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Analysis of temperature difference driven heat and mass transfer in the Phillips–Onsager cell

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ABSTRACT

In a series of experimental investigations Phillips and co-workers have determined the "Onsager heat of transport" in a cell with layers of a liquid and its vapor. Their results also include experimental observation of "cold to warm distillation", that is temperature difference driven mass transfer through the vapor from a cold to a warm liquid Mills and Phillips [e.g. C.T. Mills, L.F. Phillips, Distillation of a cool liquid onto a warmer surface, Chem. Phys. Lett. 372 (2002) 615–619]. Using standard irreversible thermodynamics for evaporation, condensation and transport, we present a theoretical analysis of the experimental set-up and discuss the reported measurements in terms of layer and interface properties. Necessary and sufficient criteria for a possible temperature difference driven cold to warm mass transfer are given. The criteria indicate that the occurrence of this phenomenon is highly unlikely.

1. Introduction

In many industrial and natural processes conditions for conversion of liquid to vapor, and vice versa, are of vital importance. In dynamic studies of phase transitions it has become increasingly clear that the interfacial region can play a decisive role in determining the rate of transformation. This paper concerns the importance of jumps in temperature and chemical potential at a vapor–liquid interface, in dynamic boundary conditions for transports through a series of phases. The theory of *thermodynamics of irreversible processes* (TIP, [1]) predicts the jumps at the interface [2] from the excess entropy production. The theory will also set the overall criteria for the transport processes, as the entropy production has to be positive everywhere.

Also kinetic theory predicts discontinuities at the interface [3–5]. In addition, kinetic theory predicts the Onsager coefficients of TIP [6–8]. Most kinetic theory models assume a velocity independent condensation coefficient, but more refined models for velocity dependent condensation coefficient are available [9,10]. The refined Onsager coefficients are of the same order of magnitude as those for constant condensation coefficients [11].

Recent molecular dynamics (MD) simulations of non-equilibrium interfaces have also shown interfacial discontinuities in the temperature and a difference between the pressure and the vapor pressure. The resulting Onsager coefficients depend on the interatomic potential used. For short range interatomic potentials, the MD simulations agree well with kinetic theory predictions [12]. For long range potentials, the diagonal resistivities are slightly smaller while the off-diagonal resistivities were larger by a factor of about three [13].

Measurements of Ward and co-workers on forced evaporation showed marked temperature jumps at the phase interface [14–16]. Values for the Onsager coefficients extracted from these data [17] were between one and two orders of magnitude larger than the values predicted by kinetic theory. As pointed out by Bond and Struchtrup [18] the experimental geometry and boundary conditions have a marked influence on the experimental observation. We refer to their paper for details. A better understanding of the origin of the difference in magnitude between simulated and measured coefficients is needed.

In a series of papers Phillips and co-workers [19–22] describe measurements in a device which they call "Onsager cell", to which we shall refer as the "Phillips–Onsager cell". In the cell, a liquid–vapor phase interface with adjacent bulk phases is subjected to a temperature gradient. The cell pressure is measured as a function of the temperature difference between an upper and a lower plate, and the slope of the pressure curve is used to determine the so-called Onsager heat of transport Q^*. Phillips and co-workers report observation of what they call "cold to warm distillation", that is the transport of matter through the vapor from the colder to the warmer side of the cell. This surprising result has as yet not be confirmed elsewhere.

We shall perform a theoretical analysis of the Phillips–Onsager cell using thermodynamics of irreversible processes [1,2,23]. We shall combine a description of the three homogeneous phases in

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the cell, with a description of two interface layers, thereby describing the heterogeneous system. The analysis will show that the heat of transport Q^* determined by Phillips et al. is a property of all layers in the whole Phillips–Onsager cell, and not just of the liquid–vapor interface. In particular it is determined by the interfacial coefficients and the thermal conductivities and thicknesses of the bulk phases, with the latter being dominant in thicker cells, and at higher cell pressures. The overall heat of transfer is related to the interface heat of transfer, q^*, however.

In Section 2 we describe the geometry of the Phillips–Onsager cell, and apply the theory to the cell. We shall distinguish between the case of a wet and a dry upper plate in the cell. Our aim is to provide a more detailed basis for analysis of these important experiments, than available so far. Section 3 gives a detailed discussion and necessary and sufficient criteria for cold to warm mass transfer. Section 4 focusses on the cell pressure, and heat of transfer for the cell. A short discussion of the expected temperature profile is presented in Section 5, before the final conclusions are presented in Section 6.

2. Thermodynamic model of the Phillips–Onsager cell

2.1. Set-up of the cell

The Phillips–Onsager cells that were used in the experiments are described in [19,22], and we shall not discuss their geometry in detail. In principle a cell consists of a chamber of large base area and relatively low height to ensure that the transport processes in vertical direction are essentially one-dimensional. The upper and lower plates that enclose the chamber are carefully thermostatted by circulating fluids above and below.

The chamber is filled with a substance, e.g. aniline [19] or water [22], which is carefully cleaned and degassed, so that only pure substance is in the chamber. Filling amount and temperatures are such that some of the substance is liquid and the remainder in the vapor state. In other experiments the cell was filled with mixtures, but this is outside the scope of our present consideration.

Typically, for an experimental run the temperature T_L of the bottom plate is kept constant and the temperature T_H of the upper plate is varied while the cell pressure p is measured. A series of measurements results in a curve $p(T_H)$, with T_L as parameter. From that measurement Phillips and co-workers determine their heat of transport as (in dimensionless form)

$$Q^* = -\frac{T_L}{p_{sat}(T_L)}\frac{dp(T_H)}{dT_H}. \tag{1}$$

In the cited papers, pressure is typically plotted over the temperature difference $(T_H - T_L)$, which corresponds to a simple shift in the temperature scale.

For the full thermodynamic evaluation of the cell, we need to resolve the temperature field within the cell, which we will consider as a simple 1-dimensional system. Fig. 1 shows a schematic of the temperatures and layer thicknesses in the cell. In part of the experiments liquid droplets are observed at the upper plate as a result of condensation. Therefore we have to consider two different configurations, one with wet upper plate, the other with dry upper plate.

For the cell with wet upper plate (right), we have highlighted the temperatures T_L and T_H of the cell walls as well as the temperatures T_l and T_v of liquid and vapor directly at the lower phase boundary, and the temperatures T_V and T_Δ of vapor and liquid directly at the upper phase boundary. The liquid directly at the bottom and upper plates assumes the temperatures of the plates. The lower liquid layer has thickness x_L, the vapor layer has thickness x_V, and the upper liquid layer has thickness Δ, which is typically much less than x_L. To simplify the treatment, we shall consider only a fully wetted upper plate in our calculations.

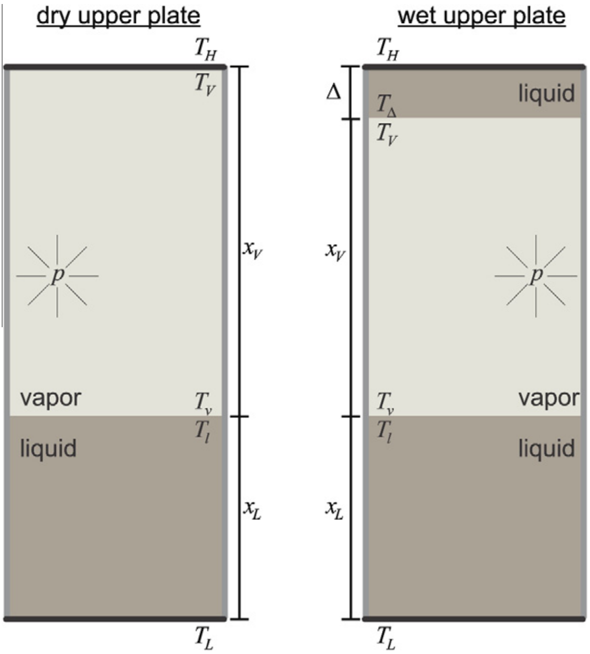

Fig. 1. Schematic of temperatures T_α and layer thicknesses in the Onsager cell with dry upper plate (left) and wet upper plate (right). The temperatures T_L and T_H at bottom and upper plate are controlled by thermostats, all other temperatures $(T_l, T_v, T_V, T_\Delta)$ and the pressure p result from the transport processes within the cell.

For the cell with dry upper plate (left), we have highlighted the temperatures T_L and T_H as well as the temperatures T_l and T_v of liquid and vapor directly at the phase boundary, and the temperature T_V of the vapor in front of the upper plate. For low vapor pressures a temperature jump between vapor and wall can exist, so that $T_V \neq T_H$. The liquid at the bottom plate, however, assumes the temperature of the plate, T_L. The liquid layer has thickness x_L and the vapor layer has thickness x_V.

To simplify the discussion of Phillips' experiments, we model the vapor as an ideal gas, and the liquid as an incompressible ideal liquid, and we shall assume constant thermal conductivities throughout. These assumptions are well justified at the low pressures in the experiments, and the rather small temperature differences employed. In particular, to mimic the experiments, we shall consider data for water and aniline. For water, we use the modelling and data employed in [18], for aniline we use the same modelling with data from a public database [24].

2.2. Liquid–vapor interface conditions

Irreversible thermodynamics for a liquid vapor phase interface reveals that transport of mass and heat across the interface follows the interface conditions [2]

$$\begin{bmatrix} \frac{p_{sat}(T_l)-p}{\sqrt{2\pi R T_l}} \\ \frac{p_{sat}(T_l)}{\sqrt{2\pi R T_l}}\frac{T_l - T_v}{T_l} \end{bmatrix} = \begin{bmatrix} \hat{r}_{11} & \hat{r}_{12} \\ \hat{r}_{12} & \hat{r}_{22} \end{bmatrix} \begin{bmatrix} J \\ \frac{q_v}{R T_l} \end{bmatrix}, \tag{2}$$

where R is the specific gas constant, T_l and T_v are the temperatures of liquid and vapor directly at the interface, $p_{sat}(T_l)$ is the equilibrium saturation pressure at the liquid interface temperature, p is the actual pressure of the system, J is the mass flux (positive for evaporation, negative for condensation), and q_v is the measurable heat flux in the vapor, as given by Fourier's law. The above equation is written such that the matrix of Onsager resistivities $\hat{r}_{\alpha\beta}$ is