Stability of evaporating water when heated through the vapor and the liquid phases

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(Received 15 August 2009; revised manuscript received 11 January 2010; published 23 March 2010)

The stability of a water layer of uniform thickness held in a two-dimensional container of finite or semi-infinite extent is examined using linear stability theory. The liquid-vapor interface can be heated both through the liquid and through the vapor, as previously experimentally reported. The need to introduce a heat transfer coefficient is eliminated by introducing statistical rate theory (SRT) to predict the evaporation flux. There are no fitting or undefined parameters in the expression for the evaporation flux. The energy transport is parameterized in terms of the evaporation number, $E_{ev}$, that for a given experimental circumstance can be predicted. The critical Marangoni number for the finite, $Ma_{fr}$, and for the semi-infinite system, $Ma_{sc}$, can be quantitatively predicted. Experiments in which water evaporated from a stainless-steel funnel and from a polymethyl methacrylate (PMMA) funnel into its vapor have been previously reported. Marangoni convection was observed in the experiments that used the stainless-steel funnel but not with the PMMA funnel even though the Marangoni number for the PMMA funnel was more than 27 000. The SRT-based stability theory indicates that the critical value of the Marangoni number for the experiments with the PMMA funnel was greater than the experimental value of the Marangoni number in each case; thus, no Marangoni convection was predicted to result from an instability. The observed convection with the stainless-steel funnel resulted from a temperature gradient imposed along the interface.

DOI: 10.1103/PhysRevE.81.036318

PACS number(s): 47.20.Dr, 47.55.dm

I. INTRODUCTION

The conditions at the liquid-vapor interface during phase-change processes have proven to be surprisingly complex. Earlier experimental studies have indicated that on the center line of an axisymmetric liquid phase evaporating into its vapor while maintained at the circular mouth of a stainless-steel funnel, there are interfacial-temperature discontinuities in which the interfacial-vapor temperature is greater than that of the liquid and that the magnitude of the discontinuity depends on the evaporation flux [1–4]. Although these measurements were made with microthermocouples, the measurements have been used with statistical rate theory (SRT) [5] to predict the latent heat and constant pressure specific heat of water as functions of temperature that are in agreement with independently measured values of these properties [6]. We emphasize that the measured interfacial temperatures were used in the analysis, as opposed to temperatures measured at the funnel throat.

In contrast, Bond and Struchtrup used temperatures measured at the funnel throat as part of the inputs to their analysis to calculate the interfacial temperatures. They concluded that the energy flux is the dominant factor in determining the interfacial-temperature discontinuities and noted that the parameters in their analysis could be chosen to give good agreement with the experiments of Refs. [1,3] but that the classical-kinetic-theory-based Hertz-Knudsen and Schrage laws could not. The validity of the Hertz-Knudsen relation was also questioned by Holyst and Litniewski [7] who used molecular dynamics to examine the evaporation into a vacuum from a liquid film. They also examined the evaporation of an enclosed nanosized droplet and concluded that the temperature discontinuity depended, in part, on how the vapor interacted with the enclosing walls [8]. It remains an open question of how the evaporation and condensation coefficients of the Hertz-Knudsen relation may be determined other than empirically [9,10].

However, neither the study by Bond and Struchtrup nor those of Holyst and Litniewski included surface-tension-driven (or Marangoni or thermocapillary) convection in their analysis. Since in the experiments of references [1–3] the interfacial temperature was measured only on the funnel center line, from those measurements alone, it could not be established whether Marangoni convection existed. Even if buoyancy-driven convection was eliminated in these experiments, Marangoni convection could have contributed significantly to the energy transport in the bulk liquid [11–15].

In subsequent water evaporation experiments conducted with the same stainless-steel funnel, the interfacial temperatures were measured along the interface. In each experiment, the interfacial-temperature discontinuity persisted at positions along the interface, but as the interfacial evaporation flux was increased, a transition from quiescent water evaporation to evaporation with Marangoni convection occurred [16], but the mechanism by which the Marangoni convection was initiated was unclear (see below). Nonetheless, it was shown that an extraordinary amount of energy was transported by the Marangoni convection. The energy transport was defined in terms of the surface-thermal capacity, $c_{sf}$, and for one value of this surface property, the conservation-of-energy principle was satisfied for each of nine water evaporation experiments conducted over a range of conditions [17]. The value of $c_{sf}$ was confirmed in a second set of experiments in which the liquid-vapor interface was converted from spherical to cylindrical and the area increased by a factor of 4 [18]. It was hypothesized that the large value of

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due to the polar interactions of the water molecules. This hypothesis was supported by a third set of evaporation experiments that used D$_2$O as the test fluid. These experiments indicated the value of $c_r$ was similar to that of H$_2$O [19].

Since Marangoni convection is indicated to transport an extraordinary amount of thermal energy during water evaporation [20], it is important to determine under what conditions Marangoni convection is initiated in volatile liquids because it potentially offers a means of enhancing the efficiency of evaporation and thus has a number of important applications.

II. INITIATION OF MARANGONI CONVECTION DURING LIQUID EVAPORATION

In a recent paper, experiments were discussed in which water evaporated into its vapor while maintained at the circular mouth of a PMMA funnel with the funnel throat maintained at a constant temperature of $\sim 3.5$ °C [21]. No Marangoni convection was observed, even though the experimental Marangoni number was more than 12 times greater than the value of the Marangoni number predicted to be critical by the Pearson-Nield model [22,23]. Thus, on the basis of the Pearson-Nield model, Marangoni convection was expected, but no evidence of its presence was found.

In contrast, when H$_2$O and D$_2$O each evaporated into their respective vapors while maintained at the circular mouth of a stainless-steel funnel with the funnel throat also maintained at $\sim 3.5$ °C, Marangoni convection was clearly present [16,17,19], but the mechanism by which the convection was initiated was not clear. The value of the critical Marangoni number, $Ma_c$, was in reasonable agreement with that predicted by the Pearson-Nield model (81 compared with $\sim 147$), but the possibility of thermal conduction from the funnel throat through the funnel walls to the periphery of the funnel mouth, resulting in a temperature gradient along the interface from the periphery to the funnel centerline, could not be eliminated [21]. The thermal conductivity of stainless steel is $\sim 78$ times that of PMMA, the funnel designs were similar, and the temperatures at the funnel throats were very nearly the same in all experiments. If this hypothesis is accepted, it leaves unanswered the question of how a Marangoni number of 27 847 could have existed in the experiments with the PMMA funnel without Marangoni convection having been initiated by the mechanism proposed by Pearson [22].

It is argued in [21] that since the heat transfer coefficient is an arbitrary coefficient in the Pearson model—there is no way within that model to determine its value [24]—and it can not be zero if the liquid is evaporating, the Pearson model only applies to nonvolatile liquids in semi-infinite containers. The experimental support for the Pearson model has been found only with nonvolatile liquids, primarily silicone oil [25–27]. Chai and Zhang [28] considered volatile liquids, and proposed a modification of the expression for the critical Marangoni number that had been proposed by Pearson. Barnes and colleagues [29,30] used interferometry to examine the temperature profile in water as it evaporated steadily under hydrodynamic conditions where Pearson’s model indicated Marangoni convection would be present, but no evidence of Marangoni convection was found. Cammena et al. [31] also measured the temperature profile near the interface of evaporating water under hydrodynamic conditions that Pearson’s model would have suggested Marangoni convection should be present, but they did not find the evidence they expected. The existence of Marangoni convection in water was therefore questioned [32]. Since Marangoni convection in water has been clearly demonstrated [16,33], and the Pearson model is not strictly valid when evaporation is present, the relevant question is: under what conditions is Marangoni convection initiated when the liquid is evaporating?

Rosenblat et al. [34,35] considered a change in one of the parameters in the Pearson model. They took the system to have a finite aspect ratio (width over depth) but otherwise used an approximation similar to that of Pearson. They did not consider evaporation but allowed the liquid to be cooled using a heat transfer coefficient that they assigned arbitrary values. The side walls were taken to be adiabatic, but they were not then able to obtain an analytical solution with the no-slip boundary condition imposed at the walls. They introduced the “slippery” walls approximation, in which the fluid could not penetrate the walls, but could move parallel to them. Their prediction with these approximations was that as the aspect ratio is decreased, the critical Marangoni number is increased. The role of the aspect ratio in determining the stability of nonevaporating liquids was later investigated by several authors [36–38]. These investigators also used the “slippery side walls” approximation. Rather than use this approximation, we take the side walls to be isothermal and apply the no-slip condition at the walls.

Investigations of the effect of evaporation on the stability of a semi-infinite liquid layer have been made using the Hertz-Knudsen relation and assuming the interfacial temperatures of the liquid and vapor phases have the same value [39–42]. When the Hertz-Knudsen relation is adopted, it is necessary to introduce the accommodation coefficient. This parameter has proven to be difficult to determine experimentally. An investigation of the values reported for it has indicated it varies by several orders of magnitude [9]. There is strong evidence that during evaporation the interfacial temperatures are discontinuous.

Margaret et al. [43] also used the Hertz-Knudsen relation to describe an evaporating, semi-infinite liquid film, but allowed the interfacial temperature to be discontinuous. Their approach introduces four parameters that were ultimately combined into an “equivalent” Biot number. They concluded that as the temperature discontinuity was increased the system became less stable, but evaporation has a stabilizing influence on the liquid. The value of the critical Marangoni number found in this approach appears to be approximately the same as those of Pearson. Thus, there would be no indication from this approach of how a Marangoni number of more than 27 000 could exist without initiating convection.

Prosperetti and Plesset considered the stability of a semi-infinite evaporating liquid layer [44] in which the energy transport through the vapor phase was neglected. As justification, they say: “it is known [45,46] that in the presence of
any appreciable evaporation flux the temperature gradient in the vapor is very nearly zero.” When Refs. [45,46] are examined, no experimental evidence is found to support their claim. The evaporation of a thin film was considered by Bulrlbach et al. [47], and they also neglected the energy transport through the vapor in their analysis. A similar approach has been adopted in considering the evaporation of a sessile droplet [48,49]. In contrast, in [21], we described experiments with the stainless-steel funnel in which water evaporated with an average flux of 68 mg/m² s, and all of the energy to evaporate the liquid came through the vapor. When the evaporation flux was raised to 100 mg/m² s, the thermal conduction through the vapor was still more than that through the liquid: 133 compared with 117 W/m².

In the model developed below, we impose the conservation-of-energy condition at the liquid-vapor interface, and take the energy transport from both phases into account. We examine the stability of a liquid layer with a finite aspect ratio that is heated from below and is evaporating. We consider the stability for the evaporation flux does not contain any fitting account. We examine the stability of a liquid layer with a finite aspect ratio that is heated from below and is evaporating into its vapor. We eliminate the heat transfer coefficient at the liquid-vapor interface by introducing the SRT expression for the evaporation flux. Importantly, the SRT expression for the evaporation flux does not contain any fitting parameters, and it has been examined experimentally [5,6,50]. When it is incorporated in a linear stability analysis quantitative predictions of the critical Marangoni number, Ma₂, can be made from knowledge of the interfacial conditions. When the proposed theory is used to examine the experiments with the stainless-steel funnel, it is predicted that the observed Marangoni convection was not initiated by a Pearson-type instability. For the experiments with the PMMA funnel, it is predicted that the experimental Marangoni number is less than the predicted critical value. Hence, no Marangoni convection is predicted for the PMMA funnel, even though the Marangoni number was greater than 27 000 and none was observed.

III. PROBLEM DEFINITION

Consider an incompressible, gravity-free liquid of uniform depth, δ, that is confined in a two-dimensional container with lateral isothermal side walls separated by a distance of 2L. The fluid velocity,  \( \bar{V}(x,z,t) \), with component \( U(x,z,t) \) in the x direction and \( W(x,z,t) \) in the z direction, and the temperature, \( T(x,z,t) \), must satisfy the following conditions at the boundaries:

\[
\bar{V}(L,z,t) = \bar{V}(-L,z,t) = 0 ,
\]

\[ T(\pm L,z) = T^L_I , \]

where \( T^L_I \) is a constant and is equal to the temperature in the liquid at the interface before the system is subject to the perturbation,

\[ T(x, \delta,0) = T^L_I . \]

At the bottom surface of the container

\[ \bar{V}(x,0,t) = 0 , \]

and the temperature at this position is constant, \( T_{th} \), and has the same value for all values of \( x \) and \( t \),

\[ T(x,0,t) = T_{th} . \]

At the liquid-vapor interface, there is an evaporation flux, \( j_{ev} \), and if the enthalpy on the vapor side of the interface is denoted \( h^V_I \) and that on the liquid side as \( h^L_I \); then, if the temperature in both phases is uniform along the interface [17–20], conservation-of-energy gives

\[ -k^V(\nabla T)_{x=\delta} \cdot \mathbf{i} + k^L(\nabla T)_{x=\delta} \cdot \mathbf{i} = j_{ev}(h^V_I - h^L_I) , \]

where \( k^V \) and \( k^L \) are the thermal conductivities of the liquid and vapor phases, respectively. The change in enthalpies may be written in terms of the specific heats, \( c_p^L, c_p^V \), evaluated at the triple point temperature, \( T_{th} \), and the latent heat at this point, \( h_{fg} \) [16]:

\[ (h^V_I - h^L_I) = h_{fg}(T_{th}) + c_p^V(T_{th} - T_{th}) - c_p^L(T^L_I - T_{th}) , \]

where the interfacial-vapor temperature is denoted \( T^V_I \).

The SRT expression for the evaporation flux [1,3,5,6,50,51] may be written in terms of the change in entropy that results from a molecule transferring from the liquid phase to the vapor phase, \( \Delta s_{LV} \), and the equilibrium exchange rate between the liquid and vapor phases, \( K_x \). If the chemical potentials of the molecules in the liquid and the vapor phases at the interface are denoted \( \mu^L_I, \mu^V_I \), then the net rate of molecular flux from the liquid to the vapor phase is given by [5,52]

\[ j_{ev} = 2K_x \sinh \left( \frac{\Delta s_{LV}}{k_b} \right) , \]

where \( k_b \) is the Boltzmann constant, and \( \Delta s_{LV} \) may be written as

\[ \Delta s_{LV} = \left( \frac{\mu^L_I}{T^L_I} - \frac{\mu^V_I}{T^V_I} \right) + h_I^L \left( \frac{1}{T^L_I} - \frac{1}{T^V_I} \right) . \]

We assume the local equilibrium approximation is valid for the flat liquid-vapor interface that we consider, and apply statistical thermodynamics to determine the expressions for \( \mu^L_I \) and \( h^L_I \). Provided the isothermal compressibility \( \kappa_T \) and the saturation-vapor pressure, \( P_s \), satisfies

\[ \kappa_T |P^V - P_s| \ll 1 , \]

for the triatomic water molecule, with the internal molecular vibration frequencies (phonons) denoted as \( \omega_i \), the expression for \( \Delta s_{LV} \) may be written as [3,5,52]

\[
\Delta s_{LV} \frac{k_b}{h_{\omega_1}} = 4 \left( 1 - \frac{T^V_I}{T^L_I} \right) + \left( \frac{1}{T^L_I} - \frac{1}{T^V_I} \right) \sum_{i=1}^{3} \frac{h_{\omega_i}}{2k_b} \left( \frac{\omega_i}{k_b} \exp(h_{\omega_i}/k_b T^L_I) - 1 \right) + \frac{v_f}{k_b} \left( \frac{P_f(T^L_I)}{P_s} \right) \left( \frac{P_s(T^V_I)}{P_f(T^V_I)} \right) \left( \frac{q_{eb}(T^V_I)}{q_{eb}(T^L_I)} \right) .
\]
\[ q_{\text{evap}}(T) = 3 \sum_{i=1}^{\infty} \frac{\exp(-\tilde{h} \omega_i^2 k_b T)}{1 - \exp(-\tilde{h} \omega_i k_b T)}, \] (11)

and

\[ K_e = \frac{P_e(T_e^i) \exp[(\nu_j/\nu_e)(P_e/P_e(T_e^i) - 1)]}{\sqrt{2 \pi m_v k_b T_e^i}}, \] (12)

where \( \nu_j \) is the molecular specific volume, \( m_v \) is the molecular weight of the fluid, and \( P_e \) is the pressure in the liquid and vapor phases at the interface.

When Eqs. (10) and (12) are combined with Eq. (8), one obtains an expression for the evaporation flux that is in terms of the instantaneous interfacial properties \( T_e^i, T_e^f, P_e \), the material properties of water \( P_e(T_e^i), \nu_e \), and the molecular phonons of the water molecule, \( \nu_i \). We take the material properties and the internal molecular vibration frequencies to be known from previous, independent experiments. Note that there are no free or fitting parameters in the SRT equation for \( E_e \).

Interface observed in Table I

\[ \frac{\partial \delta}{\partial t} = (\tilde{V}(x,0,t) - \tilde{V}(x,\delta,t)) \cdot \hat{z}, \] (13)

and at the liquid-vapor interface

\[ \tilde{V}(x,\delta,t) \cdot \hat{z} = \nu_j \tilde{e}_v. \] (14)

The liquid film is maintained of constant thickness by fluid entering the container uniformly at the bottom,

\[ \tilde{V}(x,0,t) \cdot \hat{z} = \nu_j \tilde{e}_v. \] (15)

Thus, as seen from Eq. (13), \( \delta/t \) is constant, an approximation that is consistent with recent experimental observation [53].

If \( \gamma_f \) denotes the change in surface tension with temperature and \( \eta \) the dynamic viscosity, a stress balance at the interface requires

\[ \eta \left( \frac{\partial \tilde{U}}{\partial z} \right)_{\zeta = \delta} = \gamma_f \left( \frac{\partial \tilde{T}}{\partial x} \right)_{\zeta = \delta}. \] (16)

If the pressure is denoted as \( P(x,z,t) \), the conservation of mass, linear momentum, and energy requires

\[ \tilde{\nabla} \cdot \tilde{\nabla} = 0, \] (17)

\[ \frac{\partial \tilde{V}}{\partial t} + (\tilde{V} \cdot \tilde{\nabla}) \tilde{V} = -\frac{1}{\rho} \tilde{\nabla} p + \nu \tilde{\nabla}^2 \tilde{V}, \] (18)

\[ \frac{\partial \tilde{T}}{\partial t} + (\tilde{V} \cdot \tilde{\nabla}) T = \alpha \tilde{\nabla}^2 T, \] (19)

where \( \nu \) is the kinematic viscosity, \( \rho \) is the liquid density and \( \alpha \) is the liquid thermal diffusivity. Viscous dissipation is neglected in Eq. (19) since we only consider an infinitesimal perturbation from the initial state in which there is no flow, but only energy transport by thermal conduction.

IV. EXPERIMENTAL OBSERVATIONS

In the experiments reported in [21], the evaporation took place either from a stainless steel or a PMMA funnel. The throat diameter in both cases was 1.09 mm, giving \( L \) a value of 0.54 mm. The funnel mouth was 3.55 mm above the throat, and we take this height to be the value of \( \delta \) in each experiment. Thus, the aspect ratio, \( A \), was 0.15 in these experiments. The experiments were performed under steady-state conditions and the measured temperatures on the funnel center lines at the liquid-vapor interface are listed in Tables I and II. Also, for each experiment, the interface was investigated for the presence of Marangoni convection (see Interface observed in Table I). The temperatures in these tables were used to calculate the experimental Marangoni numbers using the properties listed in the Appendix.

V. INITIAL STATE OF THE EVAPORATING LIQUID

At the initial time, we suppose the liquid is evaporating steadily, and is stably stratified. For water, this means the temperature at the interface is less than the \( \sim 3.5 \) °C throat temperature. At the highest evaporation rate, the Reynolds number of the flow entering the throat of the stainless-steel funnel was \( 5 \times 10^3 \) and that for the PMMA funnel was \( 1.8 \times 10^4 \). Thus, we neglect the flow entering the funnels, and take the \( z \) component of the liquid velocity at the throat as approaching zero. At the liquid-vapor interface, the liquid speed perpendicular to the interface would be even smaller than that at the throat; thus we neglect the flow at this interface as well. As indicated by Eqs. (13)–(15), \( \delta \) is constant in time, and that the initial state may be approximated as a steady conduction state with negligible convection.
the constant $H^{0}$jecting it to a perturbation. Now we investigate the vapor as being time independent. We take the temperature gradient in the liquid film depth and the temperatures in the liquid at the liquid-vapor interface and at the bottom of the system.

From Eqs. (13)–(17) are linearized by introducing the perturbations and nondimensionalized by scaling the length with $\delta$, time with $\delta^2/\nu$, velocity with $\alpha/\delta^2$, pressure with $\rho\nu\alpha/\delta^2$ and temperature with $\beta\delta$, one finds

$$\nabla \cdot \mathbf{\tilde{V}}_l = 0,$$

(29)

and the difference in the interfacial enthalpies may be expressed as

$$(h^V_l - h^F_l) = (h^V_0 - h^F_0) - c^L\theta(x, \delta t).$$

(28)

The expression for $j_{ev}$ is given in Eqs. (8)–(12).

If Eqs. (13) and (17)–(19) are linearized by introducing the perturbations and nondimensionalized by scaling the length with $\delta$, time with $\delta^2/\nu$, velocity with $\alpha/\delta^2$, pressure with $\rho\nu\alpha/\delta^2$ and temperature with $\beta\delta$, one finds

$$\nabla \cdot \mathbf{\tilde{V}}_l = 0,$$

(29)

$$\frac{\partial \mathbf{\tilde{V}}_l}{\partial t} = \nabla p + \nabla^2 \mathbf{\tilde{V}}_l,$$

(30)
Thus, temperature perturbation also vanishes there, where Pr is the Prandtl number, $v/\alpha$.

We can eliminate the pressure term by taking the curl of Eq. (30) which yields the vorticity equation. After taking the curl of the vorticity equation and combining the result with the continuity equation, one finds [54]

$$\nabla^2 \left( \frac{\partial \theta}{\partial t} - \nabla^2 \right) w = 0. \tag{32}$$

The linearized energy equation in the perturbed state may be written as

$$\left( Pr \frac{\partial}{\partial t} - \nabla^2 \right) \theta = -w. \tag{33}$$

At $z=0$, we assume the perturbation vanishes

$$w(x,0,t) = 0, \tag{34}$$

and since $u(x,0,t)$ vanishes for all values of $x$, so does

$$\left( \frac{\partial u}{\partial x} \right)_{z=0} = 0. \tag{35}$$

Then from continuity

$$\left( \frac{\partial w}{\partial z} \right)_{z=0} = 0. \tag{36}$$

If the aspect ratio, $A$, is defined as $L/\delta$, then on the isothermal side walls, $x=\pm A$, one finds from Eqs. (2) and (26)

$$\theta(\pm A,z,t) = 0. \tag{37}$$

Similarly, from Eqs. (1) and (24),

$$w(\pm A,z,t) = 0. \tag{38}$$

We write the solution to the continuity equation in terms of the stream function $\psi$,

$$w = \frac{\partial \psi}{\partial x}, \tag{39}$$

and

$$u = \frac{\partial \psi}{\partial z}, \tag{40}$$

then Eq. (1) gives

$$\left( \frac{\partial \psi}{\partial z} \right)_{x=\pm A} = \left( \frac{\partial \psi}{\partial x} \right)_{x=\pm A} = 0. \tag{41}$$

Thus, $\psi$ is a constant and we take the constant to be 0,

$$\psi(\pm A,z,t) = 0. \tag{42}$$

Since $T$ has the value $T_{th}$ at $z=0$, as seen from Eq. (26), the temperature perturbation also vanishes there,

$$\theta(x,0,t) = 0. \tag{43}$$

For the evaporation fluxes before the onset of convection, one finds from Eqs. (13)–(15) that for $\delta$ to remain constant

$$w(x,1,t) = 0. \tag{44}$$

From Eqs. (16) and (29)

$$\left( \frac{\partial^2 w}{\partial z^2} \right)_{z=1} = -Ma \left( \frac{\partial^2 \theta}{\partial x^2} \right)_{z=1}, \tag{45}$$

where the Marangoni number $Ma$ is given by

$$Ma = \frac{\gamma e B_\ell^2}{\eta \alpha}. \tag{46}$$

After substituting Eqs. (27) and (28) into Eqs. (6) and (7), linearizing, and nondimensionalizing, the conservation-of-energy equation becomes

$$E_{ev} \left( \frac{\partial \theta}{\partial \zeta} \right)_{\zeta=1} + \theta(x,1,t) = 0, \tag{47}$$

where the evaporation number $E_{ev}$ is defined

$$E_{ev} = \frac{\kappa}{\delta} \left[ (h_0 - h_{\ell}) \left( \frac{\partial h_{je}}{\partial T} \right)_I - C_{\ell}/\theta_{ev} \right]^{-1}. \tag{48}$$

We note that $E_{ev}$ may be evaluated for the given instantaneous interfacial properties ($T_{th}, T_{th}, P_{th}$) using SRT, Eqs. (8)–(12), and the liquid-layer thickness. Thus, there is no need to introduce a phenomenological heat transfer coefficient [55,56] into the analysis.

A. Conditions for marginal stability of a finite-sized system

We suppose $w(x,z,t)$ and $\theta(x,z,t)$ to be of the form

$$w(x,z,t) = -w_s(x,z) \exp(\alpha t), \tag{49}$$

$$\theta(x,z,t) = \theta_s(x,z) \exp(\alpha t), \tag{50}$$

where $\alpha$ is the growth rate and is in general complex. Then

$$\frac{\partial w}{\partial t} = -w_s \alpha \exp(\alpha t), \tag{51}$$

$$\frac{\partial \theta}{\partial t} = \theta_s \alpha \exp(\alpha t). \tag{52}$$

As indicated by Eq. (20), in the initial state $w_s$ is equal zero, but now we wish to determine the expression for $w_s$, $\theta_s$ in the state of marginal stability. This state exists when Re($\alpha$) vanishes. We will show that when this state is reached Im($\alpha$) is also zero, indicating the marginally stable state is stationary in time [57–59] for the finite aspect ratio problem defined in the previous section.

When $w(x,z,t)$ and $\theta(x,z,t)$ are substituted into Eqs. (32) and (33), one finds

$$\sigma \nabla^2 w_s - \nabla^4 w_s = 0, \tag{53}$$

$$\sigma Pr \theta_s - \nabla^2 \theta_s = w_s. \tag{54}$$

If the real and imaginary portions of Eq. (51) are considered separately, one finds

$$Re(\alpha) \nabla^2 w_s - \nabla^4 w_s = 0, \tag{55}$$
It will be shown below that for Eqs. (53) and (55) to be satisfied, \( \text{Im}(\sigma) \) must vanish; thus, Eqs. (56) and (57) must be solved to determine \( w_s \) and \( \theta_s \) in the marginally stable state.

The boundary conditions in the marginally stable state at \( x=\pm A \) are

\[
w_s(\pm A, z) = 0;
\]

and since

\[
w_s = -\frac{\partial \psi_s}{\partial x},
\]

and

\[
u_s = \frac{\partial \phi_s}{\partial z},
\]

from Eqs. (37) and (42), we have at \( x=\pm A \),

\[
\theta_s(\pm A, z) = 0,
\]

\[
\phi_s(\pm A, z) = 0.
\]

At \( z=0 \), the boundary conditions, Eqs. (34), (36), and (43), give

\[
w_s(x, 0) = \left( \frac{\partial w_s}{\partial z} \right)_{z=0} = 0,
\]

\[
\theta_s(x, 0) = 0.
\]

And at \( z=1 \), one finds from Eqs. (44), (45), (47), and (50) that in the marginally stable state

\[
w_s(x, 1) = 0,
\]

\[
\left( \frac{\partial^2 w_s}{\partial z^2} \right)_{z=1} = \text{Ma} \left( \frac{\partial^2 \theta_s}{\partial x^2} \right)_{z=1},
\]

\[
E_{ve} \left( \frac{\partial \theta_s}{\partial z} \right)_{z=1} + \theta_s(x, 1) = 0.
\]

For the system to be marginally stable, one condition that the velocity perturbation in the \( z \) direction must satisfy is given by the biharmonic equation [Eq. (56)]. The corresponding condition that the temperature perturbation must satisfy may be seen in Eq. (57). The boundary conditions for these perturbations are listed in Eqs. (58)–(65).

**B. Conditions for marginal stability of a system that is infinite in the horizontal direction**

For comparison with the results obtained when the system is finite, we first consider a system with infinite aspect ratio (i.e., \( A \rightarrow \infty \)). Following the procedure outlined above, one is again led to Eqs. (56) and (57), but the boundary conditions are now different. There is no longer an eigenvalue problem in the horizontal direction. We suppose the solution is periodic in this direction with wave number \( k \),

\[
w_s = f(z) \cos(kx),
\]

and that

\[
\theta_s = g(z) \cos(kx).
\]

Substituting the forms of \( w_s \) and \( \theta_s \) into Eqs. (56) and (57) gives

\[(D^2 - k^2)^2 f(z) = 0,
\]

and

\[(D^2 - k^2) g(z) = -f(z).
\]

At \( z=0 \), Eqs. (34), (36), and (43) now give

\[f(0) = \left( \frac{\partial f}{\partial z} \right)_{z=0} = 0,
\]

\[g(0) = 0.
\]

And at \( z=1 \), one now finds from Eqs. (44), (45), and (47)

\[f(1) = 0,
\]

\[E_{ve} \left( \frac{\partial g}{\partial z} \right)_{z=1} + g(1) = 0.
\]

The problem thus reduces to the solution of ordinary differential equations and once the solution is available, the Marangoni number can be obtained from Eq. (73),

\[ \text{Ma}_{\infty} = \frac{a[(k^2 - 2K)k \cosh(k) + (1 - K)k^2 \sinh(k)]}{g(1)k^2},
\]

where

\[ K = \frac{k \cosh(k) - \sinh(k)}{\sinh(k)},
\]

and after simplification \( g(1) \) is given by

\[ g(1) = a \frac{E_{ve}(-k^3 \cos(k) + (\sinh(k))^2)}{4k^2(E_{ve} k \cosh(k) + \sin(k))}. \]

Note that the arbitrary constant \( a \) divides out in the final expression for the Marangoni number.
As seen in Eqs. (75)–(77), $M_{ac}$ depends on two parameters, $E_{ev}$ and the wave number $k$. In Fig. 1, for the experimental values of $E_{ev}$ listed in Table II, $M_{ac}$ is shown as a function of the wave number. The most unstable mode, $k_c^*$, for each value of $E_{ev}$ corresponds to $k_c^* = 3$. For the most unstable mode, as observed in Fig. 1, the critical value of the Marangoni number, $M_{ac}$, is determined by the value of $E_{ev}$, and as $E_{ev}$ is increased $M_{ac}$ is decreased. In Table II, it is seen that as $E_{ev}$ is increased, the evaporation flux increases. Thus, the prediction is that evaporation destabilizes the system in the sense that evaporation reduces the critical Marangoni number.

In the experiments conducted with the PMMA funnel (Table II), the evaporation flux was progressively raised. For a semi-infinite liquid that had the measured values of $T_f^*$, $T_f^*$, and $P$ at the interface, the calculated value of the critical Marangoni number, $M_{ac}$, is listed, along with the calculated value of the Marangoni number for each experiment, $M_{ac,exp}$. Note that for the experiments with the lower evaporation fluxes (experiments 1–3) $M_{ac,exp} > M_{ac}$. Thus, for these experiments the prediction is that there would be no transition from a quiescent to a convecting interface, but if the liquid were approximated as semi-infinite, in experiments 4 and 5, $M_{ac} < M_{ac,exp}$. Thus, the prediction is that if the liquid film were semi-infinite, Marangoni convection would have occurred in experiments 4 and 5. However, Marangoni convection was not observed in these cases either, as indicated by the last line of the experimental conditions (Table II). This suggests that the finite size of the liquid phase was important for these two experiments.

**VII. EXPRESSION FOR $w_y$ FOR A MARGINALLY STABLE SYSTEM THAT HAS A FINITE ASPECT RATIO**

For a system with a finite aspect ratio, the solution to Eq. (56) may be expressed as

$$ w_y = \sum_{n=1}^{\infty} \left[ \sinh k_n z + K_n \sinh k_n z - k_n z \cosh k_n z \right] $$

$$ \times \left( C_n \sin k_n x + D_n \cos k_n x \right), $$

(78)

where $C_n$ and $D_n$ are arbitrary constants, and $k_n = n \pi / A$, 

(79)

and

$$ K_n = \frac{k_n \cosh k_n - \sinh k_n}{\sinh k_n}. $$

(80)

The no-slip boundary conditions that we consider are given in Eqs. (58) and (60). The conditions at the liquid-vapor interface and at the heating surface are given in Eqs. (60) and (61). For the system that we consider, $D_n$ vanishes, but we note that if slip were allowed at $x = \pm A$ [34, 36–38], $D_n$ would be nonzero, and the cos $k_n$ modes would be the only ones present. One may verify that $w_y$ with $D_n = 0$ is the exact solution for the biharmonic equation with the boundary conditions given in Eqs. (58), (60), (61), and (63).

Since we now have the expression for $w_y$, Eq. (78), we can complete the proof that the marginally stable state is stationary. From the expression for $w_y$, one finds

$$ \nabla^2 w_y \neq 0; $$

thus, from Eq. (53),

$$ \text{Im}(\sigma) = 0. $$

Hence, the marginally stable state is stationary in time since both $\text{Re}(\sigma)$ and $\text{Im}(\sigma)$ vanish.

From the definition of the stream function, one finds for each mode

$$ w_y^n = - \frac{\partial \psi'^{n}}{\partial x}. $$

If $w_y^n$ is integrated, first from $-A$ to $x$ and then from $A$ to $x$ since $\psi'(\pm A, z) = 0$, one finds

$$ \psi'^{n} = \int_{-A}^{x} w_y^n(x', z) dx' = - \int_{A}^{x} w_y^n(x', z) dx'. $$

(81)

Also, by integrating the continuity equation and applying the boundary conditions given in Eq. (60)

$$ u_y^n(x, z) = - \int_{-A}^{x} \frac{\partial \psi'^{n}}{\partial z}(x', z) dx' = - \int_{-A}^{x} \frac{\partial \psi'^{n}}{\partial z}(x', z) dx'. $$

(82)

Note that the expression for $u_y^n$ may be constructed from the expression for $w_y^n$. From Eqs. (78) and (82), one finds

$$ u_y^n(x, z) = \frac{C_n}{k_n} (\cos n \pi - \cos k_n x)((k_n - k_n z) \sinh k_n z + (k_n k_n z) \cosh k_n z). $$

(83)

Note $u_y^n(x, z)$ is an even function of $x$, and at $z = 1$, the direction of the flow is determined by the sign of $((-1)^n \cos k_n x)$. For $-A < x < A$, the sign of this term is determined by the sign of $(-1)^n$. Thus, for each mode, the surface flow is
unidirectional, but the direction changes for successive modes. Using the data in Table II corresponding to the highest value of $M_a_{exp}$, experiment 5, this behavior is demonstrated in Figs. 2–4 and has not been previously predicted. This mode was obtained from the new expression for the $z$ component of the perturbed velocity [Eq. (78)].

As may be seen from Eqs. (78) and (83) for $x = 0$, $w_0(x, z)$ is zero for all modes, but $u_0'(0, z)$ is zero only for the even modes. Thus, as indicated in Fig. 2 for an even mode, the centerline is a stagnation line. Apart from the stagnation lines, the other positions where both $w_0''$ and $u_0'$ vanish are at the center of the rolls.

For a given $A$ and $n$, the value of $k_n$ can be determined from Eq. (79) and the positions, $z_i$, where $u_0'(x, z_i)$ vanishes may be obtained from Eq. (83) for any $x$.

\[
\sin(k_{\mu} x_i) = 0. \quad (85)
\]

At the positions other than the stagnation lines where $u_0'(x, z_i)$ and $w_0''(x, z_i)$ vanish are illustrated in Figs. 2–4 as the roll centers. The values of $x_i$ and $z_i$ corresponding to the roll centers calculated by the outlined procedure are listed in Table III. If the boundary condition at the side walls had required slip, then $w_0''$ would have been expressed in terms of $\cos k_{\mu} x$ modes. These modes do not exhibit unidirectional surface flow [34].

The expression for $\psi''_0(x, z)$ may be obtained from Eq. (81),

\[
\psi''_0(x, z) = \frac{C_n}{\kappa_n} \cos(n \pi - 2z) \times (k_{\mu} \cosh k_{\mu} z - (1 + k_{\mu} \sinh k_{\mu} z)). \quad (86)
\]

The position on the liquid-gas interface where $u_0''$ has its maximum value, $x_{0\mu}$, may be determined from

**TABLE III. Positions of roll centers.**

<table>
<thead>
<tr>
<th>$n$</th>
<th>$A$</th>
<th>$x_0$</th>
<th>$z_0$</th>
<th>$(x_1, z_1)$</th>
<th>$(x_2, z_2)$</th>
<th>$(x_3, z_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.68</td>
<td>(0.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.68</td>
<td>(-1, 5)</td>
<td>(1, 5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.68</td>
<td>(-3.3, 0.68)</td>
<td></td>
<td>(0, 0.68)</td>
<td>(3.3, 0.68)</td>
</tr>
</tbody>
</table>
\[
\left( \frac{\partial u_s^i(x,1)}{\partial x} \right)_{x=x_0} = 0. \tag{87}
\]

Then
\[
u^{\text{max}}_s = u_s(x_0,1).
\]

The speeds may now be scaled in terms of \( u^{\text{max}}_s \) and the constant \( C_n \) eliminated. As seen in Figs. 2–4, the \( x \)-component of velocity, \( u_s \) (lower panel) is symmetric about \( x \) equal to zero, but the flow at \( z=1 \) is unidirectional.

**VIII. EXPRESSION FOR \( \theta_1 \) IN THE STATE OF MARGINAL STABILITY**

The expression for the temperature perturbation \( \theta_1 \) must satisfy Eq. (57) and the corresponding boundary conditions Eqs. (60), (62), and (65). We choose to represent \( \theta_1 \) in a sine series,
\[
\theta_1 = \sum_{s=1}^{\infty} C_s g_s(z) \sin k_s x, \tag{88}
\]

where \( C_s \) are the coefficients of the expansion. Note that \( \theta_1 \) satisfies the isothermal boundary conditions at the sidewalls. Moreover each mode of \( \theta_1 \) corresponds to a mode of \( w_s \), since the latter is also a sine series. Note that \( w_s \) and \( \theta_s \) are related through Eq. (57).

This choice of \( \theta_1 \) and the expression of \( w_s \) from Eq. (78) are inserted into Eq. (57) to yield
\[
\sum_{s=1}^{\infty} C_s \left[ \frac{d^2 g_s}{dz^2} - k_s^2 g_s \right] \sin k_s x
= - \sum_{s=1}^{\infty} C_s \left[ \sinh k_m z + K_m \sinh k_m z \right]
- k_m \sinh k_m z \sin k_m x. \tag{89}
\]

After multiplying both sides by \( \sin(n \pi x / A) \) and integrating over \( x \) from \( x=-A \) to \( x=+A \), on one obtains,
\[
\left( \frac{d^2 g_n}{dz^2} - k_n^2 g_n \right)
= - \left[ \sinh(k_n z) + K_n \sinh(k_n z) \right]
- k_n \sinh(k_n z). \tag{90}
\]

The general solution of the Eq. (90) may now be written as
\[
g_n(z) = C_1 \cosh(k_n z) + C_2 \sinh(k_n z) - \frac{K_n}{4k_n^2} (k_n^2 \cosh(k_n z) - k_n \sinh(k_n z))
- z \sinh(k_n z)) + \frac{1}{4k_n} (k_n^2 \sinh(k_n z) - 3z \cosh(k_n z)). \tag{91}
\]

When this expression for \( \theta_1 \) is required to satisfy the boundary conditions at the top and bottom surfaces,
\[
E_{ev} \frac{d g_n(1)}{dz} = - g_n(1), \tag{92}
\]

one obtains \( \bar{C}_1 = 0 \) and
\[
\bar{C}_2 = \frac{1}{4k_n^2 (k_n E_{ev} \cosh(k_n) + \sinh(k_n))} \left[ E_{ev} (k_n K_n \cosh(k_n)
+ k_n^2 K_n \sinh(k_n) - K_n \sinh(k_n) + k_n^2 \sinh(k_n) - k_n^3 \cosh(k_n)
+ 3k_n \cosh(k_n)) + (k_n K_n \cosh(k_n) - K_n \sinh(k_n)
- k_n^2 \sinh(k_n) + 3k_n \cosh(k_n)) \right]. \tag{93}
\]

Thus, the expression for \( \theta_1 \) has now been obtained in terms of the parameters \( E_{ev} \) and \( A \). The value of \( E_{ev} \) was calculated from the experimental results listed in Table II using Eq. (48). The values of \( A \) for each case are given in the captions of Figs. 2–4. The temperature perturbation at the interface is shown in the upper panel of each of these figures. Note that for the second mode, Fig. 2, the temperature gradient near the side walls does not determine the direction of the surface velocity. The viscous effects arising from the side walls have an influence on the direction of the surface flow. For the second mode, Fig. 2, in the core of the fluid, the reversal of the temperature gradient, results in a stagnation point of the flow at the centerline. There are, however, two stagnation points for the third mode (Fig. 4). An investigation indicates the number of stagnation points depends on the mode. For the \( n^{th} \) mode, \( n-1 \) stagnation points are predicted in the flow.

**IX. CRITICAL MARANGONI NUMBER FOR FINITE-SIZED SYSTEMS**

The critical Marangoni number for a finite-sized system is determined from the only boundary condition that has not yet been satisfied. For this type of system, Eq. (64), the tangential stress boundary condition at the interface (\( z=1 \)) for each mode may be expressed as
\[
\frac{\partial^2 w_n}{\partial z^2} = M_n \frac{\partial^2 \theta_n}{\partial x^2}, \tag{94}
\]

The expression for \( w_n \) is given in Eq. (78) and the expression for \( \theta_n \) in Eqs. (88)–(93). After putting these expressions into Eq. (94), one finds
\[
M_n = \frac{[(k_n^2 - 2K_n)k_n \cosh(k_n) + (1 - K_n)k_n^2 \sinh(k_n) \cosh(k_n)]}{k_n^2}. \tag{95}
\]

Using this expression, calculating the value \( E_{ev} \) for experiment 5 of Table II, choosing a mode (or value of \( n \)), \( M_n \) may be plotted as a function of the aspect ratio \( A \). The type of results found is illustrated in Fig. 5 for the first eight modes. The horizontal dashed line in this figure indicates the value of the critical Marangoni number obtained for a semi-infinite liquid layer when \( E_{ev} \) has a value of \( 1.473 \times 10^{-3} \) (see Fig. 36318-10)}
1). Note that at certain values of the aspect ratios, $A$, the critical Marangoni number for the finite system, $M_{a,cr}$, is equal to that for the semi-infinite system $M_{a,cr}$. This occurs when $A$ is such that the critical wave number of the horizontal motion, $k_c=n\pi/A$, is equal to that of the semi-infinite system, $k_c$, for that value of $E_{ev}$. We denote this value of the aspect ratio as $A_{\infty}$. For the experiments described in Table II, $k_c \approx 3$. The value of $A_{\infty}$ may, in general, be written as

$$k_c = k_{0c}.$$

$$A_{\infty} = \frac{n\pi}{k_c}.$$  

(96)

When $A > A_{\infty}$ or $A < A_{\infty}$, the system is stabilized compared to that when $A = A_{\infty}$. For the funnel used for the experiments described in Table II, $A$ is approximately 0.15. For this value of $A$ and the values of $E_{ev}$ calculated for experiments 4 and 5 of this table, the value of $M_{a,cr}$ is greater than $M_{a,exp}$, thus the transition from quiescent to a convecting interface is not predicted for these experiments either.

At certain values of $A$, two modes are equally unstable, and there is the possibility of mode switching, as has been observed experimentally by Johnson and Narayanan [60]. As indicated in Figs. 2–4, a change in the mode changes the flow pattern.

**X. DISCUSSION AND CONCLUSION**

A linear stability analysis has been performed to determine the conditions under which an evaporating liquid layer of thickness $\delta$ heated from below is marginally stable. Both an infinite and finite values of the aspect ratio are considered. When the liquid evaporates, the interface can be heated both through the liquid and through the vapor phases. For finite aspect ratio systems, the liquid is taken to be held in a two-dimensional container that has isothermal side walls. The fundamental difference between the proposed approach and earlier ones is that for both finite and semi-infinite systems, statistical rate theory is applied at the liquid-vapor interface to predict the evaporation flux [Eqs. (8)–(12)]. This removes the necessity of introducing phenomenological coefficients such as the heat transfer coefficient [56] or the accommodation coefficient [9] or the Onsager coefficients [43]. The expression obtained for the evaporation flux from SRT [5] has significant experimental support [6,50], and allows the interfacial temperatures and chemical potentials to be discontinuous. The temperature in the vapor at the interface has been found experimentally to be greater than that of the liquid [1–4,16–19,50,61–63] and this disequilibrium at the interface is included in the SRT calculation of the evaporation flux.

The steady-state solution of the coupled system of equations is perturbed by considering small changes in the interfacial-liquid temperature. For both finite and semi-infinite systems, this leads to the boundary condition given in Eq. (47) that contains the evaporation number, $E_{ev}$. Using SRT, Eqs. (8)–(12), the value of this parameter may be determined from values of the instantaneous interfacial properties, $T_L^v, T_v^v, P$ and the liquid-layer thickness, $\delta$. There are no fitting or undefined parameters in this procedure; thus, the value of $E_{ev}$ may be calculated for a given physical circumstance. If the conditions at the interface are changed so as to increase the value of $E_{ev}$, the total-energy flux to the interface increases, as does the average evaporation flux (see Table II).

When the aspect ratio is taken to be infinite and the solution of the linearized equations is assumed to be periodic in the horizontal direction with wave number $k$, the Marangoni number $M_{a,cr}$ depends on $k$ and $E_{ev}$. For each value of $E_{ev}$, there is a critical value of $k$, denoted $k_c$. This case is depicted in Fig. 1. Note that for the range $E_{ev}$ values considered in the experiments, as $E_{ev}$ is increased, $M_{a,cr}$ decreases; thus, for these experimental conditions, evaporation is predicted to destabilize even the semi-infinite system.
The opposite effect of evaporation on the stability of semi-infinite systems was predicted by Margerit et al. [43]. They used nonequilibrium thermodynamics and a linearized-Hertz-Knudsen expression for the evaporation flux. The thermodynamic forces were taken to be the interfacial-temperature discontinuity and the deviation of the liquid-interface temperature from the saturation value. They concluded the interfacial-temperature discontinuity destabilizes the system, but the deviation of the interfacial-liquid temperature from the saturation temperature (Hertz-Knudsen-evaporation flux) had a stabilizing effect on the system. When SRT is applied both the interfacial-temperature discontinuity and the deviation from equilibrium are included in the value of $E_{ev}$, and one predicts the net effect of the evaporation.

In Ref. [21], it is argued that the Pearson model does not apply when the liquid evaporates because: (1) at the liquid-vapor interface, energy conservation is not satisfied. For example, the latent heat plays no role in that model. (2) Also, the temperature discontinuity that he assumed is in the opposite direction of that found in the experiments. (3) The value of the Marangoni number that is predicted to be critical is much smaller than those observed in the experiments with the PMMA funnel.

For a finite-sized system, the predictions are more complex: consider a finite-sized and a semi-infinite layer of the same liquid. For isothermal side walls and the no-slip conditions at all walls, a separation-of-variables type solution is obtained in which each mode depends on the aspect ratio, $A$, and $E_{ev}$. Remarkable new modes are predicted (Figs. 2–4): for each mode, the surface flow is unidirectional, but the direction is predicted to change with successive modes. For evenly numbered modes, there is a flow stagnation point on the center line of the container. In general, flow rolls are present in the bulk liquid, and the number of rolls depends on the flow mode. Because of viscous effects at the side walls, on the liquid-vapor interface, there is a portion of the interface where the flow direction is different than that expected from the predicted temperature gradient: the flow is in the direction of increasing temperature. For example, as indicated in Fig. 2, the prediction is that the flow must be some distance away from the viscous effects of the side walls before the flow direction is controlled by the temperature gradient. Under certain conditions the finite and semi-infinite systems are predicted to have the same value of their critical Marangoni numbers. If the same conditions exist at the interface $(T_f^L, T_f^V, P)$ and the liquid layers have the same thickness, then they would have the same value of $E_{ev}$. If the finite-sized system had aspect ratios of $n\pi/k_c$, denoted $A_{nc}$, the wave length in the horizontal direction in the two systems would be the same. This circumstance is depicted in Fig. 5. Thus, for a finite-sized system with one of these aspect ratios, the aspect ratio plays no role in determining the critical Marangoni number: $Ma_{cf} = Ma_{nc}$. However, if the aspect ratio is either greater or less than $A_{nc}$, the effect is predicted to stabilize the system because the critical value of the Marangoni number is increased for these values of $A$. The amount of the increase depends on the value of $E_{ev}$ and the mode. An example for one value of $E_{ev}$ and several modes is given in Fig. 5.

For the experiments described in Table II, the value of $E_{ev}$ was determined from the measured values of $T_f^L$, $T_f^V$, $P$, $\delta$, and $A$ in each experiment was less than $A_{nc}$. The predicted value of $Ma_{cf}$ is listed in the Table. Note that for each experiment, $Ma_{cf} > Ma_{exp}$. Since the liquid was stably stratified, the Rayleigh number would be negative, and the Nield model would indicate the critical Marangoni number would be even larger than $Ma_{cf}$ [21,23]. Thus, no transition to Marangoni convection is predicted for any of the water evaporation experiments described in Table II, and none were observed: the interface was observed to be quiescent in each experiment. This supports the hypothesis of [21] suggesting that the Marangoni convection observed in the experiments with the stainless-steel funnel, Table I, resulted from thermal conduction in the funnel walls imposing a temperature gradient along the liquid-vapor interface rather than from an instability.

**ACKNOWLEDGMENTS**

We wish to acknowledge the support of the Canadian and European Space Agencies and the Natural Sciences and Engineering Research Council of Canada.

**APPENDIX**

The correlations used to calculate water properties (in SI units, $T$ in °C) are listed below. The density was taken to be [64]

$$
\rho(T) = 999.867 876 9 + 0.068 252 345 12 T
- 0.009 172 478 57 T^2 + 0.000 108 280 327 T^3
- 0.172 307 755 6 \times 10^{-5} T^4 + 0.438 663 578 8
\times 10^{-7} T^5 - 0.956 189 531 5 \times 10^{-9} T^6,
$$

(A1)

the surface tension [65]

$$
\gamma(T) = 0.075 478 7 - 0.000 138 489 T - 0.336 392
\times 10^{-6} T^2 + 0.475 362 \times 10^{-9} T^3 + 0.264 479
\times 10^{-12} T^4,
$$

(A2)

the dynamic viscosity [64]

$$
\eta(T) = 0.001 792 - 6.267 241 \times 10^{-5} T + 1.567 118 5
\times 10^{-8} T^2 - 5.306 324 2 \times 10^{-11} T^3
- 1.764 882 744 \times 10^{-14} T^4
- 2.799 21 \times 10^{-15} T^5,
$$

(A3)

the thermal conductivity [66]

$$
\kappa(T) = 0.560 43 + 0.002 074 97 T - 7.919 24 \times 10^{-6} T^2
- 1.043 04 \times 10^{-8} T^3,
$$

(A4)

and the saturation-vapor pressure [6]
STABILITY OF EVAPORATING WATER WHEN HEATED

\[ P_s = 611.2 \exp[1045.851 157 7 - 21 394.666 262 9/(T + 273.12) + 1.096 904 4(T + 273.12) - 1.300 374 1 \times 10^{-3}(T + 273.12)^2 + 7.747 298 4 \times 10^{-7}(T + 273.12)^3 - 2.164 900 5 \times 10^{-12}(T + 273.12)^4 - 211.389 655 9 \ln(T + 273.12)] \]  \hspace{1cm} (A5)

We also use the following thermodynamic relations to determine \( \kappa_T \) and \( c_p \) [6]:

\[ \kappa_T = -\frac{1}{\rho} \frac{\partial P}{\partial T}; \]  \hspace{1cm} (A6)

\[ c_p^T(T) = c_p^V(T) - \frac{d}{dT} \left( \frac{RT^2}{P_s} \frac{dP_s}{dT} \right). \]  \hspace{1cm} (A7)