Surface thermal capacity and its effects on the boundary conditions at fluid-fluid interfaces

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We have formulated a generalization of the energy boundary condition for fluid-fluid interfaces that includes the transport of the Gibbs excess internal energy. A newly measured surface property—the surface thermal capacity $c_\sigma$—appears in the result, and couples the temperature and velocity fields. If this term is not included in the energy boundary condition at liquid-vapor interfaces, the energy-conservation principle cannot be satisfied during steady-state evaporation of H$_2$O(l) or D$_2$O(l). The $c_\sigma$ term is possibly important in a number of other circumstances, and its importance can be determined from the magnitude of two nondimensional numbers.

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The proper boundary conditions to be applied at fluid-fluid interfaces are the subject of intense study [1–9]. But none of these earlier studies have included the transport of the Gibbs excess internal energy $u^{LV}$ [10] by surface-tension-driven (STD) convection. The Gibbs approximation treats the interface as a separate phase with excess moles $n^{LV}$ and temperature $T^{LV}$. Recent evaporation studies indicate that transport of $u^{LV}$ by STD convection is important during evaporation of both H$_2$O(l) and D$_2$O(l) [11–13].

For example, when water was pumped into the throat of a stainless-steel funnel (Fig. 1), where its temperature was maintained just below 4 °C, and onto the funnel mouth where it evaporated steadily and where its temperature was less than that at the funnel throat, buoyancy-driven convection was eliminated, since H$_2$O(l) has its maximum density at 4 °C. If STD convection is neglected, thermal conduction must supply the energy to evaporate the liquid at the measured rate. The apparatus indicated in Fig. 1 was used to determine if thermal conduction fulfilled this role. The evaporation rate was measured by adjusting the chamber pressure surrounding the funnel and the rate at which water was pumped by a syringe pump into the funnel throat so the water-vapor interface at the funnel mouth did not move. Thus, the evaporation rate was equal to the pumping rate, and the latter could be accurately measured (0.05% of the set value). The temperature profiles in the liquid and vapor phases were measured with a microthermocouple mounted on a positioning micrometer. From these profiles, the energy transport to the interface by thermal conduction was determined and compared with that required to evaporate H$_2$O(l) at the observed rate. When the Marangoni number $M_\alpha$ [14] was less than approximately 100 (i.e., $M_\alpha$), thermal conduction provided the energy transport required to evaporate H$_2$O(l) at the observed rate. But when the evaporation rate was raised, energy transport by thermal conduction fell progressively further below the required energy transport rate (see Fig. 1), reaching a minimum of approximately 40% at the highest evaporation rate, and indicating there had to be another mechanism of energy transport.

An approximate energy boundary condition was developed in which STD convection of $u^{LV}$ was included. This required the introduction of the surface-thermal capacity $c_\sigma = n^{LV} (\partial u^{LV}/\partial T^{LV})_{n^{LV}}$ [11,12]. When $c_\sigma$ was assigned one value, energy conservation was completely satisfied in each of the nine experiments (see Fig. 1), but the assigned value of $c_\sigma$ was $10^5$ times larger than what a simple estimation of

![Diagram](https://example.com/diagram.png)

**FIG. 1.** (a) Schematic of the evaporation apparatus and (b) comparison of the energy transport required to evaporate the water with the energy transport by thermal conduction and by STD convection in the absence of buoyancy-driven convection [12]. The onset of STD convection occurs at $M_\alpha$. The vertical scales for the left and right lines and the position of the same point in the two scales are indicated by arrows.

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its value indicated. A second set of experiments was undertaken in which the circular-mouthed funnel was replaced by one with a rectangular mouth that had a surface area more than four times larger than the circular-mouthed funnel, and the experiments were repeated. The value of $c_r$ was confirmed by the second set of experiments [13]. It was hypothesized that the reason for the surprising magnitude of $c_r$ results from the polar interaction of water molecules. Another set of experiments with the circular-mouthed funnel was undertaken using $D_2O(l)$, another polar liquid. The value of $c_r$ for $D_2O(l)$ was found to be a few percent larger than that for $H_2O(l)$ [12].

Our objective in this study is to carefully derive the energy boundary condition (EBC) at fluid-fluid interfaces and to ensure that all effects that could account for the magnitude of $c_r$ have been taken into account. We allow for both interface movement and flow parallel to the interface, and show that the velocity and temperature fields are coupled by the EBC, even for the flow of a nonvolatile liquid with negligible viscous dissipation. This coupling comes through $c_r$, but this effect vanishes if the interface is quiescent. The equations are general enough to show that $c_r$ is a property not only of water, but of any system with an interface. We obtain an explicit expression for the interfacial energy dissipation $\Phi$, and determine the magnitude of the terms appearing in the EBC for water evaporation. Also, we show how $c_r$ modifies the EBC for evaporating menisci in which the interface is moving, e.g., evaporating droplets or thin film evaporation.

To derive the EBC, we choose a control volume which includes the interface between two fluids. The total material volume $V$ is thus bounded by the surfaces of the bulk phases $\partial V^L$ and $\partial V^V$ with the outward normal vectors $\hat{n}^L$ and $\hat{n}^V$, respectively. The interface, approximated as a Gibbs dividing surface $I$, divides $V$ into volumes $V^L$ and $V^V$. The portion of $I$ located inside the volume $V$ is limited by the curve $\partial I$. The unit-normal vector to $I$, pointing from the liquid to the vapor is denoted $\hat{n}$, and the unit tangent vector to $I$, denoted $\hat{T}$, is normal to the intersection of the surface $\partial V$ and $I$, and points out of $\partial I$. When changes in the momentum in $V$ due to (1) traction on the Gibbs dividing surface, (2) body forces, and (3) interfacial stress are taken into account, the general momentum balance can be written [15]

$$\frac{d}{dt} \int_V \rho \vec{v} \, dV = \int_{\partial V^L} \hat{n} \cdot \vec{a} \, dS + \int_{\partial V^V} \hat{n} \cdot \vec{a} \, dS + \int_{\partial I} \gamma^L \hat{\gamma} \cdot dI,$$

where $\rho$ is the fluid density, $\vec{v}$ the fluid velocity, $\vec{X}$ the body force, and $\hat{\gamma}$ the traction. The traction is related to the stress tensor $T$ by $\vec{\gamma} = T \hat{n}$. For a Newtonian fluid with dynamic viscosity $\eta$, $T = -p I + 2\eta \hat{\gamma}$, where $p$ is the isotropic pressure and $I$ is the rate-of-strain tensor.

If each of the fields involved, say $f(\vec{x}, t)$, is allowed a simple discontinuity at $I$, assumed to have smooth derivatives on either side of $I$, then the magnitude of the discontinuity may be defined $[f] = f^L - f^V$. The transport theorem and surface Gauss theorem [15,16] may be applied to rewrite Eq. (1) as

$$\int_V \left( \rho \frac{d\vec{v}}{dt} - \vec{T} - \rho \vec{X} \right) \, dV + \int_I (-j_{en} [\vec{v}]) \cdot [\vec{T}] = \int_I \gamma^L \hat{\gamma} \cdot dI + \int_{\partial I} \gamma^L \vec{v} \cdot \hat{n} \, dI,$$

where we have neglected any mass storage in the interface; thus, the net mass flux at the interface is given by

$$j_{en} = \rho \vec{v}^L \cdot \hat{n} - \rho \vec{v}^V \cdot \hat{n}.$$

The surface gradient operator is defined as $\vec{\nabla} = \vec{\nabla} - \hat{n} \vec{\nabla} \hat{n}$ and the mean curvature of $I$ as $\hat{C}$ where $2\hat{C} = \vec{\nabla} \cdot \hat{n}$. Equation (2) holds for any material volume containing a surface phase. Separating the bulk and the interface portions of Eq. (2), we get the Navier-Stokes (NS) equations in the bulk phases:

$$\rho \frac{d\vec{v}}{dt} - \vec{T} = 0 \quad \text{where} \quad i = L \text{ or } V,$$

and the interface momentum balance from the interface portion of Eq. (2):

$$j_{en} [\vec{v}] - [\vec{T}] = -\hat{C} (\vec{\nabla} \cdot \vec{v}) + 2 \hat{C} \vec{\nabla} \cdot \vec{v} \hat{n}.$$

In the absence of any net mass transfer ($j_{en}=0$), the scalar product of $\hat{n}$ with Eq. (5) leads to the Laplace equation, which relates the bulk pressure to the surface tension of the fluid, while the scalar product with $\hat{\gamma}$ leads to the Marangoni stress balance equation. However, when there is evaporation, the modification of the Laplace equation due to vapor recoil $[\hat{C}^2 (\rho' - 1) \rho] \hat{n}$ [5] is obtained from the first term of Eq. (5).

The conservation-of-energy principle may also be applied to the control volume, and if both the excess internal energy per unit area of the interface, $u' (\equiv \mu' V dV)$, and the thermal flux vector $\vec{q} = -\kappa \vec{\nabla} T$ are included, one finds

$$\frac{d}{dt} \int_V \rho (\vec{v}^2/2) \, dV + \int_{\partial V} \vec{v} \cdot \vec{a} \, dS = -\int_{\partial V} \hat{q} \cdot \hat{n} \, dA + \int_I \vec{v} \cdot \hat{\gamma} \, dI + \int_V \rho \vec{v} \cdot \vec{X} \, dV$$

$$+ \int_{\partial I} \gamma^L \hat{\gamma} \cdot \vec{v} \hat{n} \, dI,$$

where $\rho$ is the specific internal energy of the fluid, and we have neglected radiation. In previous energy balance equations, we emphasize that the term $(d/dt)\int_{\partial I} u' dI$ was neglected [4,8,9].

The surface transport theorem [17] may be applied to write

$$\frac{d}{dt} \int_I u' dI = \int_I \left( \frac{d}{dt} \vec{u} + \vec{\nabla} \cdot (u' \vec{u}) \right) \, dI,$$

and the second surface Gauss theorem used to obtain

$$\int_{\partial I} \gamma^L \vec{v} \cdot \hat{\gamma} \, dI = -2\hat{C} \gamma^L \vec{v} \cdot \hat{n} \, dI + \int_I \vec{\nabla} \cdot (\gamma^L \vec{v}) \, dI. \quad \text{(8)}$$

The conservation-of-energy principle now becomes
\[
\int_I \left[ \frac{d}{dt} \left( u + \frac{|\nabla|^2}{2} \right) + \text{div} \, \tilde{q} - \text{div}(T \tilde{v}) - \rho \tilde{v} \cdot \tilde{X} \right] dV = \int_I \left( j_v v + \frac{|\nabla|^2}{2} + \left[ q \cdot \hat{n} - \left[ v \cdot T \hat{n} \right] - \frac{D \rho u}{dt} \right. \right.
\]
\[
- (u' - \gamma T') \tilde{v}_i \cdot \tilde{v}_i + \tilde{v}_i \cdot \nabla_{\tilde{v}} (2C \gamma T') \hat{n} \cdot \hat{n} \right) \]dI,
\]
(9)

where \( D/I d = \partial \lambda / \partial t + \delta \tilde{v}_i \cdot \nabla_{\tilde{v}}. \) Equation (9) may be separated into the bulk-energy equation
\[
\rho \frac{d}{dt} \left( u + \frac{|\nabla|^2}{2} \right) + \text{div} \, \tilde{q} - \text{div}(T \tilde{v}) - \rho \tilde{v} \cdot \tilde{X} = 0,
\]
(10)

and the EBC
\[
j_v = \left[ u + \frac{|\nabla|^2}{2} \right] + \left[ q \cdot \hat{n} - \left[ v \cdot T \hat{n} \right] - \frac{D \rho u}{dt} - (u' - \gamma T') \tilde{v}_i \cdot \tilde{v}_i 
\right.
\]
\[
+ \tilde{v}_i \cdot \nabla_{\tilde{v}} (2C \gamma T') \hat{n} \cdot \hat{n} = 0.
\]
(11)

Eliminating the contribution of mechanical energy from the total by taking the scalar product of \( \tilde{v} \) with the NS equations [Eq. (4)], and subtracting it from Eq. (10), the heat equation in the bulk fluid is obtained. If a similar procedure is followed and the scalar product of \( \tilde{v}_i \) is taken with Eq. (5) and the result subtracted from Eq. (11), one finds as the energy balance for an element of the interface
\[
\left[ (\kappa T') \cdot \hat{n} = j_v \left[ u + \frac{1}{2} (\tilde{v} - \tilde{v}_i) \cdot \hat{n} \right]^2 - \left[ (\tilde{v} - \tilde{v}_i) \cdot \nabla_{\tilde{v}} \right] - \frac{\partial \lambda}{dt} \right.
\]
\[
- \tilde{v}_i \cdot \nabla_{\tilde{v}} (u' - \gamma T') \tilde{v}_i \cdot \tilde{v}_i.
\]
(12)

Equation (3), the relation \( T = -p \mathbf{I} + 2 \rho \mathbf{I} \), and the definition of \( c_\sigma = n_{LV}(\partial T^L / \partial T^L)_{\lambda} \) may be simplified to yield Eq. (12). After neglecting the variation of \( n_{LV} \) along \( I \), indicating \( \tilde{v}_i : \tilde{v}_i = 0 \), one obtains the EBC
\[
\left[ (\kappa T') \cdot \hat{n} = j_v [h] + \frac{\rho c}{2} \left[ 1 \right] - \left[ \eta (\tilde{v} - \tilde{v}_i) \cdot \mathbf{II} \hat{n} \right] \right.
\]
\[
- c_\sigma \tilde{v}_i \cdot \nabla_{\tilde{v}} (2C \gamma T') \hat{n}.
\]
(13)

An additional equation that relates the interfacial velocity to the bulk velocity and net evaporation flux is given by Eq. (3). A final constitutive relation of the form
\[
j_{vc} = j_{vc} (T^L, T^V, P^V, P^L)
\]
(14)
is obtained from statistical rate theory [18] to close the system of equations.

Since earlier investigations of the EBC [4,8,9] did not include the transport of \( u_{LV}, c_\sigma \) does not appear in their proposed EBC, but Eq. (13) indicates that the coupling between the velocity and temperature fields that results from a non-zero value of \( c_\sigma \) is possibly important in a number of different circumstances. (1) Even for a nonvolatile liquid (\( j_{vc} = 0 \)) with negligible viscous dissipation, thermal flux to the interface is coupled to the velocity field through \( c_\sigma \). (2) For a fluid in a finite container with differentially heated sidewalls [19,20], \( c_\sigma \) appears in the EBC, even in the linear order. (3) For problems in which the interface is at position \( \Lambda = \Lambda (x, y, t) \) and evaporation is occurring, \( \tilde{v}_i \hat{n} = \Lambda (x, y, t) / \partial t \), Eq. (13) is general enough to be considered with the kinematic boundary condition, Eq. (3). Thus the equations developed herein may be applied to examine the stability and evolution of evaporating liquid films. The EBC appears crucially important in modeling thermocapillary fluid flow and thin film evolution.

The relative magnitude of the terms in Eq. (13) may be examined by nondimensionalization. Length may be scaled with \( d \) and temperature with \( \Delta T \). In the experiments (Fig. 1) [12], \( d \) is the distance between the funnel throat and the interface on the funnel centerline, and \( \Delta T \) is the difference in temperature between these positions; speed may be scaled with \( [(\partial T^L / \partial t)_{\lambda}] / \Delta T / \eta / \rho c \), and mass flux \( j_{vc} \) with \( k^2 \Delta T / h \sqrt{d} \). The nondimensional mass flux is denoted \( J_{vc} \). After introducing these scaling factors, Eq. (13) becomes
\[
\left[ \tilde{v} T^L \cdot \hat{n} - \left( \frac{\kappa V}{k^2} \right) \tilde{v} T^V \cdot \hat{n} \right]
\]
\[
= J_{vc} \left[ \frac{h L}{h V} - 1 \right] + \frac{\sqrt{3}}{\kappa^2} \left( \frac{\rho v^2}{\rho v^2 - 1} - \frac{16 \cdot \text{Ma}^2}{9 \cdot \text{Ev} \cdot \text{Pr}} \right)
\]
\[
\times \left( \frac{v^2 - v_i^2}{\kappa^2} \right) (\tilde{v} - \tilde{v}_i) \cdot \mathbf{II} \hat{n}
\]
\[
- \text{Ma} \tilde{v}_i \cdot \nabla_{\tilde{v}} (T^L).
\]
(15)

In Eq. (15), \( \text{Ev} = k^2 \Delta T / \eta / h \sqrt{V} \) is the evaporation number; \( D_v = 3 \sqrt{2} / 2 \rho \sqrt{V} \) is approximately the ratio of densities; \( \text{L} = 8 \delta d h \sqrt{V} \rho / 9 (\eta / \rho c)^2 \) compares thermal to viscous effects; \( \text{Ma} = (\partial T^L / \partial t)_{\lambda} / \Delta T d / \eta / \rho c \) is the Marangoni number. If the thermal diffusivity is denoted \( \alpha \), \text{Pr} = \eta / \alpha \rho c \) is the Prandtl number of the liquid, and if the constant pressure specific heat of the liquid is denoted \( c_p \), then a new nondimensional number \( \gamma = c_\sigma / \rho c_p d \) appears. It determines the coupling between surface properties and those in the liquid phase. In general \( k^2 / \kappa^2, \rho v^2 / \rho v^2, (\eta / \rho c)^2 / \eta^2, h^2 / h \sqrt{V} \approx 1 \), and we can decouple the hydrodynamic equations of the liquid from those of the vapor. The values of these nondimensional numbers for water near \( 4 \text{ C} \) give \( \text{Ev} \approx 10^{(2)}, \text{D_v} \approx 10^{(4)}, \text{L} \approx 10^{(11)}, \text{Pr} \approx 10^{(1)}, \) and \( \gamma \approx 10^{(1)} \).

We can identify three steady-state, water-evaporation regimes in the experiments of [12]. (1) \( \tilde{v}_i = 0, \text{Ma} < 100 \): There is evaporation, but contributions due to kinetic energy and viscous dissipation are negligible, since \( \text{Ev} / D_v \text{L} \approx 1 \), and \( \text{Ma}^2 / \text{Ev} \sqrt{\text{Pr}} \text{L} \approx 1 \). Under these conditions, Eq. (15) reduces to the nondimensional Stefan equation
\[
\left[ \tilde{v} T^L \cdot \hat{n} - \left( \kappa V / k^2 \right) \tilde{v} T^V \cdot \hat{n} \right] = J_{vc} \left( \frac{h L}{h V} - 1 \right).
\]
(16)

and indicates that the energy transport to the interface is by thermal conduction. The results presented in Fig. 1 support this conclusion. (2) \( \tilde{v}_i \neq 0, \) but \( \tilde{v}_i \cdot \hat{n} = 0 \) and \( 100 < \text{Ma} < 22 \times 10^{(2)} \): the boundary between the liquid and vapor phases is stationary, but there is convection within the surface phase.
The kinetic energy and viscous dissipation effects remain negligible because (a) $\text{Ev}^2/D_p^2\mathcal{L} \ll O(1)$, and (b) $Ma = O(10^4)$; hence $Ma^2/\text{Ev} Pr^2\mathcal{L} \ll O(1)$. The resultant EBC reduces to

$$\hat{v}^T \cdot \hat{n} - \left( \frac{\kappa}{k^2} \right) \hat{v}^T \cdot \hat{n} + J_{ev} \left( \frac{h^k}{h^v} - 1 \right) - \Gamma Ma \hat{u}_L \cdot \hat{V}^T \hat{n},$$

which is the dimensionless form of the equation used to measure $c_\sigma$ [11–13]. Thus, the new effects do not change the value determined for $c_\sigma$, and the results in Fig. 1 indicate that only one value of $c_\sigma$ is required to satisfy conservation of energy in the experiments. (3) $\hat{u}_L \neq 0$, but $\hat{u}_L \cdot \hat{n} = 0$, and $Ma > 22,000$. There is convection in the interface between the liquid and vapor phases, but, provided $J_{ev} < O(10^{7/3})$, kinetic energy effects remain negligible because $Ev^2/D_p^2\mathcal{L} \sim O(10^{7/3})$; however, the viscous dissipation

$$\Phi = \frac{16}{9} \frac{Ma^2}{\text{Ev} Pr^2\mathcal{L}} \left( (\hat{u}^L - \hat{u}_L) \cdot \Pi_L \hat{n} - \frac{\eta'}{\eta} (\hat{u}^V - \hat{u}_L) \cdot \Pi^V \hat{n} \right)$$

cannot be neglected when $Ma > O(10^4)$, since $Ma^2/\text{Ev} Pr^2\mathcal{L} \geq O(1)$. In order for kinetic energy effects to be of importance, $j_{ev} > 10^{7/3} k^2 \Delta T h^k d \sim 0.1$ kg/m$^2$ s. The largest value of $j_{ev}$ in the experiments was less than 0.01 kg/m$^2$ s.

In summary, when the transport of $u^L$ by STD convection is included, the boundary condition obtained from the energy-conservation principle is given by Eq. (13), and is seen to couple the temperature and velocity fields. The importance of this coupling is determined by the relative magnitude of $c_\sigma \hat{u}_L \cdot \hat{V}^L$. For the conditions considered in [11–13], Eq. (15) reduces to the EBC used to determine the value of $c_\sigma$. As indicated by Fig. 1, if this coupling is not taken into account, the energy-conservation principle cannot be satisfied.

Also, $c_\sigma$ provides an essential coupling in other areas of potential application. (1) It appears in the flow of a nonvolatile liquid with a temperature gradient along the interface. (2) For a fluid held in a finite sized container with differentially heated sidewalls, $c_\sigma$ appears in the EBC even in the linear approximation, independently of whether there is evaporation. (3) For evaporation of a thin liquid film, $c_\sigma$ through $j_{ev}$ couples the film thickness to the EBC. Finally, in an arbitrary circumstance, the importance of this coupling may be determined by examining the relative magnitude of the nondimensional parameter $\Gamma Ma$.

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