

SURFACES AS NON-AUTONOMOUS THERMODYNAMIC SYSTEMS

Wilhelm Schneider

Institute of Fluid Mechanics and Heat Transfer
Vienna University of Technology
Resselgasse 3/2
1040 Vienna
Austria
wilhelm.schneider@tuwien.ac.at

ABSTRACT

To deal with negative surface heat capacities that are observed for many liquids, surfaces are treated as non-autonomous thermodynamic systems, i.e. together with the liquid that forms the surface. First, a few examples of lumped heat capacities are presented. Both quasistatic and non-static area changes of plane liquid films are considered. To provide a criterion for the applicability of the quasistatic limit, one-dimensional thermo-capillary waves in liquid films are investigated. Next, heat transfer at surfaces is considered. Various forms of the energy equation of surfaces are presented, non-dimensional parameters characterizing the relative importance of the surface heat capacity are defined, and a few applications are given. If the surface heat capacity is negative, a heat pulse supplied to the surface initially leads to a decrease of the surface temperature. Furthermore, negative surface heat capacities give rise to amplifications of small perturbations of the surface temperature. This physical instability may also cause numerical instabilities when solving heat conduction problems. Finally, the dependence of the surface tension on the radius of nano-droplets serves as a motivation for extending the relevant thermodynamic relations to systems with area-dependent surface tension. The implications for Kelvin's equation for the vapour pressure at small droplets are discussed.

INTRODUCTION

In classical thermodynamics, the surface of a chemically pure liquid is considered as a thermodynamic system, whose thermodynamic equilibrium state is uniquely given by the surface area, A , and the (absolute) temperature, T . The surface tension, σ , is then defined by the relation

$$d_e W = \sigma dA \quad (1)$$

for the work required to change the surface area by the infinitesimal amount dA in a quasistatic process. It is commonly assumed in classical thermodynamics that the surface tension is independent of A , i.e. a function of T only, with $\sigma = \sigma(T)$ representing the thermal equation of state of the surface. Furthermore, measurements as well as molecular models indicate that the value of the surface tension of common liquids is nearly independent of the surrounding gas, which may be a vapour or an inert gas.

The entropy, S_σ , of the surface is defined by Gibbs' fundamental equation

$$T dS_\sigma = dU_\sigma - \sigma dA \quad (2)$$

for a quasistatic process. Since the internal energy, U_σ , and the entropy, S_σ , are quantities of state, dU_σ and dS_σ have to satisfy the conditions for total differentials, leading to the following relation between the thermal and caloric quantities of state:

$$\left(\frac{\partial U_\sigma}{\partial A} \right)_T = u_\sigma = \sigma - T \frac{d\sigma}{dT}, \quad (3)$$

where u_σ is the internal energy of the unit surface area, while the heat capacity of the unit surface area, c_σ , is defined by the relation

$$\left(\frac{\partial U_\sigma}{\partial T} \right)_A = A c_\sigma. \quad (4)$$

Since σ is a function of T only, the same is true for u_σ and c_σ , i.e. $u_\sigma = u_\sigma(T)$ and $c_\sigma = c_\sigma(T)$, and from equations (3) and (4) one obtains

$$c_\sigma = \frac{du_\sigma}{dT} = -T \frac{d^2\sigma}{dT^2}. \quad (5)$$

Note that sometimes the temperature dependence of the surface tension is approximated by assuming $d\sigma/dT = \text{const}$. This, however, implies a vanishing surface heat capacity according to Eq.(5).

As u_σ is independent of A , Eq.(3) can easily be integrated. There appears an unknown function of T , which, however, must be a constant in order to be in accord with Eqs.(4) and (5). Thus $U_\sigma = Au_\sigma + \text{const}$, or

$$U_{\sigma 2} - U_{\sigma 1} = A_2 u_{\sigma 2} - A_1 u_{\sigma 1}. \quad (6)$$

Here, and in what follows, the subscripts 1 and 2 refer to an initial and a final state, respectively.

Making use of Eq.(3), Gibbs' fundamental equation, Eq.(2), gives

$$\left(\frac{\partial S_\sigma}{\partial A}\right)_T = -\frac{d\sigma}{dT}. \quad (7)$$

Introducing, finally, the entropy of the unit surface area, s_σ , according to $S_\sigma = As_\sigma$, gives

$$s_\sigma = -\frac{d\sigma}{dT} = \frac{u_\sigma - \sigma}{T}. \quad (8)$$

Note that the entropy of a surface can be responsible for the irreversibility of evaporation processes [1]. For instance, in order to completely evaporate a plane liquid film with surface area A under isothermal conditions, a supply of heat is required that is smaller than the evaporation enthalpy of the liquid by the amount Au_σ , cf. Eq.(3). The entropy change due to the disappearance of the surface, however, is not equal to $-Au_\sigma/T$, but only equal to $-As_\sigma = -A(u_\sigma - \sigma)/T$. The difference, which represents the work that is necessary to generate the surface in an isothermal process, indicates that the process of complete evaporation of a plane liquid film, being associated with the disappearance of the surface, is inherently irreversible. In most cases, however, it turns out that the entropy change due to the disappearance of the surface is very small in comparison with the entropy change due to the evaporation of the liquid. This justifies, in general, the idealization of a quasistatic isothermal evaporation process as a reversible process.

Since, according to the second law, the entropy is an extensive quantity of state, it follows from Eq.(7) that

$$\frac{d\sigma}{dT} < 0. \quad (9)$$

Note, however, that σ and u_σ vanish as the critical point is approached. From Eq.(3) it follows that $d\sigma/dT \rightarrow 0$ for $T \rightarrow T_c$, with T_c denoting the critical temperature.

While, according to Eq.(9), positive values of $d\sigma/dT$ are excluded as a consequence of the second law, the second law does not tell us anything about the sign of du_σ/dT or c_σ . A Carnot cycle, for instance, can be constructed for the surface as a thermodynamic system irrespective of the sign of c_σ . While the isothermal changes of state are characterized by $\sigma = \text{const}$, the isentropic changes of state satisfy the relation

$$dA = \frac{Ac_\sigma}{T} \left(\frac{d\sigma}{dT}\right)^{-1} dT, \quad (10)$$

which follows from Eqs. (2) to (4). Observing Eq.(9), one can see from Eq.(10) that the isentropic temperature increase in the Carnot cycle is associated with a decrease or increase of the surface area, depending on whether c_σ is positive or negative, and vice versa for the isentropic temperature decrease. But the thermal efficiency of the cycle is smaller than 1 in both cases, in accord with the second law.

In fact, positive as well as negative values of c_σ have been measured, and also calculated on the basis of molecular models, for various liquids in certain temperature regimes [1] [2] [3]. There is, however, a problem of stability. Let us assume that the thermodynamic equilibrium state (T, A) is perturbed by a small surface-area change, $\delta A > 0$. According to Eq.(10) together with Eq.(9), the system reacts with a temperature change $\delta T < 0$ and $\delta\sigma > 0$ if $c_\sigma > 0$. The increase of the surface tension will then lead to $dA < 0$, driving the surface back to the equilibrium state. The opposite is true in the case $c_\sigma < 0$, leading to the thermodynamic instability that is to be expected of any system with a negative heat capacity. Thus it is usually argued that the surface must not be considered as an "autonomous" system, but rather ought to be treated together with the liquid that forms the surface [4]. This, however, is sometimes easier said than done. The present contribution to the symposium is intended to provide a basis for the discussion of problems associated with considering the surface as a non-autonomous system. In accord with many applications, the discussion will be restricted to thermodynamic systems that consist of only one chemical substance, i.e. mixtures will not be considered, and phase transitions will not be taken into account in what follows.

LUMPED HEAT CAPACITIES

Isentropic film-area change

Consider a quasistatic, adiabatic, i.e. isentropic, change of the surface area, A , of a plane liquid film of constant mass, m . The liquid film is surrounded by an inert gas. The mass density of the liquid may be assumed constant, thereby allowing to neglect work due to volume changes. Accounting for the internal energy of the liquid with isochoric specific heat capacity c_v , one obtains in the same way as above the following relation [1]:

$$dA = \frac{mc_v + Ac_\sigma}{T} \left(\frac{d\sigma}{dT}\right)^{-1} dT. \quad (11)$$

Note that $mc_v + Ac_\sigma$ represents the "lumped" heat capacities of the two parts of the system, i.e. of the bulk liquid and the surface. As an approximation, lumped heat capacities are well known from the theory of heat transfer, but in the present case they result from the quasistatic limit, which implies thermal equilibrium between all parts of a system.

With $m = \rho\delta A/2$, where ρ is the mass density of the liquid and δ is the thickness of the film with two free surfaces, the condition for a positive lumped heat capacity, as required for stability reasons, becomes $\delta > -2c_\sigma/c_v\rho$. Estimates on the basis of known properties of various liquids, e.g. water (cf. [1], p. 94, and [5]) or argon (cf. [6], p. 12), show that a film thickness of the order of the size of molecules is sufficient to give a positive lumped heat capacity.

For film thicknesses that are much larger than the molecular size, Ac_σ may be neglected in comparison with mc_v , and upon integration one obtains from Eq.(11) the following relation between the area change $A_2 - A_1$ and the temperature change from T_1 to T_2 :

$$A_2 - A_1 = m \int_{T_1}^{T_2} \frac{c_v}{T} \left(\frac{d\sigma}{dT} \right)^{-1} dT, \quad (12)$$

or, using Eq.(3),

$$A_2 - A_1 = m \int_{T_1}^{T_2} c_v (\sigma - u_\sigma)^{-1} dT. \quad (13)$$

Equation (13) shows that the internal energy of the surface has to be taken into account, even if the heat capacity of the surface is negligible. This, perhaps surprising, result can be understood by considering the energy balance. As u_σ and σ are of the same order of magnitude, cf. Eq.(3), the contribution of the surface-energy change to the energy balance, i.e. $u_\sigma dA$, is of the same order of magnitude as the work performed by the surface tension, i.e. σdA .

Non-static film area change

Consider a plane liquid film that is stretched in a rectangular frame with a frictionless movable bar of length L forming one side of the frame. As before, the mass and the mass density of the film are assumed constant. In addition, the isochoric specific heat capacity, c_v , of the liquid is also assumed constant. In the initial state (surface area A_1 , temperature T_1) the film is in thermodynamic equilibrium. This implies that the force acting on the bar is $F_1 = 2L\sigma$. (The coefficient 2 is due to the fact that the film has two surfaces.) At a certain moment, the force acting on the bar suddenly changes to the value F_2 , which is then kept constant. Heat exchange with the surroundings may be neglected, i.e. the change of state is non-static, but adiabatic. The new state of thermodynamic equilibrium (surface area A_2 , temperature T_2) is to be determined [1].

Since thermodynamic equilibrium implies mechanical equilibrium, the surface tension in the final state is $\sigma_2 = F_2/2L$, and the temperature T_2 can be determined by inverting the thermal equation of state of the surface, i.e. $\sigma = \sigma(T)$. As the force acting on the system is constant, the work performed in the non-static process is

$$W_{12} = \sigma_2(A_2 - A_1), \quad (14)$$

and the energy balance, together with Eq.(6), gives

$$A_2 = [mc_v(T_1 - T_2) + A_1(u_{\sigma_1} - \sigma_2)] / (u_{\sigma_2} - \sigma_2). \quad (15)$$

Estimates for common liquids show that, with the exception of extremely thin films, the term with the coefficient A_1 in Eq.(15) is negligibly small, but the internal energy of the surface remains of importance via the term u_{σ_2} . As in the case of the isentropic process considered above, the negligible term is associated with the (positive or negative) surface heat capacity, as can be seen by making use of Eq.(3) and rewriting the term $(u_{\sigma_1} - \sigma_2)$ as

$$(u_{\sigma_1} - \sigma_2) = u_{\sigma_1} - u_{\sigma_2} - T_2(d\sigma/dT)_2, \quad (16)$$

with $u_{\sigma_1} - u_{\sigma_2} \approx c_{\sigma_1}(T_1 - T_2)$ for approximately constant surface heat capacity.

One-dimensional thermo-capillary waves

To justify the assumption of a quasistatic change of state, the rate of change of the surface area of the liquid film must be sufficiently small to allow the equalization of perturbations at any point in time. For the present treatment it suffices to consider a plane liquid film that is in thermodynamic equilibrium and at rest in the base state (subscript 0). Small perturbations of the film thickness, δ , and temperature, T , according to $\delta = \delta_0 + \varepsilon\delta_1$, $T = T_0 + \varepsilon T_1$, with $\varepsilon \ll 1$, are associated with small film velocities, εv_1 , in the direction of the longitudinal coordinate, x . Neglecting viscosity, the net force acting on a film element per length is $\partial\sigma/\partial x = \sigma'(T)\partial T/\partial x$, with $\sigma' = d\sigma/dT$. With regard to the energy balance, we assume local thermodynamic equilibrium and neglect heat transfer to the surroundings as well as heat conduction in the film in longitudinal direction. This allows us to apply Eq.(11), which describes quasistatic adiabatic changes of state. For unsteady one-dimensional flow of an incompressible liquid in a thin film, the linearized equations of continuity, momentum and energy can then be written as follows:

$$\frac{\partial\delta_1}{\partial t} + \delta_0 \frac{\partial v_1}{\partial x} = 0; \quad (17)$$

$$\rho\delta_0 \frac{\partial v_1}{\partial t} = \sigma'(T_0) \frac{\partial T_1}{\partial x}; \quad (18)$$

$$\frac{1}{T_0} \frac{\partial T_1}{\partial t} = - \frac{\sigma'(T_0)}{\rho\delta_0 c_v + c_\sigma} \frac{1}{\delta_0} \frac{\partial\delta_1}{\partial t}. \quad (19)$$

Eliminating δ_1 and v_1 from Eqs.(17)-(19), one obtains the linear wave equation

$$\frac{\partial^2 T_1}{\partial t^2} - C_0^2 \frac{\partial^2 T_1}{\partial x^2} = 0, \quad (20)$$

with

$$C_0^2 = \frac{T_0[\sigma'(T_0)]^2}{\rho\delta_0(\rho\delta_0 c_v + c_\sigma)}, \quad (21)$$

or

$$C_0 = -\sigma'(T_0) \sqrt{\frac{T_0}{\rho\delta_0(\rho\delta_0 c_v + c_\sigma)}}. \quad (22)$$

Since $\sigma'(T_0) < 0$ according to the second law, cf. above, the minus sign has been chosen for the square root in Eq. (22). C_0 can be identified as the wave speed, i.e. the propagation speed of small perturbations.

To justify the idealization of a quasistatic change of state of a film that is stretched in one direction, the wave speed must be much larger than the velocity of the film, i.e. $C_0 \gg v = \varepsilon v_1$. Note that the wave speed increases with

decreasing film thickness, δ_0 . The lumped heat capacity per surface area, $(\rho\delta_0c_v + c_\sigma)$, appears in the denominator on the right-hand side of Eq.(21). If the lumped heat capacity were negative, C_0^2 would be negative according to Eq.(21), and Eq.(20) would lose the character of a wave equation and become of elliptic type.

To give an idea about the orders of magnitude, a wave speed of about 1 m/s is obtained from Eq.(21) for a film of water at 300 K with a thickness of 50 nm.

HEAT TRANSFER AT SURFACES

Energy equation of a moving surface

If the energy balance of the surface is disregarded, as it is often done - though not always with sufficient justification - in problems of fluid mechanics and heat transfer, the temperature-dependent surface tension appears only in the momentum equation. Marangoni convection is a well-known example. In an attempt to clarify the effect of the internal energy, or the heat capacity, of the surface on the heat transfer at the surface, the energy balance of the surface is investigated in what follows. Local thermodynamic equilibrium will be assumed. It allows applying the relations given in the Introduction, locally and at any moment of time, as if any surface element or any volume element were in thermodynamic equilibrium. In particular, there is no temperature jump at the surface. In the interest of simplifying the presentation, the discussion will be restricted to one-dimensional motion of the surface, but the generalization to more dimensions will be obvious, cf. also the survey [7].

Consider a surface element of length dx , with x being the tangential coordinate at the surface, while the coordinate normal to the surface is denoted by z . The surface element is assumed to be fixed in space. The liquid is assumed to be surrounded by an inert gas, i.e. condensation and evaporation are disregarded. For a liquid that moves with the tangential velocity component v_x in x -direction, the energy balance of the surface may be written as

$$\frac{\partial u_\sigma}{\partial t} + \frac{\partial(v_x u_\sigma)}{\partial x} = \frac{\partial(v_x \sigma)}{\partial x} + [\dot{q}]_\pm - v_x [\tau]_\pm, \quad (23)$$

where \dot{q} is the heat flux in z -direction, τ is the shear stress at one side of the surface, and the symbol $[]_\pm$ stands for the difference across the surface ("jump" at the surface). The terms in Eq.(23) have the following physical meaning (in this order, from left to right): Rate of change of internal energy; net convective flux of internal energy; net work done by the surface tension due to moving the surface into, and out of, the surface element; net heat flux; net work done by the shear stresses at both sides of the surface.

Equation (23) may be re-written in various ways. A rather nice formulation is obtained by introducing the surface heat capacity according to Eq.(5), and, furthermore, the surface enthalpy (per surface area), h_σ , according to

$$h_\sigma = u_\sigma - \sigma = Ts_\sigma = -T d\sigma/dT. \quad (24)$$

Making then use of the force balance at the surface, i.e.

$$[\tau]_\pm = \frac{\partial \sigma}{\partial x}, \quad (25)$$

one finally obtains that at the surface the following boundary condition has to be satisfied:

$$\begin{aligned} c_\sigma \left(\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} \right) &= -h_\sigma \frac{\partial v_x}{\partial x} + [\dot{q}]_\pm \\ &= -h_\sigma \frac{\partial v_x}{\partial x} - \left[k \frac{\partial T}{\partial z} \right]_\pm, \end{aligned} \quad (26)$$

where k is the thermal conductivity of the fluid on the respective side of the surface.

To check the analysis for self-consistency, Eq.(26) is applied to the quasistatic adiabatic, i.e. isentropic, change of the area of a plane surface in a rectangular frame with the bar on one side moving in x -direction. With $T = T(t)$ and $[\dot{q}]_\pm = 0$, Eq.(26) shows that the velocity is a linear function of x , which gives $v_x = (x/A) dA/dt$. With $h_\sigma = -T d\sigma/dT$ according to Eq.(24), one obtains from Eq.(26) the isentropic relation, Eq.(10).

Equation (26) shows that a material (substantial) time derivative of the surface temperature is, in general, associated with a jump in the normal component of the heat flux at the surface. For steady flow, the effects of the surface energy on the heat flux jump are characterized by the following two non-dimensional parameters:

$$N_1 = |c_\sigma^*| v_x^* / k^*; \quad (27)$$

$$N_2 = h_\sigma^* v_x^* / k^* T^*, \quad (28)$$

where $*$ denotes reference quantities. In the case of time-dependent processes, there is the additional non-dimensional parameter

$$N_3 = |c_\sigma^*| L^* / k^* t^*, \quad (29)$$

defined in terms of a characteristic length, L^* , and a characteristic time, t^* . If N_1 and N_2 are either irrelevant (liquid at rest) or much smaller than 1, and if, in addition, N_3 is either irrelevant (stationary state, steady flow) or much smaller than 1, the heat flux jump at the surface is negligible as far as the bulk of the liquid is concerned. In a very thin boundary layer at the surface, however, the solution may be substantially affected by the small heat flux jump. To give an example, the following problem is considered.

Heat pulse at surface

Consider the horizontal surface of a semi-infinite body of liquid. The liquid is at rest. In the initial state ($t=0$) the temperature of the liquid is independent of the downward-pointing vertical coordinate, z , i.e. $T = T_0 = \text{const}$. In the time interval $0 < t < t_e$ a constant heat flux \dot{q}_0 is supplied from the surroundings to the surface, e.g. by radiative heat transfer. Afterwards, the surface is adiabatic. Assuming constant thermal conductivity, k , it is convenient to formulate the

problem in terms of the heat flux, $\dot{q} = -k \partial T / \partial z$, as the dependent variable. The heat diffusion equation gives

$$\frac{\partial \dot{q}}{\partial t} = \alpha \frac{\partial^2 \dot{q}}{\partial z^2}, \quad (30)$$

where α is the thermal diffusivity, which is assumed to be constant, like all other material properties of the liquid. Equation (30) is to be solved subject to the initial condition

$$\dot{q} = 0 \quad \text{for } t = 0, z > 0, \quad (31)$$

and the boundary conditions

$$\dot{q} = 0 \quad \text{for } z \rightarrow \infty, \quad (32)$$

$$\dot{q} - l \frac{\partial \dot{q}}{\partial z} = \dot{q}_0 \quad \text{for } z = 0, 0 < t < t_e, \quad (33)$$

$$\dot{q} - l \frac{\partial \dot{q}}{\partial z} = 0 \quad \text{for } z = 0, t > t_e, \quad (34)$$

with the parameter l defined by

$$l = c_\sigma / \rho c_p, \quad (35)$$

where c_p is the isobaric specific heat capacity of the liquid. The parameter l has the physical dimension of a length, but, depending on the value of c_σ , it may be positive, zero or negative. Based on available data [1]-[3], [5],[6], $|l|$ is of the order of nanometers. Note that the second term on the left-hand sides of Eqs.(33) and (34), which follow from Eq.(26) with $v_x \equiv 0$ and the heat diffusion equation in terms of T , represents the heat-flux jump at the surface due to the surface heat capacity.

As it happens, the solution of the heat diffusion equation with initial and boundary conditions of the form of Eqs.(31)-(34) is given in [8], §2.8, case (i), though the problem is a different one. In the present notation the solution reads

$$\frac{\dot{q}}{\dot{q}_0} = G(z, t) \quad \text{for } 0 < t < t_e; \quad (36)$$

$$\frac{\dot{q}}{\dot{q}_0} = G(z, t) - G(z, t - t_e) \quad \text{for } t > t_e. \quad (37)$$

with

$$G(z, t) = \operatorname{erfc} \left(\frac{z}{2\sqrt{\alpha t}} \right) - \exp \left(\frac{z}{l} + \frac{\alpha t}{l^2} \right) \operatorname{erfc} \left(\frac{z}{2\sqrt{\alpha t}} + \frac{\sqrt{\alpha t}}{l} \right). \quad (38)$$

Of particular interest is, of course, the surface temperature, T_σ . With the solution according to Eqs.(36)-(38), one obtains from Eq.(26) the following differential equations for T_σ :

$$\frac{dT_\sigma}{dt} = (\dot{q}_0 / c_\sigma) G_0(t) \quad \text{for } 0 < t < t_e; \quad (39)$$

$$\frac{dT_\sigma}{dt} = (\dot{q}_0 / c_\sigma) [G_0(t) - G_0(t - t_e)] \quad \text{for } t > t_e, \quad (40)$$

with

$$G_0(t) = \exp \left(\frac{\alpha t}{l^2} \right) \operatorname{erfc} \left(\frac{\sqrt{\alpha t}}{l} \right). \quad (41)$$

A plot of the function G_0 can be found in [9], Fig. 7.1.

Equations (39)-(41) can easily be integrated numerically, but a qualitative discussion of the solution suffices for the present purpose. First of all, the influence of the surface heat transfer is remarkable. If $c_\sigma < 0$, the heat supply at the surface gives rise to a decrease of the surface temperature for times of the order of $t^* = l^2 / \alpha$. For $c_\sigma > 0$, $t/t^* \rightarrow \infty$, however, Eq.(39) gives

$$\frac{dT_\sigma}{dt} \sim \frac{\dot{q}_0}{\rho c_p \sqrt{\pi \alpha t}}, \quad (42)$$

i.e. the surface temperature changes in the classical manner as if there were no surface heat capacity. Since l is very small, cf. above, the time scale t^* is also very small, but well within the range of presently available pulsed lasers. Thus one could envision the application of picosecond lasers to reduce the surface temperature step by step. The analysis may be based on Duhamel's theorem, but cannot be given here.

Associated with the decrease of the surface temperature is, of course, a decrease of the temperature in the liquid near the surface. It follows from the solution for the heat flux, i.e. Eq.(36) together with Eq.(38), that the decrease is restricted to a boundary layer whose thickness is as small as $|l|$. For $z/|l| \rightarrow \infty$ the classical result, represented by the first term on the right-hand side of Eq.(38), is obtained even for times as small as t^* .

Instability due to negative surface heat capacity

When heat is supplied locally to a surface with negative heat capacity, the surface temperature will decrease, at least initially, in the region of heat supply. The temperature gradient in the liquid will then give rise to a heat flow from the bulk of the liquid to the surface, thereby enhancing the decrease of the surface temperature. Obviously, this effect may lead to an instability of the initial state. The following linear perturbation analysis is intended to provide a quantitative description of the instability. For non-linear phenomena far from thermodynamic equilibrium cf. [4].

As in preceding section, a semi-infinite body of liquid with horizontal surface is considered. However, it is now assumed that there is no heat transfer from the surroundings to the surface. Furthermore, it is assumed that the temperature in the liquid may depend not only on the vertical coordinate, z , but also on the horizontal coordinate, x . Thermo-convective motion of the liquid will be neglected in the energy balance, which, therefore, reduces to the heat diffusion equation

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial z^2} \right), \quad (43)$$

with the boundary conditions

$$c_\sigma \frac{\partial T}{\partial t} = k \frac{\partial T}{\partial z} \quad \text{for } z = 0; \quad (44)$$

$$T = T_\infty = \text{const} \quad \text{for } z \rightarrow \infty. \quad (45)$$

Of interest is now the evolution of spatially periodic perturbations of the thermodynamic equilibrium state, which is characterized by the uniform temperature $T = T_\infty$. Thus solutions of the form

$$(T - T_\infty)/T_\infty = f(z) \exp(\beta t + i\kappa x) \quad (46)$$

are sought, with the amplification rate, β , and the wave number, κ , being taken as real numbers. Of course, the wave number is always positive, whereas the amplification rate may be positive (amplified perturbations), zero (stationary perturbations), or negative (damped perturbations).

Eq.(46) satisfies the heat diffusion equation, Eq.(43), together with the boundary condition at infinity, Eq.(45), if

$$f = \exp\left(-\sqrt{\kappa^2 + \beta/\alpha} z\right), \quad (47)$$

while the boundary condition at the surface, Eq.(44), gives

$$\beta = \frac{\alpha}{2l^2} \left(1 \pm \sqrt{1 + 4K^2} \right), \quad \begin{array}{l} + \text{ for } K < 0, \\ - \text{ for } K > 0, \end{array} \quad (48)$$

with the non-dimensional wave number

$$K = l\kappa = c_\sigma \kappa / \rho c_p \quad (49)$$

and the parameter l according to Eq.(35). For $K = 0$, i.e. the surface heat capacity not taken into account, the classical result $\beta = -\alpha\kappa$ is obtained, of course. But note that Eq.(48) gives the classical result in the limit $K \rightarrow 0+$, whereas the solution diverges as $K \rightarrow 0-$ for a fixed value of l .

Equation (47) shows that the penetration depth of the perturbations is of the order of δ , with

$$\delta = (\kappa^2 + \beta/\alpha)^{-1/2}, \quad (50)$$

or

$$\delta = 2|l| \left(\pm 1 + \sqrt{1 + 4K^2} \right)^{-1}, \quad \begin{array}{l} + \text{ for } K < 0, \\ - \text{ for } K > 0. \end{array} \quad (51)$$

Equations (48) and (51) allow the following conclusions with regard to the stability of the state of thermodynamic equilibrium of the system consisting of the liquid and the surface. If the surface heat capacity is negative, K is also negative, while β is positive, i.e. the perturbations increase with time, and the state of thermodynamic equilibrium is unstable. However, the perturbations are confined to a

boundary layer, whose thickness is of the order of $|l|$, i.e. nanometers for common liquids, cf. above. In the case of amplified perturbations, the maximum value $\delta_{\max} = |l|$ of the penetration depth is obtained for $K \rightarrow 0-$, i.e. in the limit of long waves in the scale of $|l|$. For fixed values of c_σ , with $c_\sigma < 0$, the amplification rate attains the minimum value $\beta_{\min} = \alpha/l^2$ in this long-wave limit. In the limit of very short waves, on the other hand, $\delta/|l| \sim 1/(-K) \rightarrow 0$ and $\beta \sim |K| \alpha/l^2 = \kappa\alpha/|l|$ as $K \rightarrow -\infty$.

As the unstable perturbations are confined to a very thin layer near the surface, the physical relevance may be seen as rather limited. For numerical solutions of heat transfer problems, however, the instabilities may cause severe problems, in particular, when high resolution is desirable, or required, for small systems. It may be necessary to introduce a boundary layer at the surface in order to deal properly with the (numerical) stability problem.

NANO-DROPLETS: AREA-DEPENDENT SURFACE TENSION

It has been observed that the surface tension of very small droplets depends not only on the temperature, but also on the radius of the droplet, cf. [10], pp. 112 and 126-130, and [11], [12]. For constant temperature, the surface tension decreases, in general, with decreasing droplet radius. In view of recent discussions on the applicability of macroscopic thermodynamics to nano-droplets [13], it is investigated in what follows whether, and perhaps how, the dependence of the surface tension on the radius affects the classical thermodynamic relations given in the Introduction. As the surface tension is then no longer only a local quantity of the surface, but also depends on properties of the bulk of the liquid, this is another example of considering the surface as a non-autonomous system.

For the present purpose it is convenient to introduce the surface area instead of the droplet radius as an independent variable. Thus the thermal equation of state of the surface is formally written as

$$\sigma = \sigma(T, A). \quad (52)$$

Gibbs' fundamental equation, Eq.(2), remains valid, of course, but in Eq.(3) the ordinary derivative is to be replaced by the partial derivative to obtain

$$\left(\frac{\partial U_\sigma}{\partial A} \right)_T = u_\sigma = \sigma - T \left(\frac{\partial \sigma}{\partial T} \right)_A, \quad (53)$$

with $u_\sigma = u_\sigma(T, A)$. Similarly, Eq.(4) remains valid as the definition of the surface heat capacity, but Eq.(5) is to be replaced by

$$c_\sigma + A \frac{\partial c_\sigma}{\partial A} = \frac{\partial u_\sigma}{\partial T} = -T \frac{\partial^2 \sigma}{\partial T^2}, \quad (54)$$

with $c_\sigma = c_\sigma(T, A)$.

The entropy of the unit surface, s_σ , is defined as

$$s_\sigma = \left(\frac{\partial S_\sigma}{\partial A} \right)_T. \quad (55)$$

Based on this definition, the classical relation Eq.(8) is re-obtained, apart from the partial derivative instead of the ordinary one, i.e.

$$s_\sigma = - \left(\frac{\partial \sigma}{\partial T} \right)_A = \frac{u_\sigma - \sigma}{T}. \quad (56)$$

In addition, the classical relation

$$\left(\frac{\partial S_\sigma}{\partial T} \right)_A = \frac{1}{T} \left(\frac{\partial U_\sigma}{\partial T} \right)_A = \frac{Ac_\sigma}{T} \quad (57)$$

is also re-obtained from Eq.(3).

There are further thermodynamic relations that follow from Gibbs' fundamental equation together with the integrability conditions for the differentials of quantities of state. In particular, one re-obtains the classical "potential" relations for the surface internal energy, U_σ , and the surface free energy, $F_\sigma = U_\sigma - TS_\sigma$, i.e.

$$\left(\frac{\partial U_\sigma}{\partial S} \right)_A = T ; \quad \left(\frac{\partial U_\sigma}{\partial A} \right)_S = \sigma ; \quad (58)$$

and

$$\left(\frac{\partial F_\sigma}{\partial T} \right)_A = -S_\sigma ; \quad \left(\frac{\partial F_\sigma}{\partial A} \right)_T = \sigma , \quad (59)$$

as well as Maxwell's relations

$$\left(\frac{\partial S_\sigma}{\partial A} \right)_T = - \left(\frac{\partial \sigma}{\partial T} \right)_A ; \quad (60)$$

$$\left(\frac{\partial T}{\partial A} \right)_S = \left(\frac{\partial \sigma}{\partial S_\sigma} \right)_A. \quad (61)$$

$()_S$ indicates a partial derivative with S_σ kept constant.

Based on the thermodynamic relations given above, the problem of the vapour pressure, p_v , at a small droplet in thermodynamic equilibrium can be re-considered, e.g. following [14], §22. To be consistent, the surface area of the droplet, A , is related to the mole number, n , of the droplet according to the relation $dA/dn = 4\tilde{V}_l/d$, where \tilde{V}_l is the molar volume of the liquid, and d is the droplet diameter. It turns out that the classical result, i.e. the famous Kelvin equation

$$\ln \frac{p_v}{p_s} = \frac{4\sigma}{d} \frac{\tilde{V}_l}{\tilde{R}T}, \quad (62)$$

is re-obtained, with \tilde{R} as the universal (molar) gas constant, and p_s as the saturation pressure at a plane surface. This is not in accord, however, with the results of molecular

simulations for droplets with diameters of the order of a few nanometers, cf. [10], p. 127, although Laplace's equation

$$p_l - p_v = 4\sigma/d, \quad (63)$$

which follows from mechanical equilibrium, has been found to be in good agreement ([10], pp. 112 and 126). Preliminary investigations by the present author seem to indicate that the assumption of constant density of the liquid, which is – often implicitly – made in deriving Kelvin's equation, may be the reason for the discrepancies, but a further discussion of that question is beyond the scope of the present paper.

CONCLUSIONS

Treating surfaces as non-autonomous thermodynamic systems leads to interesting and sometimes strange results. The change of state of a liquid film that is sufficiently thin to allow neglecting the – possibly negative – surface heat capacity is, nevertheless, affected by the internal energy of the surface. Short pulses of heat supplied to a surface with negative surface heat capacity give rise to a decrease of the surface temperature and of the temperature in a boundary layer of liquid near the surface. For the case of no heat supply from the surroundings, thermal instabilities in the boundary layer are predicted for negative surface heat capacities. It is true that the boundary layers are of the order of nanometers, i.e. of the molecular size, for common liquids, but the macroscopic description of nano-systems has recently found much interest, cf. [15] for an example. Furthermore, numerical solutions of the macroscopic equations of fluid mechanics and heat transfer may face difficulties associated with those instabilities.

As far as the dependence of surface tension on the radius of nano-droplets is concerned, treating the surface as a non-autonomous system, but retaining the other assumptions, has not lead to a generalization of Kelvin's equation for the vapour pressure. Thus other generalizations, in particular accounting for the compressibility of the liquid, are desirable.

ACKNOWLEDGMENTS

The author is indebted to Mr C. Buchner and Dr R. Jurisits for providing valuable references to other authors' work on surface heat capacities. Furthermore, Dr R. Jurisits performed numerical evaluations that have been of much help for a better understanding of the analytical solutions. Financial support by Androsch International Consulting Ges.m.b.H, Vienna, is also gratefully acknowledged.

NOMENCLATURE

Symbol	Quantity	SI Unit
A	Surface area	m^2
c_p	Isobaric specific heat capacity	J/kgK
c_v	Isochoric specific heat capacity	J/kgK
c_σ	Surface heat capacity	J/m ² K
d	Droplet diameter	m
f	Auxiliary function	-
F	Force	N
F_σ	Free energy of surface	J
G	Auxiliary function	-

h_σ	Enthalpy of unit surface area	J/m ²
i	Imaginary unit	-
k	Thermal conductivity	W/mK
L	Length	m
l	Parameter, see Eq.(35)	m
m	Mass	kg
n	Mole number	mole/m ³
p	Pressure	N/m ²
\dot{q}	Heat flux	W/m ²
\tilde{R}	Universal gas constant	J/mole K
S_σ	Surface entropy	J/K
s_σ	Entropy of unit surface area	J/Km ²
T	Absolute temperature	K
T_c	Critical temperature	K
t	Time	s
U_σ	Internal energy of surface	J
u_σ	Internal energy of unit surface area	J/m ²
\tilde{V}	Molar volume	m ³ /mole
v	Velocity of liquid or surface	m/s
W	Work	J
x, z	Spatial coordinates	m

Greek symbols

α	Thermal diffusivity	m ² /s
β	Amplification rate	1/s
δ	Thickness of liquid film, or penetration depth	m
κ	Wave number	1/m
ρ	Mass density	kg/m ³
σ	Surface tension	N/m
τ	Shear stress	N/m ²

Subscripts

e	End of time interval
l	Liquid
v	Vapour
s	Saturation
x	Component in x -direction
0	Base state, or at surface
1	Initial state, or perturbation
2	Final state
σ	Surface
∞	At infinity

Superscript

* Reference quantity

Other symbol

[]_± Difference across surface

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