

Surfing the Nanowaves: Progress in Understanding the Gas–Liquid Interface

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ABSTRACT

Recent work on the gas–liquid interface is discussed with emphasis on theoretical studies of the small-scale motion of the capillary-wave zone, experimental and theoretical studies of the ultra-small-scale surface roughness of liquids, experimental measurements of the Onsager heat of transport at a gas–liquid interface, the likely origin of the heat of transport at a molecular level, and the resolution of several types of paradoxical behavior that have been observed or predicted to occur at a liquid–vapor interface.

Introduction

Transport of matter through a gas–liquid interface is important in an enormous variety of chemical, biological, geophysical, and industrial processes and many of these processes have been characterized in great detail by chemists, physicists, and chemical engineers. It has also been a topic of theoretical interest for many years,¹ and there are encouraging signs that the interface itself is beginning to be understood.

The current view of gas–liquid transfer is that it is a two-stage process, adsorption of some fraction of the incident molecules onto the surface being followed by either desorption or accommodation into the bulk, and that the accommodation and desorption processes are both likely to involve a free energy of activation.² There is a considerable body of experimental data relating to gas–liquid exchange, including measurements of absolute evaporation rates³ and of accommodation and uptake coefficients,⁴ thermochemical⁵ and nonlinear optical⁶ studies of species adsorbed on liquid surfaces, and measurements of both inelastic and reactive scattering of atoms and molecules by liquid surfaces.⁷ Studies of the properties of the liquid surface itself include measurements of the scattering of visible light⁸ and of X-rays, including synchrotron radiation,⁹ measurements of ordinary X-ray absorption and extended x-ray absorption fine structure (EXAFS),¹⁰ and measurements of the Onsager heat of transport at the surface of a pure liquid.¹¹

Leon Phillips was born in Thames, New Zealand, on Bastille Day, 1935. He was educated at the University of Canterbury (M.Sc.) and Cambridge University (Ph.D., Sc.D.) and spent a year as a postdoctoral fellow at McGill University, Montreal, before returning to a chemistry lectureship at Canterbury, where he has been a full professor since 1966. His research deals with the kinetics and dynamics of small molecules, especially in relation to the chemistry of planetary atmospheres. He has held visiting appointments in many research institutions around the world, has been a Harkness Fellow and a Visiting Fellow of Balliol College, Oxford, and is currently a member of an ongoing NSF-funded international collaboration at the University of California, Irvine.

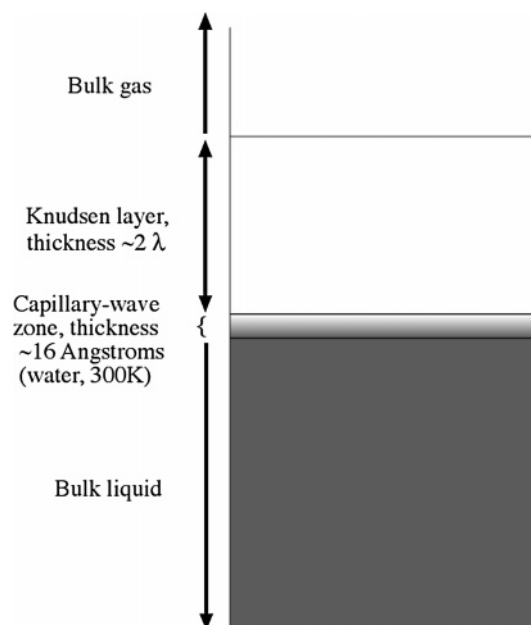


FIGURE 1. Structure of a gas–liquid interface, not to scale. Here λ is the mean free path in the gas.

Theoretical studies include a large number of molecular dynamics simulations,¹² many solutions of the Boltzmann equation,¹³ and several treatments based on irreversible thermodynamics.¹⁴ Nevertheless, there is at present no satisfactory dynamical treatment, as opposed to a simulation, of either the evaporation process or the interaction of an incoming molecule with the mobile capillary-wave zone.

The basic structure of a gas–liquid interface is shown in Figure 1. Two features of this diagram are largely responsible for the rather slow rate of progress since J. C. Maxwell's pioneering effort of 1879.¹ The first is the Knudsen layer, the thickness of which is on the order of a mean free path (the average distance a molecule travels between collisions). In this layer, molecules traveling away from the surface generally have a different velocity distribution from those moving toward the surface. The second is the capillary-wave zone, where the liquid surface is in a state of continuous, rapid motion.

Pao's solutions of the Boltzmann equation for the Knudsen layer¹³ led him to conclude that, during trap-to-trap distillation under quite ordinary conditions, the temperature gradient in the gas-phase is inverted with the higher temperature adjacent to the cooler surface. This conclusion has been confirmed by many other theoretical treatments and has generated quite a substantial literature. Nevertheless it has been suggested that the existence of this paradox shows that there is something basically wrong with the underlying theory. Our work shows that this is merely one of several interesting kinds of paradoxical behavior that can occur at a gas–liquid interface.

Capillary waves are waves for which the restoring force is provided by surface tension, and they are the dominant form of surface motion over a range of wavelengths, which extends downward from the macroscopic scale almost to

molecular dimensions. A superposition of thermally excited capillary waves, which can be regarded as Brownian motion of the membrane created by surface tension, provides an excellent description of the mobile liquid surface over this range.¹⁵ However, capillary-wave theory is a continuum theory and can therefore be expected to break down at distance scales where the presence of discrete molecular units is important. The nature of the surface motion on the scale at which capillary-wave theory is beginning to break down is one of the topics discussed here. Motion of a liquid surface on a molecular scale, which is the domain of molecular modelers,¹² is outside the scope of the present Account and clearly would be an excellent topic for some other author.

On the time scale of a fast incoming molecule, with kinetic energy on the order of 100 kJ/mol or more, the surface appears as a frozen landscape and the resulting similarity to the gas–solid interface can provide useful insight. However, molecules striking the surface at ordinary thermal energies must undergo a complicated series of interactions with the mobile layer. These interactions give rise to several important phenomena, including the adsorption–accommodation sequence that is responsible for transfer of material from the bulk gas into the body of a liquid and the coupling of heat and matter fluxes that is encapsulated in the Onsager heat of transport.

The heat of transport, Q^* , arises in Onsager's treatment of simultaneous steady-state flows of heat and matter through a region not far from equilibrium. The factor $Q^*/(RT)$ (where R is the ideal gas constant and T the temperature) controls the extent to which the flow of matter is affected by the temperature gradient in addition to the usual effect of the concentration gradient or, more generally, the chemical potential gradient. Because gas–liquid exchange nearly always takes place in the presence of a temperature gradient, the heat of transport is potentially quite important, yet its role has often been neglected. The present Account discusses our measurements of the Onsager heat of transport at a gas–liquid interface and presents some ideas about the origin of the heat of transport in terms of processes occurring at the molecular level.

Capillary Waves and Surface Roughness

During gas–liquid transfer, the adsorption process is complicated, and surface–bulk exchange is facilitated by the liquid surface being in a continual state of agitation. The surface motion can be regarded as a superposition of a large number of thermally excited capillary waves¹⁵ the nature of which changes as the scale of observation decreases from macroscopic to molecular dimensions.¹⁶ Capillary waves behave as harmonic “normal modes” when damping by viscosity can be neglected, which implies motion on a distance scale that is significantly larger than the critical-damping wavelength of about 8.6 μm on a water surface at 300 K. Normal modes are conveniently expressed in terms of wave packets con-

structed from ordinary trigonometric functions. The wavelength range of normal modes extends upward from the critical damping wavelength to the transition from capillary waves to gravity waves, which occurs at a wavelength of a few centimeters on water.¹⁷ In place of wavelength λ , it is often more convenient to work with the wave vector $\mathbf{k} = 2\pi/\lambda$. Critical damping occurs when $\mathbf{k} = \rho\gamma/\eta$, where ρ is the liquid density, η the coefficient of viscosity, and γ the coefficient of surface tension. Moving toward larger values of \mathbf{k} , on distance scales between the critical damping wavelength and a small multiple of the molecular diameter, the motion is a superposition of a large number of “local modes”, which are excited by positive- or negative-going impacts from the direction of the bulk liquid. In this range, it is still mathematically possible to express the surface motion in terms of a basis set of sine and cosine functions, but the basis functions have no physical significance.

The surface displacement due to a single local mode is the product of a Bessel function, $J_0(\mathbf{k}r)$, with a time-dependent function, $A\{1 - \exp(-t/\tau_1)\} \exp(-t/\tau_2)$.¹⁸ Here \mathbf{k} is the wave vector for the limiting cosine form of the Bessel function at large values of $\mathbf{k}r$, r being the radial distance from the point of impact. The constant A is fixed by the initial state of motion of the surface at the point of impact and can be positive or negative. The quantity $\tau_1 = \rho/2\mathbf{k}^2\eta$ is the rise time and $\tau_2 = 2\eta/\mathbf{k}\gamma$ the (longer) fall time of the displacement. Thus the typical over-damped motion resembles that of a geothermal mud pool or boiling porridge with a fast rise time and slow fall time. The maximum possible value of \mathbf{k} is $\mathbf{k}_{\text{max}} = 4.806/\sigma$, where σ is the molecular diameter and the factor 4.806 appears because 2.403 is the first zero of the Bessel function $J_0(\mathbf{k}_{\text{max}}r)$, which has to occur at $r = \sigma/2$. For water, with $\sigma \approx 3 \text{ \AA}$, this gives $\mathbf{k}_{\text{max}} = 1.6 \times 10^8 \text{ cm}^{-1}$.

An arbitrary surface displacement with circular symmetry can be written as a sum of local modes, having different \mathbf{k} values, in a Fourier–Bessel series. For a displacement that takes the form of a Gaussian dome, with height proportional to $\exp(-r^2/2d^2)$, the component \mathbf{k} values are clustered together near the lower end of the available spectrum of \mathbf{k} , so that a Gaussian dome largely retains its shape throughout the rise and fall process. For a displacement of any other shape, the high-frequency components decay first with the result that the displacement evolves more or less quickly into a Gaussian dome. Consequently, if a liquid surface is viewed on a very small scale, it will be found to spend most of its time in the slow falling phases of many overlapping Gaussian or near-Gaussian domes.

The root-mean-square (rms) displacement of an isolated local mode on water at 300 K is $1.34 \times 10^{-8} \text{ cm}$.¹⁸ When overlap with other local modes is taken into account this increases to $1.4 \times 10^{-8} \text{ cm}$, and the contributions of normal and local modes to the rms displacement become almost equal. The number of modes of a given \mathbf{k} value is proportional to \mathbf{k}^2 , so there are many more local than normal modes. However, normal modes extend over the whole of the available surface area, whereas local modes

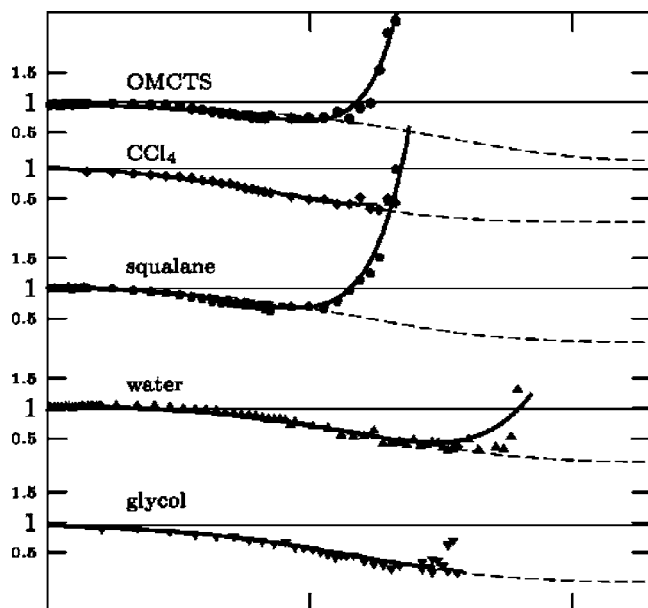


FIGURE 2. Measured values of γ/γ_0 as a function of the wave vector \mathbf{k} for a variety of liquids, adapted from Mora et al.⁹ Points are experimental data. Curves are theoretical fits from their density-functional-theory treatment.

are obliged to live up to their name. For local modes having positive amplitude and high values of \mathbf{k} , it is fairly easy for thermal excitation to result in the loss of a molecule into the gas phase, which is a plausible model for evaporation. Normal modes promote accommodation by continually creating and destroying surface area in a molecular-scale version of the “surface-renewal” process¹⁹ but play little or no part in evaporation.

As noted above, the capillary-wave model breaks down on distance scales at which the discrete molecular structure of the surface is important and surface tension ceases to be a very useful concept. Mora et al.⁹ have investigated the time-averaged small-scale roughness of liquid surfaces experimentally, by synchrotron X-ray scattering, and theoretically, using density functional theory. Their experimental results for a variety of liquids—octamethylcyclotetrasiloxane (OMCTS), carbon tetrachloride, squalane, ethylene glycol, and water—are strikingly similar (Figure 2). All show a marked increase in surface roughness over the value predicted by capillary-wave theory at \mathbf{k} -values greater than about $3 \times 10^6 \text{ cm}^{-1}$, the roughness decreasing again at large \mathbf{k} . In parallel to the change in surface roughness, the apparent surface tension value falls to about half the macroscopic value at large \mathbf{k} , then rises sharply when \mathbf{k} is very large, though still significantly below the upper limit that is set by the molecular diameter. These observations amount to a clear and unambiguous demonstration of the departure of the surface motion from the predictions of capillary-wave theory on short distance scales, and the observed \mathbf{k} -dependence of surface tension provides an invaluable testing ground for theory.

In their density functional theory calculations, Mora et al.⁹ were able to model the variation of surface roughness with \mathbf{k} for all of the liquids studied with the assump-

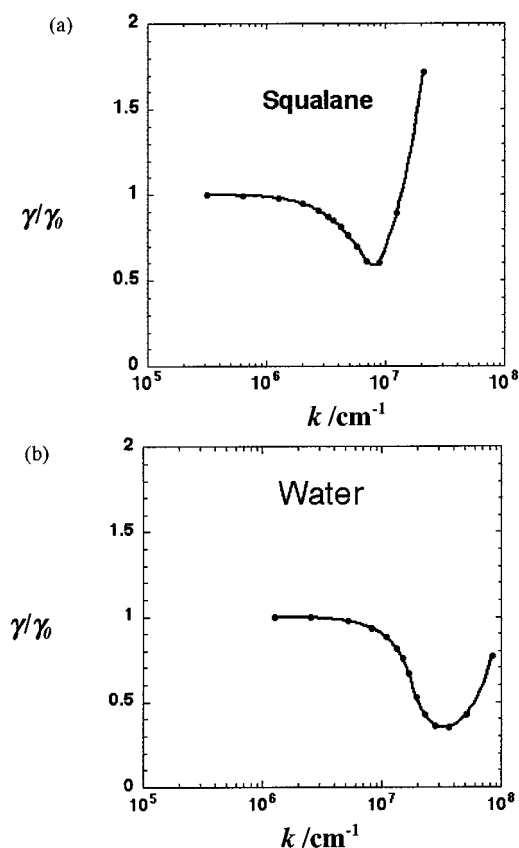


FIGURE 3. Theoretical values of γ/γ_0 as a function of \mathbf{k} from a calculation with no adjustable parameters for squalane (a) and water (b).¹⁶ The calculations used a $1/r^6$ potential for squalane and a $1/r^3$ potential for water.

tion of a Lennard-Jones intermolecular potential in every case. This result is surprising, because the long-range part of the potential was considered to be particularly important in their treatment and the Lennard-Jones potential varies as $1/r^6$ at long range, whereas the properties of hydrogen-bonded liquids such as water and glycol are well-known to be dominated by the dipole–dipole potential, which varies as $1/r^3$ at long range.

An alternative treatment¹⁶ shows that the enhanced roughness at high \mathbf{k} values can be understood as a consequence of the anharmonicity of small-scale local modes. For a large-scale (= low \mathbf{k}) mode, the restoring force during a displacement is parallel to the liquid surface and the motion is perfectly harmonic. In the limiting case of a small-scale mode, where a single column of quasi-close-packed molecules is displaced vertically relative to its neighbors, the restoring force is perpendicular to the surface and highly anharmonic. The anharmonicity results from the periodic nature of the nearest-neighbor potential during vertical displacement of the column of molecules and is due to short-range rather than long-range interactions. Because the important interactions are short-range, essentially the same results are obtained for a $1/r^3$ potential as for a $1/r^6$ potential. Representative results for the variation of surface tension with \mathbf{k} value are shown in Figure 3, where the points correspond to individual calculations. Results for the other liquids studied by Mora

et al. are given in the paper.¹⁶ No fitting is involved, and the only parameters that enter the calculations are the macroscopic value of surface tension and the molecular diameter. Both the observed minimum values of γ/γ_0 and the \mathbf{k} values at which the effective surface tension begins to rise are well-reproduced by the calculations.

For very small-scale modes, the displacement due to thermal excitation at room temperature can exceed the elastic limit of the bonds holding a molecule in the surface layer. In the case of a negative displacement, the molecule at the peak becomes incorporated into the layer below the surface, while for a positive displacement, the molecule at the peak escapes into the gas phase. In both cases, the peak of the motion is truncated, which explains why the apparent surface tension of water, for example, increases sharply for \mathbf{k} -values well below the upper limit of $1.6 \times 10^8 \text{ cm}^{-1}$. These calculations comprise a simple but remarkably successful treatment of the transition from the domain of capillary-wave theory to the discrete-molecule regime.

The Onsager Heat of Transport

The heat of transport governs the extent to which the matter flux through a region is affected by the local temperature gradient, in addition to its normal dependence on the chemical potential gradient, and is expected to be significant in connection with the air–sea exchange of gases such as CO_2 .²⁰ The heat of transport arises in the irreversible thermodynamic treatment of processes in which there are simultaneous coupled fluxes of heat and matter.²¹ Onsager expressed a general pair of coupled fluxes, J_1 and J_2 as linear functions of their driving forces, X_1 and X_2 , according to the equations

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \quad (2)$$

where the quantities L_{mn} are numerical coefficients that depend on the nature of the flux J_n , while the L_{mn} with $m \neq n$ are “coupling coefficients”. From considerations of microscopic reversibility, Onsager showed that any pair of corresponding coupling coefficients L_{mn} and L_{nm} are equal provided the departure from equilibrium is small. If J_1 corresponds to heat conduction and J_2 to diffusion, the driving force X_1 is given by $-(\text{grad } T)/T$ and driving force X_2 is $-T \text{grad}(\mu/T)$, where μ is the chemical potential of the substance being transferred. Coefficient L_{11} is closely related to the thermal conductivity and coefficient L_{22} to the diffusion coefficient. The exact relationships are obtainable from the limiting forms of eqs 1 and 2, as Fourier’s law of heat conduction and Fick’s law of diffusion, when coupling effects are negligible.

The term $L_{12}X_2$, which is the contribution to the heat flow that results from the driving force X_2 for the flow of matter, can also be written as J_2Q^* , where Q^* is the heat absorbed or released at the boundary of the region as a consequence of the matter flux J_2 . We use this as our definition of the heat of transport, Q^* . This leads to eqs 3

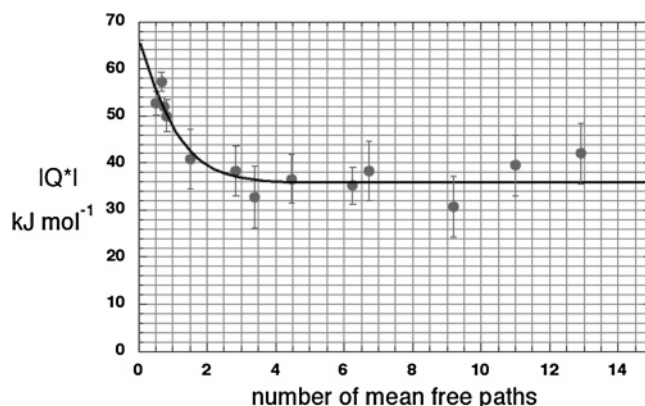


FIGURE 4. Measured values of $|Q^*|$ for *n*-heptanol as a function of the number of mean free paths in the gap over which the temperature difference was applied.

and 4 for the fluxes of heat and matter, where the matter flux is specified as a flow of gas in moles per unit area at average pressure P through the narrow region, of thickness δ , across which the pressure and temperature changes are ΔP and ΔT . When the flux J_2 is zero, eq 4 reduces to the stationary-state expression 5 that is the basis of our Q^* measurements.

$$J_1 = -\frac{L_{11}}{\delta} \frac{\Delta T}{T} + Q^*J_2 \quad (3)$$

$$J_2 = -\frac{RTL_{22}}{\delta} \left(\frac{Q^*}{RT} \frac{\Delta T}{T} + \frac{\Delta P}{P} \right) \quad (4)$$

$$\frac{Q^*}{RT} = -\frac{\Delta P}{P} \frac{T}{\Delta T} \quad (5)$$

In our experiments,^{11,27} we applied a temperature difference ΔT across the layer of vapor close to the liquid surface and measured the resulting pressure change, ΔP . The measurements were made with pure liquids (aniline, *n*-heptanol) at fairly low pressure (normally below 0.1 Torr). The effect was expected to occur within a few multiples of the mean free path, λ , from the surface, because the behavior of molecules in the gas phase should not be affected by the presence of the liquid surface when it is more than a few mean free paths away. At the highest pressure used (with aniline), the thickness of the gap across which the temperature difference was applied corresponded to 38λ . The heat of transport was found to be negative, and its absolute value increased as the number of mean free paths in the vapor gap decreased, appearing to tend toward the latent heat of vaporization when the number tended toward zero. This is shown for *n*-heptanol in Figure 4.

Measurements with pure liquids are restricted to positive values of ΔT because condensation makes it impossible to establish a stationary state with ΔT negative. Our preliminary measurements for water vapor at the surface of 50% w/w sulfuric acid have shown that eq 5 is valid for both positive and negative values of ΔT .

Denbigh and Raumann²² used an equation equivalent to eq 5 to obtain Q^* from stationary-state measurements

of the thermo-osmosis of several gases through a natural-rubber membrane, obtaining values of $Q^*/(RT)$ that ranged from about -5.6 for H_2O , through -3.1 for CO_2 and -0.43 for N_2 , to $+0.17$ for H_2 . For comparison, the largest value of $Q^*/(RT)$ from the data in Figure 4 is -24 and the smallest -15 .

If Q^* were precisely equal to the latent heat of either vaporization or solution (depending on whether the system were a pure liquid or a mixture), the steady-state vapor pressure would be equal to the pressure that the liquid would exert if its surface were at the same temperature as the gas on the other side of the Knudsen layer. The results in Figure 4 show that this situation is not far from being realized, which could have interesting consequences for the rate and direction of air–sea exchange at a location with a large air–sea temperature difference. For any volatile solute, the effective vapor pressure of a stretch of ocean surface exposed to a wind off the Sahara would be greatly enhanced, whereas the effective vapor pressure of a stretch of unfrozen ocean surface exposed to the wind off Siberia during winter would be greatly reduced.

A theoretical prediction that the heat of transport for material going from one liquid to another, via a pair of liquid–vapor interfaces, should be numerically equal to the latent heat of condensation was made by Spanner in 1954.²³ Spanner's paper, which is part of the plant physiology literature, appears to have been overlooked by physical chemists, and his theory was never tested by experiment. Essentially the same prediction for a single liquid–vapor interface was made independently by the present author in 1991.²⁴ This work and its application to air–sea exchange²⁰ were the subject of strong criticism by Doney,²⁵ criticism that our recent experiments¹¹ have shown to be unjustified except in a fairly minor respect.

By treating the transfer of matter through a gas–liquid interface as a limiting case of thermo-osmosis through a membrane, it was shown that the heat of transport for such a system should be similar to the latent heat associated with the process of solution or condensation of the gas being transferred.²⁶ Hence, if the zone in which flux coupling occurs is assumed to be the layer of gas immediately adjacent to the surface, the heat of transport might be expected to correspond to the heat of adsorption on the liquid, which is typically about 90% of the heat of solution or condensation. This is consistent with the existing, albeit limited, experimental data.^{11,27}

Coupling of heat and matter fluxes is expected to be less important within a bulk liquid because temperature gradients in a liquid are an order of magnitude smaller than in a gas, and there is no quantity that corresponds to the latent heat. However, the possibility remains that coupling might be significant in the capillary-wave zone, where the time-averaged thermal conductivity is intermediate between the values for gas and liquid. The origin of the Onsager heat of transport at a molecular level has been investigated by model calculations, which show that simple heating of the capillary-wave zone cannot account for our measured heats of transport, but the effect of an applied temperature gradient on the free energy barrier

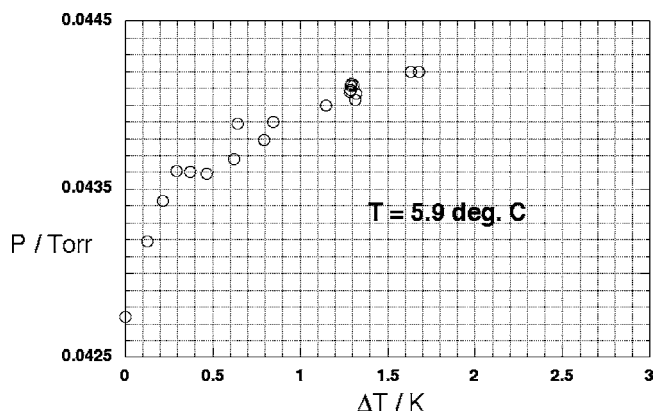


FIGURE 5. Typical experimental results for *n*-heptanol at a high liquid-surface temperature ($+5.9$ °C).

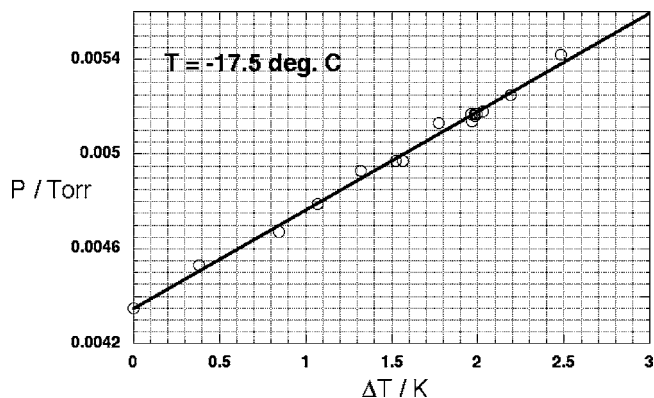


FIGURE 6. Typical experimental results for *n*-heptanol at a low liquid-surface temperature (-17.5 °C).

to evaporation is more than capable of doing so.²⁸ It is apparent that more-detailed calculations are needed.

The results of individual Q^* measurements in Figure 5 show an unanticipated feature, namely, curvature of the ΔP versus ΔT plots. This curvature is always present at higher values of the equilibrium pressure. With *n*-heptanol (though not with aniline, the first liquid we studied), it is possible to work at lower pressures such that the thickness of the layer across which the temperature difference, ΔT , is applied amounts to significantly less than one mean free path with results as shown in Figure 6. At the lower pressures, ΔP versus ΔT plots are linear for ΔT up to at least 3 K with slopes that correspond to the initial slopes of curves such as that in Figure 5.

In practice, the pressure ranges for straight lines and curves overlap, experiments in the intermediate regime sometimes giving straight lines and sometimes curves. This strongly suggests that the curvature is an artifact and probably is due to turbulence. However, changing from a glass to a metal apparatus to reduce postulated turbulence-inducing horizontal temperature gradients in the vapor gap did not remove the curvature. A referee for ref 27 pointed out that turbulence could be present as a consequence of vortices generated by the "well-known" long tail on the velocity autocorrelation function,²⁹ which is essentially a reflection of the persistence of velocity in collisions. Clearly this is a prime topic for investigation.

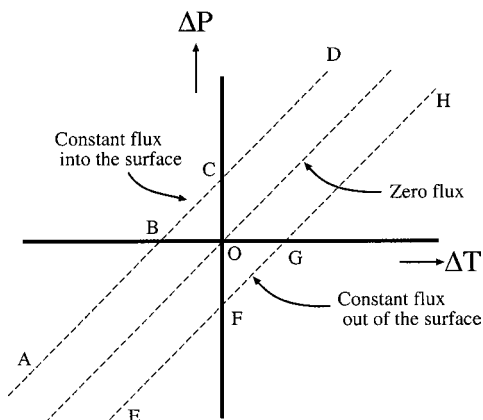


FIGURE 7. Constant flux plots from eq 4.

Paradoxical Behavior at a Gas–Liquid Interface

The possibility of paradoxical behavior at a gas–liquid interface was first noticed by Pao¹³ as an implicit consequence of his solution of the Boltzmann equation for the “two-surface problem”, in which a liquid distills from a warm surface to a cooler one. The paradox consisted of the prediction that the temperature gradient in the vapor would often be inverted, the cooler temperature being found above the warmer liquid. The theoretical prediction of this paradox has been repeated many times, by different authors and several different methods, but so far its existence has not been demonstrated by experiment.

During our measurements of the Onsager heat of transport for the aniline liquid–vapor interface, we observed an instance of anomalous behavior, which took the form of distillation of a cool liquid onto a warmer surface.³⁰ The phenomenon can readily be understood in terms of the observed effect of a surface temperature gradient on vapor pressure. The cooler liquid experiences a positive temperature gradient, which enhances its vapor pressure, and the warmer liquid experiences a negative temperature gradient, reducing its vapor pressure. Provided the absolute value of Q^* is large enough, which in practice means provided the pressure is low enough for the absolute value of Q^* to be greater than half the latent heat of vaporization, the enhanced vapor pressure of the cool liquid will exceed the reduced vapor pressure of the warm liquid, with the result that distillation occurs in the opposite direction from one’s normal expectation.

Ward and co-workers^{31,32} have made a number of observations of anomalous liquid–vapor temperature differences during steady evaporation, differences that are mostly in the opposite direction from those predicted by Pao.

All three kinds of paradoxical behavior can be rationalized on the basis of Figure 7, which plots the pressure difference ΔP against the temperature difference ΔT across the Knudsen layer in accordance with the Onsager flux equation, eq 4. Point O corresponds to the equilibrium vapor pressure with ΔP and ΔT both zero. The line passing through O is the locus of possible stationary states as observed in our Q^* measurements. The uppermost line

corresponds to the effect of applying a pressure difference greater than the stationary-state value so as to produce a steady flux of matter into the liquid, and the bottom line corresponds to maintaining a pressure difference smaller than the stationary-state value, so that there is a steady matter flux out of the liquid. These changes amount to moving away from the stationary state by adjusting the second term in eq 4. Alternatively, each line can be regarded as the locus of points with constant gas flux J_2 for different values of ΔP and ΔT . In a two-surface system, we label the pressure and temperature changes across the two Knudsen layers as $\Delta P, \Delta T$ and $\Delta P', \Delta T'$, respectively.

In Figure 7, the paradoxical behavior predicted by Pao¹³ corresponds to the region E–F, with ΔP and ΔT both negative at the surface of the evaporating liquid, and region C–D, with $\Delta P'$ and $\Delta T'$ both positive at the surface of the condensing liquid. When $|\Delta T| + |\Delta T'|$ is greater than the temperature difference between the two liquids, the gas-phase temperature profile is inverted, which results in a small conductive heat flux in the opposite direction to the much larger latent heat flux, which flows in the orthodox direction, from the warm liquid to the cool one. This kind of anomalous behavior has not been observed in its entirety (see below).

Our observed distillation of a cool liquid onto a warmer surface³⁰ corresponds to region G–H, with ΔP and ΔT both positive, at the surface of the evaporating liquid, and region A–B, with $\Delta P'$ and $\Delta T'$ both negative, at the warmer surface of the condensing liquid. If $|\Delta P| + |\Delta P'|$ is greater than the equilibrium vapor pressure difference between the two liquid surfaces, liquid distills from the cool surface to the warmer one. In this case, the flux of latent heat has to be much smaller than the conductive heat flux, which drives the process.

The evaporation experiments of Fang and Ward³¹ correspond to the region F–G at the surface of an evaporating liquid, with ΔP negative and ΔT positive. In a two-surface system this would be paired with region B–C at the surface of a condensing liquid, with $\Delta P'$ positive and $\Delta T'$ negative. However, the condensation process corresponding to region B–C has not been reported. Instead, the condensation experiment of Ward and Stanga³² appears to correspond to the condensation part of Pao’s prediction, region C–D. The sizes of regions B–C and F–G increase with increasing vapor flux, so observation of the corresponding behavior for a two-surface system depends on the presence of a large gas flux. The other anomalous phenomena occur in regions that are semi-infinite, which suggests that they ought to be easier to observe. With all of the regions in Figure 7 accounted for, we can conclude that no other forms of paradoxical behavior at the gas–liquid interface remain to be discovered.

A Concluding Note

While this Account was in preparation, Aarts and co-workers³³ reported direct visual observation of processes involving thermally excited capillary waves at a liquid–

liquid interface. Their liquids were engineered to make the interfacial surface tension extremely small with the result that the rms displacement was of the order of micrometers rather than ångströms.

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