

Kinetics of Evaporation: Statistical Rate Theory Approach

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Abstract

Currently there are three theoretical approaches to study evaporation: Continuum Mechanics, Classical Kinetic Theory, and recently Statistical Rate Theory (SRT). The assumptions being used and the predictions resulting from the first two methods have not been supported by experimental results which are in agreement with the SRT predictions. It seems that SRT can predict the conditions existing at the interface during evaporation better than other methods. This paper reviews some of the published evaporation studies, particularly evaporation rate, thermocapillary convection, and temperature discontinuity at the interface during evaporation and compares the results of different approaches.

Keywords: Evaporation, Rate of Phase Change, Surface Temperature, Convection, Statistical Rate Theory

1. The Evaporation Controversy

Evaporation is one of many phenomena in the general classification of interfacial molecular transport. In the case of evaporation, a molecule is transported across the interface between liquid and vapour phases. In spite of the immense scientific and technological importance of evaporation, this ubiquitous phenomenon is not well understood from a fundamental point of view. Specifically, the conditions existing at a liquid-vapor interface during phase change processes have become controversial. The controversy revolves around the possible existence of a temperature discontinuity at the liquid-vapor interface, its direction, magnitude, and the variables controlling the phase change rate. To identify the issues in the controversy, the results of studies regarding evaporation are first reviewed.

1.1 Transport Coefficients

Classical kinetics theory has provided the molecular basis for the understanding of evaporation for over a century (Hertz, 1882, Stefan, 1889, Knudsen, 1915, Kennard, 1938, Knacke, 1956). In 1882 Hertz tried to investigate the rate of phase change. In his experiment, the whole apparatus was evacuated and mercury in a tube was heated to a temperature between 100 and 200 °C. Then the mercury vapor was

condensed into a condenser. A thermometer was sealed in the apparatus and touched the mercury meniscus. The pressure at the evaporating surface was measured by an absolute manometer which was made of mercury itself. The rate of evaporation established from the drop of the mercury meniscus was found to be between 0.08 and 1.67 mm/min. From theoretical analysis of his experiment, Hertz arrived at the following fundamental conclusion: There exists for every substance a maximum rate of evaporation, which depends only on the temperature of the surface and on the specific properties of the substance. Experimentally, Hertz's measurements of the evaporation rate indicated a value that was approximately 10% of the maximum rate of evaporation that he calculated from kinetic theory.

In 1915, Knudsen (1915) and later others (Kennard, 1938) carried out an experimental investigation of the rate of evaporation for pure mercury. The results consistently indicated that the evaporation rate was less than the maximum rate predicted from classical kinetic theory. Knudsen's theoretical work is especially significant because he introduced the concept of the evaporation coefficient. This coefficient, although unknown, was to account for the deviation from the maximum evaporation rate.

To describe the Hertz-Knudsen formula for the rate of evaporation, we first consider the maximum rate of evaporation, as defined in classical kinetic theory, under equilibrium conditions. On a molecular level, the processes of evaporation and condensation involve a molecule escaping from a surface or an incident molecule being captured by a surface. Under equilibrium conditions, the number of molecules evaporated from the liquid phase must be equal to those condensed from the vapor phase. The vapor and condensed phases are considered to be essentially uniform and to be separated only by a mathematical plane. It is a necessary condition under equilibrium conditions that liquid and vapor temperatures are uniform, since otherwise there would be a flow of heat between the phases. However, depending on the curvature of the interface, the pressure in the condensed phase could be different from that of its vapor. The distribution function for molecular velocity far away from the interface is Maxwellian (Fowler, 1965), and if it is assumed that the interface itself is not a disturbing influence on the distribution function, then the Maxwellian distributions exists right up to the interface, i.e.

$$f_s = n \left(\frac{m}{2kT} \right)^{3/2} \exp \left(-\frac{m}{2kT} (c_x^2 + c_y^2 + c_z^2) \right) \quad (1)$$

where n is the number density of molecules, c_i is the motion of the mass center described in velocity space, k the Boltzmann constant, m the mass of the molecule, and T the temperature. If equation (1) is used to calculate the maximum rate of evaporation, one finds that

$$J_{\max} = \frac{P_{\text{sat}}(T)}{\sqrt{2pmkT}} \quad (2)$$

where P_{sat} is the saturation vapor pressure at temperature T . This implies that every incident molecule condenses.

Under non-equilibrium conditions, there could be a net mass flow across the interface. The maximum evaporation rate will not usually be achieved. This means that only a fraction of the molecules crossing a plane adjacent to the liquid surface enters the vapor, whose molecular flux is called the uni-directional (or absolute) rate of evaporation. Now consider a small departure from equilibrium. The absolute evaporation rate is expressed assuming that the Maxwell distribution in the vapor is characterized by the temperature and pressure in the liquid phase near the surface. Hence, the mechanism of molecules leaving the surface depends only on the state of the liquid and is not affected either by the state of the vapor or by the net transfer of mass, momentum, and energy. Similarly, the

approximation to obtain the expression for the absolute (or uni-directional) condensation rate is to assume that the distribution function in the vapor phase is Maxwellian at the vapor pressure and its temperature. These are the usual boundary conditions assumed at a liquid-vapor interface under nonequilibrium conditions (Barret and Clement, 1992). Then, the Hertz-Knudsen formula for the net evaporation rate is expressed as the difference of the absolute rates of evaporation and condensation such that

$$J = \frac{1}{\sqrt{2pmk}} \left(\sigma_e \frac{P_{\text{sat}}(T^L)}{\sqrt{T^L}} - \sigma_c \frac{P^V}{\sqrt{T^V}} \right) \quad (3)$$

where σ_e and σ_c are the evaporation and the condensation coefficients, superscripts L and V indicate that the parameters are evaluated in the liquid and the vapor phases individually. This equation includes the general case in which the substance does not evaporate into a vacuum, but shows an actual vapor pressure at the boundary condition. Knacke and Stranski (1956) considered the evaporation results from previous experiments and stated that in the case of substances with a vapor pressure higher than 13.3 Pa, it is no longer possible to maintain a high vacuum experimentally, and condensation has to be taken into account.

One of the major assumptions in applying kinetic theory to phase change is that the absolute rates of evaporation and condensation are uncoupled. Under equilibrium conditions, these two coefficients must be equal. However, the assumption that they have the same value under nonequilibrium conditions may not be valid (Plesset, 1956). Barrett and Clement (1992) found that there was not a complete equivalence between the evaporation and the condensation coefficients, and that the evaporation coefficient depends only on the properties of the liquid surface, while the condensation coefficient is a function of the properties of both the liquid and the vapor. Young (1991) pointed out that the condensation and evaporation coefficients are not necessarily equal. However, it is usually assumed that the evaporation coefficient and the condensation coefficient are equal. This coefficient has to then be evaluated experimentally (Barrett and Clement, 1992).

There is one consideration which will have some effect on the absolute rate of evaporation. This is the fact that if the mass transfer across an interface is occurring, the mean velocity of liquid molecules at the surface is not zero with respect to the coordinate axes which have been located there. This will probably cause the absolute rate of evaporation as well as the velocity distribution of molecules emitted from the surface to be

different from what they are in an equilibrium case. Schrage (1953) assumed that the distribution of incoming molecules in the vapor phase could be represented by a Maxwellian distribution with a net bulk velocity U_b such that

$$f_s = n \left(\frac{m}{2kpT} \right)^{3/2} \exp \left(-\frac{m}{2kT} ((c_x - U_b)^2 + c_y^2 + c_z^2) \right) \quad (4)$$

He then assumed the evaporation and condensation coefficients were equal, and gave the expression for the net rate in terms of one coefficient which he called the condensation coefficient (Schrage, 1953).

If Schrage's expression for the distribution function of the molecules leaving the liquid is used to calculate the expression for the rate of evaporation, the Maxwellian distribution is assumed to describe the condensing molecules, and both the evaporation and condensation coefficients are included, then provided the bulk vapor velocity is small one finds (Barrett and Clement, 1992) that

$$J = \frac{1}{\sqrt{2} p m k} \left(\frac{\sigma_e P_{\text{sat}}(T^L)}{1 - 0.5 \sigma_c \sqrt{T^L}} - \frac{\sigma_c P^V}{1 - 0.5 \sigma_c \sqrt{T^V}} \right) \quad (5)$$

By comparing equation (3) with equation (5), it may be seen that when $\sigma_e = \sigma_c = 1$, Schrage's formula predicts twice the flux predicted by the Hertz-Knudsen formula (Barrett and Clement, 1992). Some indirect evidence also suggests that the Hertz-Knudsen theory under predicts growth rate of small water droplets in low pressure, pure steam by a factor of about 2 (Young, 1991).

Wylie and Brodkey (1972) applied the Schrage formula with two coefficients to their experiments with mercury and found that the value of the condensation coefficient was equal to that of the evaporation coefficient, and each was approximately 0.61 under non-equilibrium conditions for a condensation flux of $3.0 \text{ g min}^{-1} \text{ cm}^{-2}$. They also stated that there is no reason for the coefficients to be less than unity. If the evaporation and condensation coefficients based on the Schrage formula are equal, Mills and Seban (1967) listed the experimentally determined values of the evaporation-condensation coefficient for water. The values vary from 0.006 to 0.1 for the evaporation of a suspended water droplet and for the evaporation of a horizontal liquid surface, and vary from 0.35 to near 1.0 for the jet evaporation (Mills and Seban, 1967). The quantitative explanation for

the variation of the coefficient has not been established. However, it is possible that the inaccurate surface temperature measurement with large temperature gradient and the contamination level would have affected the value of the evaporation coefficient. It should be noted that no direct measurement of the temperature at the interface in either phase was actually performed in these experiments.

In summary, although the Hertz-Knudsen formula and the Schrage formula have been widely used to calculate the rate of liquid evaporation, the difficulties are those of knowing the value of the evaporation coefficient and the conditions that exist at the interface of the evaporating liquid. The evaporation coefficients defined by classical kinetic theory must be determined experimentally. Marek and Straub (2001) have recently surveyed the reported values of these coefficients for water and pointed out the wide variation at nominally the same experimental conditions. The results of this survey suggest that the basic definitions of these coefficients is inadequate in some as yet undefined way or that the experiments are not being performed under the conditions assumed. One of the possible experimental difficulties is convection—either buoyancy or surface tension-driven.

1.2 Anomalous Temperature Profiles

Another major result of classical kinetic theory studies is the prediction of "anomalous" temperature profiles. Interestingly, several theoretical studies based on this theory predicted a temperature discontinuity before any experimental investigation was undertaken. The first predictions were presented by Pao (1971, 1973a) who applied the linearized Boltzmann equation to examine the energy and mass transfer between two parallel liquid films that were assumed to be maintained at different but constant temperatures. At one liquid film, evaporation was occurring and at the other, condensation was taking place. His analysis indicated that at the evaporating interface, the temperature was larger on the liquid side of the interface than on the vapor side of the interface, and at the interface where condensation took place, the relation between the interfacial temperatures was reversed. However, the predicted magnitude of the temperature discontinuity led to controversy for substances having a latent heat (h_{fg}) divided by the gas constant (R) and the temperature (T), greater than a limiting value. For example if the ratio h_{fg}/RT were greater than approximately 4.5, it was predicted that the temperature discontinuity at the liquid-vapor interface would be so large that the temperature gradient in the vapor would be the reverse of the applied temperature

gradient. Such a profile was labelled “anomalous” (or inverted), and since for many substances h_{fg}/RT is approximately 10, the prediction would be that under steady state conditions most two-film systems would exhibit anomalous temperature profiles (Pao, 1971, 1973a, 1973b).

Since such a prediction seems unreasonable, a number of theoretical investigations have been conducted to examine different assumptions in the theoretical procedure adopted by Pao. Several of these have used the linearized Boltzmann equation to perform similar investigations (Siewert and Thomas, 1973, Cipolla, Lang and Loyalka, 1974, Onishi, 1986). Others have investigated nonlinear effects using numerical methods (Cercignani, Fiszdon, and Frezzonnti, 1985, Murakami and Oshima, 1974), the six-moment method of Lees (Koffman, Plesset and Lee, 1984), and the thirteen-moment method of Grad (Young, 1991). All of these theoretical studies suggest that the reason for the prediction of anomalous temperature profiles is the boundary conditions assumed (Koffman, Plesset and Lee, 1984). Cercignani et al. (1985) used a linearized moment method to investigate the effect of different boundary conditions and concluded that predictions from classical kinetic theory would be that an anomalous temperature profile would be observed if water were evaporating at temperatures below approximately 65 °C.

The existence of an anomalous temperature profile has also been investigated using the formalism of nonequilibrium thermodynamics. Hermans and Beenakker (1986) point out that the rate of entropy production is positive when an anomalous temperature profile exists in a system; thus, an anomalous profile cannot be excluded on the basis of nonequilibrium thermodynamics. Further, Bedeaux et al. (1990) used nonequilibrium thermodynamics to investigate the same circumstance as Pao and found that the results obtained reduce to those found from kinetic theory.

One of the essential characteristics of the anomalous temperature profile is that at the interface where evaporation is occurring, the temperature in the liquid is greater than that in the vapor. This prediction is not unique to the two liquid-layer circumstance considered by Pao and subsequent investigators. Kinetic theory investigations that assumed only the evaporating liquid interface to be present and assumed the vapor to be removed at infinity also indicate that at the interface the temperature in the evaporating liquid would be greater than that in the vapor (Sone and Sugimoto, 1993).

Thus, the prediction of the temperature at an evaporating interface being larger in the liquid

than in the vapor appears to be a prediction that follows from kinetic theory and from nonequilibrium thermodynamics, and this is an essential feature of the prediction of anomalous temperature profiles. Hence, these predictions can be viewed as either the prediction of important new phenomena or as predictions that raise doubts about the fundamental theory from which the predictions were obtained. Koffman, Plesset and Lees (1984) have adopted the latter point of view. Barrett and Clement (1992) suggest that these predictions “contradict common sense”.

1.3 Experimental Investigation of the Temperature near the Interface of an Evaporating Liquid

The way the predictions from kinetic theory are viewed should be decided by experimental investigation, but the experimental results have not led to a consistent interpretation. For example, Shankar and Deshpande (1990) have reported an experimental investigation in which a liquid film was on each of two parallel metal plates. Under “quasi-steady” conditions, evaporation occurred from the liquid film on the lower metal plate and condensation on the upper film. They studied water, Freon 113, and mercury. For both water and Freon, the measured temperature profile in the lower liquid film indicates thermal conduction of energy to the interface where the evaporation took place. In other words, for these liquids, the heated plate supplies energy to the interface to evaporate the liquid—the interface is the coldest place in the evaporating liquid. The thermocouple wire used to measure the temperature had a diameter of 300 μm —the junction or bead would have been larger. For these liquids, there was no measured temperature discontinuity, but the size of the thermocouple junction would have prevented the temperature close to the interface being measured.

For mercury evaporation, the authors claim to have measured an interfacial temperature discontinuity in which the interfacial vapor temperature was less than the interfacial liquid temperature—the direction of the discontinuity predicted from classical kinetic theory— but the temperature profile in the lower liquid film indicates the highest temperature was at the interface of mercury with its vapor where evaporation was assumed to be taking place! No direct measurement of the rate of evaporation was made, and no explanation was given for why the evaporation did not cool the liquid phase. To prevent corrosion reactions, the authors report the plates had to be nickel coated and the thermocouples had to be coated with an insulating epoxy. The temperature profile in the liquid film that was evaporating suggests there

was a reaction taking place at the liquid-vapor interface.

Shankar (1993) later pointed out that in the work of Shankar and Deshpande (1990) they were unable to find “definite evidence for or against the anomalous temperature distribution” that had been predicted from classical kinetic theory.

Hisatake et al. (1993) used a 127 μm -diameter thermocouple to measure the temperature profile in both phases as water evaporated into air. The temperature profile in water shows the temperature decreasing as the thermocouple approached the interface from within the liquid and then a very sharp increase as it crossed the interface and entered the vapor-air mixture.

However, rather than interpreting their measurements as indicating a temperature discontinuity, Hisatake et al. (1993) assumed the temperature was continuous at the interface. This required the temperature to have a minimum in the liquid phase. In other words, they could not measure the temperature exactly at the interface and, therefore, interpreted their result to be consistent with the continuum approximation in which the temperature exactly at the interface is assumed continuous. However, for the temperature profile to have a minimum in the liquid phase near the interface, as the authors supposed, does not seem physically possible because it would mean that there was thermal conduction of energy to the minimum temperature location from both sides. Such a temperature profile could exist only if there were an energy “sink” at the site of the minimum temperature.

If Hisatake et al. had interpreted their results as indicating a temperature discontinuity at the interface; they would have obtained results similar to those reported later by Ward and colleagues (Ward and Duan, 2004, Ward and Fang, 1999, Fang and Ward, 1999a, 1999b). In the latter studies, water evaporating into its own vapor was examined. The apparatus used is shown schematically in *Figure 1*. Water that had been de-ionized, distilled, nano-filtered, and degassed was transferred directly into a syringe mounted in a syringe pump. The prepared water could be pushed by the pump into the throat of a stainless steel funnel where the water temperature was brought to a pre-set value and then on to the funnel mouth. The maximum height of the liquid-vapor interface above the funnel mouth was limited to approximately 1 mm. This ensured the interface was very nearly spherical. The interface could be seen from outside the evaporation chamber with a cathetometer, and its height measured with an accuracy of $\pm 10 \mu\text{m}$.

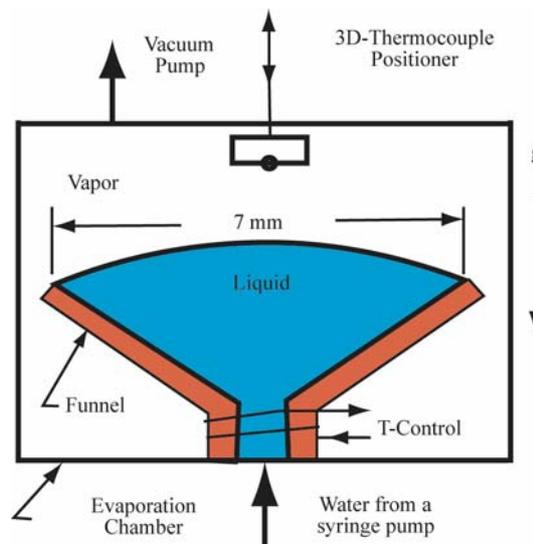


Figure 1. Schematic of the evaporation apparatus used in the experiments of Ward et al. (2004, 1999)

A 25 μm -diameter thermocouple was mounted on a positioning micrometer that allowed the water to be measured in three-dimensions. One of the temperature profiles measured on the center-line of the funnel during steady-state water evaporation is shown in *Figure 2* (Ward and Duan, 2004). Three features of this temperature profile should be noted.

1. The interface is the coldest place in the fluids: energy is conducted to the interface region from both the liquid and vapor phases.
2. At the interface a very large temperature discontinuity exists with the temperature in the vapour at the interface much larger than that in the liquid at the interface. A temperature discontinuity in this direction has also been measured under different circumstances for water and two other liquids (Fang and Ward, 1999a, 1999b). In one steady-water evaporation experiment, it was possible to get the thermocouple within approximately one mean-free-path of the interface (Fang and Ward, 1999a). In that experiment, a temperature discontinuity of 7.8°C was measured, the largest discontinuity reported to date.

A temperature discontinuity in the direction measured is in the opposite direction of that predicted by Pao (1973a, 1997b) and others from classical kinetic theory when the evaporation and condensation coefficients were assumed to be unity (Siewart and Thomas, 1973, Cipolla, Lang, Loyalka, 1974, Onishi, 1986, Cercignani, Fiszdon and Frezzoniti, 1985). Furthermore, a series of steady state experiments was conducted (Ward and Stanga, 2001) in which condensation

occurred at the water-vapor interface. These experiments indicated that there was a temperature discontinuity in the same direction as observed in the case of evaporation—the temperature in the vapor was greater than that in the liquid— but the magnitude of the discontinuity was smaller than in the case of evaporation. In view of the observed direction of the discontinuities, it seems unlikely that an anomalous temperature profile would be observed physically.

In a numerical simulation of the molecular dynamics of Argon at the liquid-vapor interface, Wang et al. reached the conclusion that a high kinetic energy component normal to the interface is an important character of the interphase transport process (Wang, Chen and Guo, 2003). This conclusion is in agreement with the measurements of Ward and Fang (1999).

3. Immediately below the liquid-vapor interface (*Figure 2*), a thin layer of liquid was observed to have a uniform temperature (Ward and Stanga, 2001). In general, below this layer, the temperature profile in the liquid phase indicated there was thermal energy transport to the interface by conduction. The source of the uniform temperature layer was initially unclear. Its presence suggests thermocapillary convection is present at the liquid-vapor interface.

However, although thermocapillary (or surface tension-driven or Marangoni-Bénard) convection has been well documented for fluids other than water (Chai and Zhang, 1998, Assenheimer and Steinberg, 1993, Buffone and Sefian, 2004), in 1984 Cammenga et al. (1984) pointed out the absence of experimental evidence for thermocapillary convection during water evaporation. Earlier work had attributed this absence to contamination. However, in the experiments of Barnes and Hunter (1982) and particularly those of Cammenga et al. (1983) and Schreiber and Cammenga (1981) measures were taken to ensure cleanliness, but they did not interpret their measurements as indicating the presence of thermocapillary convection (Cammenga et al., 1984).

To investigate the source of the uniform temperature layer, a set of experiments was conducted using the apparatus shown schematically in *Figure 1* to study water evaporation when the temperature of water entering the funnel throat was brought to a temperature of less than 4°C (Ward and Duan, 2004). Evaporative cooling at the liquid-vapor interface reduced the liquid phase temperature below that at the throat, with the minimum temperature occurring at the liquid-vapor

interface. Since water has its maximum density at 4°C and its density decreases monotonically with a decrease in temperature, the lightest liquid was at the interface. Thus, there was no potential for buoyancy-driven convection, but as indicated in *Figure 2* the uniform-temperature layer was clearly present.

The possible presence of thermocapillary convection was investigated (Ward and Duan, 2004) by inserting a 12 μm-diameter, 54 μm-in-length cantilevered wire to a depth of approximately 40 μm into water at the mid-point between the center-line and funnel rim as water evaporated under steady-state conditions while it was maintained at the circular mouth of a stainless steel funnel (*Figure 1*). The deflection of the cantilevered probe tip was measured, and, from the elastic properties of the probe material, the speed of the fluid flow required to cause the measured deflection of the cantilevered probe was determined by assuming the force on the probe resulting from drag.

This speed was determined a second way: the temperature profile parallel to the water surface was measured. As indicated in *Figure 3*, the interfacial temperature profile was found to be parabolic, with the temperature maximum at the funnel rim and a minimum on the funnel center-line. This temperature profile would have produced a gradient in the surface tension in which the maximum surface tension was on the center-line and a minimum was at the funnel rim.

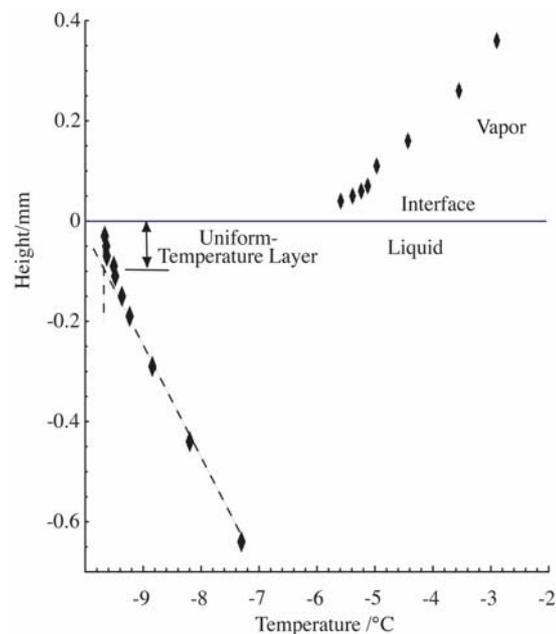


Figure 2. Temperature profile measured in the centerline of the evaporating liquid system (Ward and Duan, 2004)

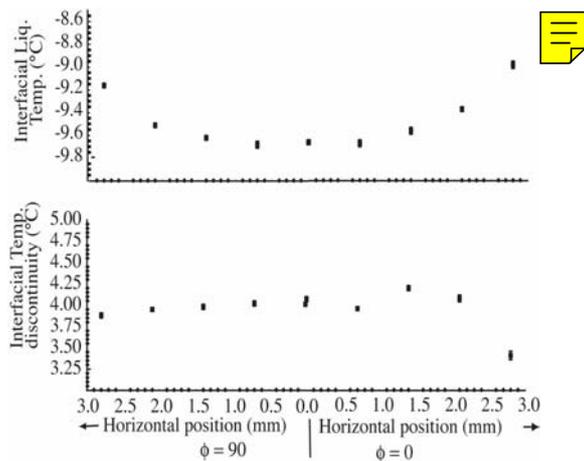


Figure 3. The abscissa indicates the position measured from the centerline in each of two horizontal directions separated by 90°. The upper ordinate gives the interfacial liquid temperature. The lower gives the interfacial temperature discontinuity

Thus, a thermocapillary flow would have been generated by this surface tension gradient that was directed from the funnel rim toward the center-line. When the flow probe was inserted between the center-line and the funnel rim, the deflection was toward the center-line, as expected. When the measured gradient in the surface tension was equated to the viscous stress parallel to the liquid surface, a second equation was developed that could be solved to determine the speed. The value of speed determined in this fashion agreed reasonably with that determined from the probe deflection (Ward and Duan, 2004). This agreement indicates that it was a gradient in surface tension that produced the fluid flow that deflected the flow probe. In a series of experiments, it was found that as the evaporation rate was increased (by lowering the pressure in the vapor phase) the thermocapillary-induced speed increased parabolically reaching a maximum of approximately 0.5 mm/s.

The uniform-temperature layer is possibly generated by the thermocapillary flow. For example, the thermocapillary flow from the rim toward the center-line and parallel to the interface for the experiment indicated in Figure 2 is two-orders of magnitude higher than the flow perpendicular to the interface that is required to maintain the evaporation at a steady rate. Also the temperature of the liquid at the interface is well below the temperature at the throat. Thus, when the lighter liquid at the interface, moving from the rim toward the center-line, reaches the center-line it must penetrate the denser liquid below the interface and return toward the funnel rim. Buoyancy would tend to push these

oppositely directed fluid streams together. The shear produced would give rise to intense mixing. The uniform-temperature layer could be the result. At the highest rates of evaporation, evidence has been cited that indicates the shear produced by these two oppositely directed streams can give rise to turbulence (Ward and Duan, 2004).

2. Statistical Rate Theory (SRT) Description of Evaporation or Condensation

Since the measured temperature discontinuity is in the opposite direction of that predicted from classical kinetic theory when the evaporation and condensation coefficient are assumed to be unity, the question arises as to the theoretical basis for the measurements. Consequently, the measured conditions during steady state evaporation have been investigated with statistical rate theory (SRT) (Ward, 1977, 1983, 2002, Ward, Findlay, and Rizk, 1982). This quantum-thermodynamic based theoretical approach has the distinct advantage of leading to an expression for the evaporation flux that is free of any fitting parameters. Also, it has been successfully applied to a number of other interfacial molecular transport processes. These include condensation (Ward and Fang, 1999), droplet evaporation (McGaughey and Ward, 2002), gas adsorption on single crystal metal surfaces (Findlay and Ward, 1982, Ward, Farahbakhsh and Venter, 1986, Ward and Elmoslehi, 1986, 1988, Elliott and Ward, 1997a, 1997b, 1995) and on heterogeneous materials (Elliott and Ward, 1997c, Panczyk and Rudzinski, 2003, 2002, Rudzinski and Panczyk, 2000, Rudzinski, Borowieck, Dominko and Panczyk, 1999, 2000a, 2000b), temperature programmed desorption (Rudzinski, Borowieck, Dominko and Panczyk, 2000c), surface diffusion of CO on stepped Pt(111) surfaces (Elliott and Ward, 1997d), rate of electron transfer reactions between ions in solution (Ward, 1977), transport gas molecules across the interface between a liquid-gas solution and a gas mixture (Torri and Elliott, 1999, Ward, Rizk, and Tucker, 1982, Ward, Tikuisis and Tucker, 1986), ion permeation across biological membranes (Tikuisis and Ward, 1992, Skinner, Ward and Bardakjian, 1993, Bordi, Cametti and Motta, 2000), crystal dissolution (Bordi, Cametti and Naglieri, 1998), and osmotic transport (Dejmek and Ward, 1998).

The expression for the net evaporative flux, J_{LV} that is obtained from SRT is in terms of two thermodynamic functions, ΔS_{LV} and K_e , and, for a spherical interface, may be written (Ward, 2002, Ward and Fang, 1999) as

$$J_{LV} = 2K_e \sinh(\Delta S_{LV}/k) \quad (6)$$

where k is the Boltzmann constant. Local equilibrium is assumed valid in each phase; and if the chemical potential at the interface in phase- i is denoted as μ^i and the temperature by T^i , then the function ΔS_{LV} may be written as

$$\Delta S_{LV} = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) + h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \quad (7)$$

where h^V is the intensive enthalpy in the vapor phase at the interface. The thermodynamic function K_e may be expressed by

$$K_e = \frac{P_{\text{sat}}(T^L) \exp\left(\frac{v_{\text{sat}}^L}{kT^L} (P_e^L - P_{\text{sat}}(T^L))\right)}{\sqrt{2\pi mkT^L}} \quad (8)$$

where the pressure P_e^L is determined as the iterative solution of

$$P_e^L = P_{\text{sat}}(T^L) \exp\left[\frac{v_{\text{sat}}^L}{kT^L} [P_e^L - P_{\text{sat}}(T^L)]\right] + \frac{2\gamma^{LV}(T^L)}{R_0} \quad (9)$$

In equation (9), R_0 is the radius of curvature and γ^{LV} is the surface tension.

An approximate expression for ΔS_{LV} has been obtained from statistical thermodynamics (Ward and Fang, 1999) such that

$$\begin{aligned} \frac{\Delta s_{LV}}{k} &= 4 \left(1 - \frac{T^V}{T^L} \right) + \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \\ &\sum_{l=1}^3 \left(\frac{h\omega_l}{2k} + \frac{h\omega_l/k}{\exp(h\omega_l/kT^V) - 1} \right) \\ &+ \frac{v_{\text{sat}}^L}{kT^L} (P^L - P_{\text{sat}}(T^L)) + \\ &\ln \left[\left(\frac{T^V}{T^L} \right)^4 \left(\frac{P_{\text{sat}}(T^L)}{P^V} \right) \right] + \ln \left(\frac{q_{\text{vib}}(T^V)}{q_{\text{vib}}(T^L)} \right) \end{aligned} \quad (10)$$

where q_{vib} is the vibration partition function given by

$$q_{\text{vib}} = \prod_{l=1}^3 \frac{\exp(-h\omega_l/2kT)}{1 - \exp(-h\omega_l/kT)} \quad (11)$$

For the water molecule, the three measured fundamental vibrational frequencies are 1590, 3651 and 3756 s^{-1} (Fang and Ward, 1999b).

The expression for the evaporation flux may be viewed as depending on three sets of variables: the instantaneous values of the local equilibrium properties in each phase: T^L , T^V , P^V and R_0 (or P^L); the material properties of the

substance evaporating, P_{sat} , v_{sat}^L and γ^{LV} ; and the molecular properties of the evaporating substance, m , ω_L and q_{vib} . For water, all of the material and molecular properties have been previously and independently determined; thus the expression for the evaporation flux does not contain any fitting parameters.

To examine the expression for the evaporation flux, one would ideally measure the local equilibrium properties in each phase and the local evaporation flux and then compare the predicted flux with that measured at each point on the interface, but a method to measure pressure at a point has not yet proven possible, nor has measuring the local evaporation flux. However, the average evaporation flux can be determined using the apparatus shown schematically in *Figure 1*. The total evaporation flux can be measured with an accuracy of approximately $\pm 0.5\%$ (by measuring the movement of the syringe pump piston). The area of the interface, A_m , can be calculated by measuring the maximum interface height above the funnel mouth, x_m , and knowing the radius of the funnel mouth, z_0 . Thus,

$$A_m \approx \pi(z_0^2 + x_m^2) \quad (12)$$

This allows the average evaporation flux to be calculated. Although the temperature varies along the interface, as indicated in *Figure 3*, the total change in the interfacial liquid phase temperature, even at the very high evaporation rate of this experiment, is only a fraction of a degree-C. Thus, on the absolute temperature scale, this is a very small percentage change in temperature along the interface. Also, as indicated in this figure, the interfacial temperature discontinuity was almost uniform at 3.8°C. Thus the variation in the interfacial vapor temperature would also have been only a fraction of a degree-C. The vapor-phase pressure for each steady-state experiment was measured with an Hg manometer and cathetometer. The accuracy of the determination was ± 13.3 Pa (Fang and Ward, 1999a, 1999b, Ward and Fang, 1999, Ward and Stanga, 2001). It is unlikely that the variation in the interfacial pressure along the interface would have been measurable with this technique.

3. Examination of the Statistical Rate Theory Expression for the Phase Change Rate

If an average is taken of equations. (6) to (11), the result may be functionally written as

$$\bar{J}_{\text{ev}} = f(\bar{T}^L, \bar{T}^V, \bar{P}^V, R_0) \quad (13)$$

A sensitivity analysis of the variables appearing in the expression for the evaporation flux has

indicated an error of ± 13.3 Pa would change the calculated value of the evaporation flux by two orders of magnitude. Thus, since \bar{J}_{ev} , \bar{T}^V , \bar{T}^L and R_0 can more accurately be measured relative to \bar{P}^V , equation (13) was inverted to obtain an expression for \bar{P}^V such that

$$\bar{P}^V = f(\bar{T}^L, \bar{T}^V, \bar{J}_{ev}, R_0) \quad (14)$$

The values of \bar{P}^V calculated from equation (14) for the series of experiments reported by Ward and Fang (1999) are shown in *Figure 4*. The values of \bar{T}^L and \bar{T}^V measured on the center-line were used in the calculations. As may be seen in the figure, the calculated values of \bar{P}^V are in agreement with the measurements to within the measurement error.

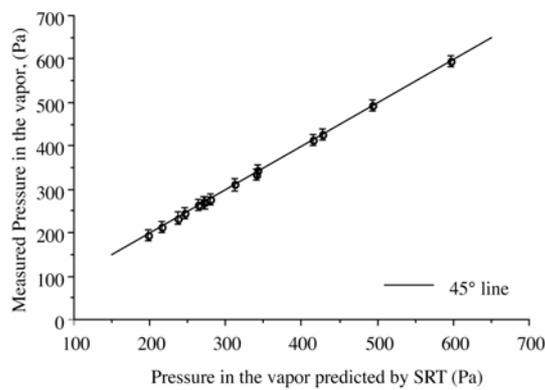


Figure 4. Pressure in the water vapor predicted by the SRT expression using measured values of temperature at the interface in the vapor and the liquid and the curvature of the interface at the measured rate of evaporation. The pressure difference between the predictions and measurements was within the measurements error of 13.3 Pa

When this result was obtained, it was thought that the close agreement may have resulted from some special property of the water molecule. Thus, two other substances were examined: octane (molecular weight 114) with its “straight chain”-like molecule with one methyl group (CH_3) at each end and six methylenes (CH_2) between, and methylcyclohexane (molecular weight 98) with its ring-like structure containing five methylenes and $\text{CH}-\text{CH}_3$ at one corner. Five experiments were performed with each of these substances.

For each, a temperature discontinuity was found at the interface during steady-state evaporation, and the direction of the discontinuity was the same as that of water: the interfacial vapor temperature was greater than that in the liquid in each case. Since the fundamental vibration frequencies of the octane

and methylcyclohexane molecules have not been measured, a prediction of the pressure at which a particular rate of evaporation is achieved cannot be as rigorous as with water. For these substances, vibration effects were neglected. equation (10) then simplifies to

$$\frac{\Delta s_{LV}}{k} = 4 \left(1 - \frac{T^V}{T^L} \right) + \frac{v_{\text{sat}}^L}{kT^L} (P^L - P_{\text{sat}}(T^L)) + \ln \left[\left(\frac{T^V}{T^L} \right)^4 \left(\frac{P_{\text{sat}}(T^L)}{P^V} \right) \right] \quad (15)$$

When the vapor-phase pressure that resulted in a particular average evaporation flux was predicted on the basis of equation (14), the results shown in *Figure 5* were obtained (Fang and Ward, 1999b). There were error bars associated with the data, but the error bars are not visible on this scale. Thus, as with the water, experiments carried out with the apparatus shown schematically in *Figure 1* did not indicate any discrepancy between the statistical rate theory predictions and the measurements.

However, it should be recalled that the statistical rate theory expression for the evaporation rate is very sensitive to the vapor-phase pressure (see below), and in these experiments, this pressure could only be measured with an accuracy of 13.3 Pa. A more accurate measurement is described below.

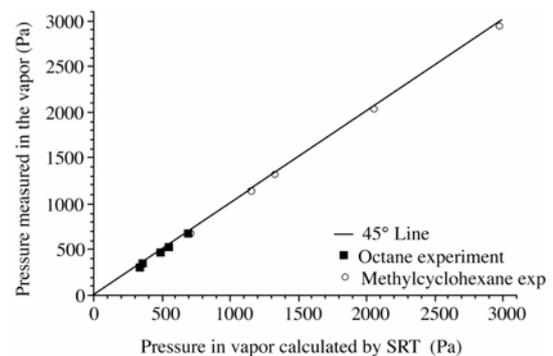


Figure 5. Pressure in the vapor predicted by the SRT expression using measured values of temperature at the interface in the vapor and the liquid and the curvature of the interface at the measured rate of evaporation

Another aspect of statistical rate theory has been examined by Ward and Stanga (2001) who noted that SRT can also be used to predict the rate of condensation. The net rate of condensation is simply the negative of J_{ev} . The apparatus shown in *Figure 1* was modified to that shown schematically in *Figure 6*. A series of experiments was performed in pairs. First, an

evaporation experiment was run and then, with water in the reservoir surrounding the funnel and maintained at a chosen temperature, the temperature in the liquid phase was inverted by cooling the liquid at the funnel throat. This produced condensation on the water interface maintained at the mouth of the funnel.

A temperature discontinuity was found to exist at the interface where condensation was taking place in each of the steady-state experiments, and the direction was the same as that found when water was evaporating: the interfacial temperature of the vapor was greater than that of the liquid. When statistical rate theory was used to predict the vapor-phase pressure at which water either condensed or evaporated at a particular rate, the results shown in *Figure 7* were obtained.

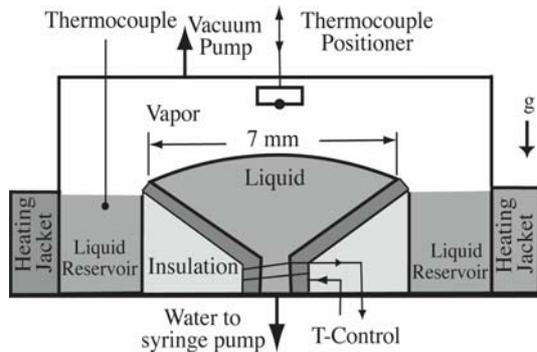


Figure 6. Schematic of the apparatus used in the condensation experiments performed by Ward and Stanga (2001)

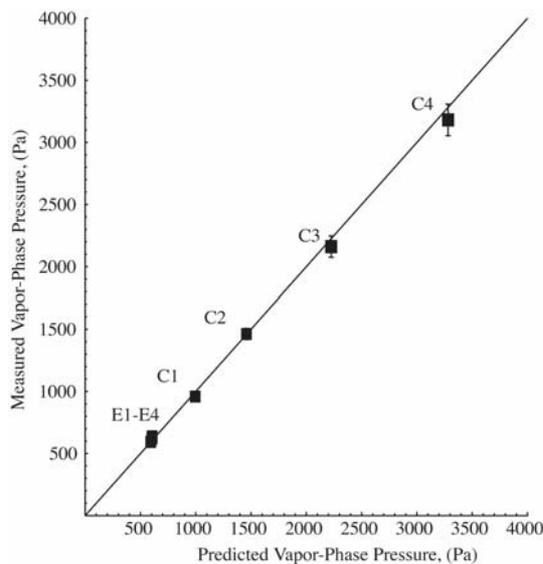


Figure 7. Comparison between the calculated vapor-phase pressure from SRT using the measured rate of evaporation (E1-E4) and condensation (C1-C4) to that measured

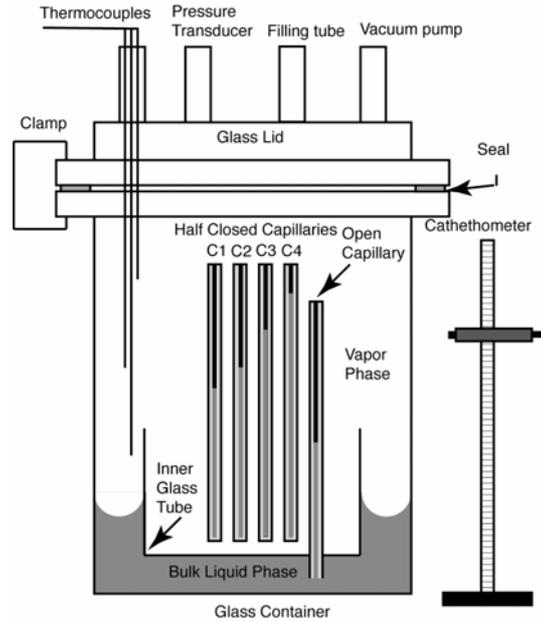


Figure 8. Schematic of the apparatus used in the evaporation studies of Rahimi and Ward (2004)

One of the major differences of the SRT expression for the rate of the phase change compared to classical kinetic theory is that based on SRT, the unidirectional liquid evaporation rate is predicted to depend on the conditions in both liquid and vapor phases whereas in classical kinetic theory it is usually assumed to be independent of the conditions in the vapor phase. As a result, based on evaporation studies using SRT, it was predicted that the rate of evaporation has an extraordinary sensitivity to the vapor-phase pressure (Fang and Ward, 1999a). Even a small change in the vapor-phase pressure on an order of magnitude of mPa is predicted to change the rate of evaporation. This sensitivity cannot be modelled by classical kinetic theory. To examine the validity of this prediction by SRT, an experimental study was performed (Rahimi and Ward, 2004).

The experimental apparatus is shown schematically in *Figure 8* and consisted of four half-closed capillaries which were open at the top and closed at the bottom. The capillaries were partially filled with liquid water to different heights. In a constant gravitational field, this meant that the vapor-phase pressure acting on the interface of each capillary was different; it was lowest at the capillary with the highest interface height and highest at the capillary with the lowest interface height. The difference between the highest and lowest interface position at the beginning of the experiment was only 42 mm corresponding to a change in vapor-phase pressure at the interface of about 3 mPa. Even though this pressure difference could not be

directly measured, it was still predicted to cause the capillary with the lowest vapor-phase pressure to have a larger evaporation rate.

The evaporation rate inside each capillary was measured by measuring the rate of change of the interface position. It was found that the capillaries were evaporating at different rates, in a way that the capillary with the lowest vapor-phase pressure (or highest interface position) was evaporating faster than the others (see *Figure 9*).

After several days, all the capillaries had the same interface position and they evaporated with the same rate from then on. The interface position inside each capillary is shown in *Figure 9*. The vapor-phase pressure acting on each interface was calculated from the measured rate of evaporation using the SRT expression for the evaporation flux. This calculated value was then compared with the calculated value from assuming equilibrium in the vapor phase and knowing the position of the interface inside each capillary compared to a reference bulk-liquid phase (see *Figure 8*). The results are listed in TABLE I. The agreement between the two values were found to be 0.004 Pa which is four orders of magnitude better than had been reported by others (Ward and Duan, 2004, Fang and Ward, 1999a, 1999b, Ward and Stanga, 2001).

4. Conclusion

Because of the disagreement of measured liquid and vapor-phase temperature at the

interface of an evaporating water system with that predicted from classical kinetic theory (and non-equilibrium thermodynamics), and the difficulties of determining the evaporation and condensation coefficients defined by classical kinetic theory, it seems that a new theoretical approach that can model the kinetics of the interface during phase change must be introduced. Based on the results of the studies discussed above it seems that statistical rate theory can model the conditions at the interface during evaporation better than classical kinetic theory. The evaporation rate of water predicted from SRT has no fitting parameter, an advantage when compared to other theoretical methods.

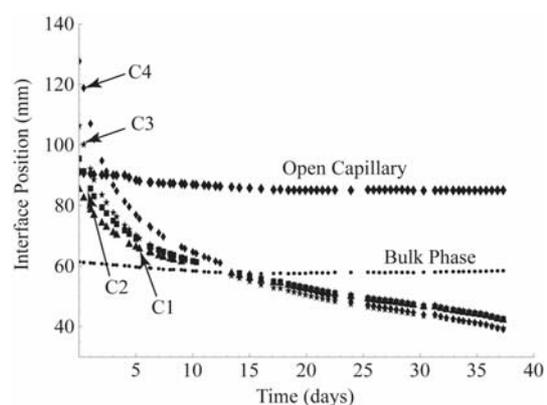


Figure 9. Liquid-vapor interface positions within capillaries and the bulk phase that were measured during the experiment of Rahimi and Ward (2004)

TABLE I. RESULTS OF THE EVAPORATION EXPERIMENT OF RAHIMI AND WARD (2004)

Day	Interface Position (mm)	Measured Evaporation Rate ($10^{-3} \text{mol/m}^2 \cdot \text{s}$)	Predicted Vapor Pressure from SRT (Pa) (± 0.0001)	Vapor Pressure from Equilibrium (Pa) ($\pm 10^{-6}$)	Agreement (Pa)
0	127.71	7.93	907.584	907.645	0.039
2	94.83	2.88	907.625	907.648	
4	81.37	1.50	907.636	907.648	
6	73.27	0.92	907.641	907.649	
10	64.67	0.52	907.644	907.650	
12	61.59	0.47	907.644	907.650	
16	55.96	0.34	907.645	907.650	
18	53.67	0.37	907.645	907.650	0.005
20	52.13	0.22	907.646	907.650	
22	50.02	0.31	907.646	907.650	
24	48.43	0.23	907.646	907.651	
26	46.61	0.18	907.647	907.651	
28	45.73	0.22	907.646	907.651	
30	43.98	0.29	907.646	907.651	
32	43.39	0.29	907.646	907.651	
34	41.92	0.20	907.646	907.651	
36	39.35	0.12	907.647	907.651	0.004

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