

HEAT AND MASS TRANSFER ACROSS PHASE BOUNDARIES: ESTIMATES OF COUPLING COEFFICIENTS

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ABSTRACT. Heat and mass transport across phase boundaries are central in many engineering problems. The systematic description offered by classical non-equilibrium thermodynamics theory, when extended to surfaces, gives the interaction between the two fluxes in terms of coupling coefficients. It is shown in this paper that these coupling coefficients are large. The few experimental and computational results that are available confirm this. Neglect of coupling coefficients, which is common in most models for surface transport, may lead to errors in the heat flux. We present values for the coupling coefficient in a one-component system in terms of the heat of transfer, as obtained from non-equilibrium molecular dynamics simulations, kinetic theory and the integrated non-equilibrium van der Waals' square gradient model.

1. Introduction

We have recently shown how to integrate fluxes and forces across phase boundaries, using the systematic theory of classical non-equilibrium thermodynamics [4, 5]. This theory has as starting point the entropy production in the heterogeneous system that consists of an interface (a separate thermodynamic system) and its two adjacent layers. The entropy production defines the independent forces as linear combinations of all fluxes. The forces and fluxes are related by a symmetric matrix of transport coefficients, the Onsager coefficient matrix. By following this systematic procedure, the transport problem in question is described in a way that is consistent with the second law of thermodynamics [4, 5]. The integrated approach [4] gives overall transport coefficients for the interface plus boundary layers.

In this paper, we repeat first the equations of transport for heat and one component across a planar surface, as given before [5]. This gives a sufficient background for analysis of the coupling coefficient for heat and mass transfer. The coefficient turns out to be large and therefore important. The system we are looking at has a heat and mass flux into as well as out of the interface. In the stationary state that we examine, the mass flux is continuous through the surface, but the heat flux is not, according to the energy balance. The large enthalpy change of the phase transition is the reason for the large coupling coefficient between heat and mass transport. We show this, using various equivalent forms of the entropy production. The interaction between the heat and mass flux, which must be symmetric according to Onsager, can not be neglected in a correct description of transport across the phase boundary. This has a bearing on phase transition modelling.

We continue to report the few values for the coupling coefficient published in the literature, for different systems and by different methods. The systems are atomic (Lennard-Jones particles) or molecular (octane, water). The methods are non-equilibrium molecular dynamics simulations, an analytical study of the non-equilibrium van der Waals square gradient model for the surface, as well as experiments. All methods show, when interpreted using non-equilibrium thermodynamics, that the coupling coefficient is large. We conclude that there is a need for more work to establish these coefficients and improve the current theoretical description.

2. Theory

The entropy production for a planar interface with boundary layers is, with the transport of heat and mass of one component into and out of the interface, equal to [3]:

$$(1) \quad \sigma^s = J_q^l \left[\frac{1}{T^s} - \frac{1}{T^l} \right] + J_q^g \left[\frac{1}{T^g} - \frac{1}{T^s} \right] - J^l \left[\frac{\mu^s(T^s) - \mu^l(T^s)}{T^s} \right] - J^g \left[\frac{\mu^g(T^s) - \mu^s(T^s)}{T^s} \right]$$

The measurable flux of heat from the l-phase into the interface is J_q^l , while the one from the interface into the g-phase is J_q^g . The corresponding mass fluxes are J^l and J^g . The conjugate forces are the differences (the value at the surface minus the value in the l-phase, and the value in the g-phase minus the value at the surface) of the inverse temperature and of minus the chemical potentials at the temperature of the surface divided by the temperature of the surface, T^s . The first superscripts l, s and g indicate values in the l-phase, at the interface and in the g-phase, respectively. The second superscript indicates the location in the phase; l,g means, for instance, in the l-phase close to the surface of the g-phase. The chemical potential in the interface is $\mu^s(T^s)$. When we write $\mu^l(T^s)$ it means that the chemical potential of the l-phase near the surface is taken at the temperature of the interface. The frame of reference for the fluxes is the interface. For simplicity we do not consider fluxes along the interface. Possible other components are not moving relative to the surface. The words surface and interface are used interchangeably.

On a macroscopic scale (say in microns), the l-phase is located in the region with $x > 0$, while the g-phase is located in the region with $x < 0$. The interface appears as a discontinuity on this scale, but with excesses in entropy, internal energy and mass. This formulation is due to Gibbs (1961), see also [5]. For evaporation and condensation in a one-component system, we take the l-phase to be the liquid and the g-phase to be the gas or the vapour. The description is also applicable to systems in which only one component is moving with respect to a stationary background of other components.

The force-flux pairs in the excess entropy production may be divided into two groups. The first group contains coupling of fluxes and forces on the incoming side of the surface and the second group contains coupling of fluxes and forces on the outgoing side. Because the processes on the two sides of the surface occur in series, it is expected that these processes are weakly coupled. We shall therefore neglect this coupling across the surface. In

that case the force-flux relations become

$$(2) \quad \begin{aligned} \frac{1}{T^s} - \frac{1}{T^l} &= r_{qq}^{s,l} J_q^l + r_{q\mu}^{s,l} J^l \\ -\frac{\mu^s(T^s) - \mu^l(T^s)}{T^s} &= r_{\mu q}^{s,l} J_q^l + r_{\mu\mu}^{s,l} J^l \end{aligned}$$

for the left hand side of the surface and

$$(3) \quad \begin{aligned} \frac{1}{T^g} - \frac{1}{T^s} &= r_{qg}^{s,g} J_q^g + r_{q\mu}^{s,g} J^g \\ -\frac{\mu^g(T^s) - \mu^s(T^s)}{T^s} &= r_{\mu q}^{s,g} J_q^g + r_{\mu\mu}^{s,g} J^g \end{aligned}$$

for the right hand side of the surface. The r -coefficients on the diagonal are resistivities to heat and mass transfer. The off-diagonal coefficients are the so-called coupling coefficients in non-equilibrium thermodynamics theory. They are here given for the l- and g-sides of the surface, respectively. They are pair-wise the same (the Onsager relations). Rather than using the coupling coefficients directly, we shall use their ratio with the thermal resistivity, the so-called heat of transfer for the i- and o-side of the surface are defined by:

$$(4) \quad q^{*,l} = \left(\frac{J_q^l}{J^l} \right)_{\Delta_{l,s}T=0} = -\frac{r_{q\mu}^{s,l}}{r_{qq}^{s,l}} \quad \text{and} \quad q^{*,g} = \left(\frac{J_q^g}{J^g} \right)_{\Delta_{s,g}T=0} = -\frac{r_{q\mu}^{s,g}}{r_{qq}^{s,g}}$$

We see that they are given by the ratios of the coupling coefficient and the resistivity to heat transfer for the l- and g-side, respectively. The definition says that the temperature of the surface in turn is equal to the temperature of the l- and the g-side.

These heats of transfer for the sides of the surface are ratios of the asymptotic values of the bulk fluxes at a constant temperature. They are therefore equal to the asymptotic values of the heats of transport in the adjacent homogeneous phases. This is a useful property as it reduces the number of new unknown resistivities for the surface to two for each side. The heats of transfer in the homogeneous phases are not normally large. They can often be neglected in descriptions of transports in these phases, at least for small temperature gradients, or small mass fluxes. In flames, where the temperature gradient can amount to 10^7 K/m, neglecting these coefficients is not advisable, however.

With the heats of transfer for the homogeneous phases, we may write for the l-side:

$$(5) \quad \begin{aligned} \frac{1}{T^s} - \frac{1}{T^l} &= r_{qq}^{s,l} [J_q^l - q^{*,l} J^l] \\ -\frac{\mu^s(T^s) - \mu^l(T^s)}{T^s} &= -r_{\mu q}^{s,l} q^{*,l} J_q^l + r_{\mu\mu}^{s,l} J^l \end{aligned}$$

Similar equations can be written for the g-side. There is mass transport into the surface due to the temperature difference between the surface and the homogeneous phase, similar to the Soret effect in the homogeneous phase. Conversely, there is also a heat effect associated with adsorption or desorption, a Dufour effect. The coefficient matrix obeys Onsager symmetry.

For stationary state conditions there is no storage or release of mass and heat at the surface. It follows that

$$(6) \quad J^l = J^g = J$$

$$(7) \quad J_q^l = J_q^g + J\Delta_{l,g}H$$

where $\Delta_{l,g}H = H^g - H^l > 0$ is the enthalpy of evaporation. There are thus only two independent fluxes. The enthalpy difference is, unless otherwise indicated, evaluated at the same temperature that the superscript of the enthalpy indicates. Using J and J_q^l as independent fluxes in the equations above, we obtain

$$(8) \quad \begin{aligned} \frac{1}{T^s} - \frac{1}{T^l} &= r_{qq}^{s,l} [J_q^l - q^{*,l}J] \\ -\frac{\mu^s(T^s) - \mu^l(T^s)}{T^s} &= -r_{qq}^{s,l} q^{*,l} J_q^l + r_{\mu\mu}^{s,l} J \end{aligned}$$

for the jumps from the left hand side to the surface and

$$(9) \quad \begin{aligned} \frac{1}{T^g} - \frac{1}{T^s} &= r_{qq}^{s,g} [J_q^l - (q^{*,g} + \Delta_{l,g}H)J] \\ -\frac{\mu^g(T^s) - \mu^s(T^s)}{T^s} &= -r_{qq}^{s,l} q^{*,g} J_q^l + (r_{\mu\mu}^{s,g} + r_{qq}^{s,g} q^{*,g} \Delta_{l,g}H)J \end{aligned}$$

for the jumps from the surface to the right hand side.

In order to obtain the jumps *across* the surface, we add Eqs.(8) and (9):

$$(10) \quad \begin{aligned} \frac{1}{T^g} - \frac{1}{T^l} &= (r_{qq}^{s,l} + r_{qq}^{s,g})J_q^l - [r_{qq}^{s,l} q^{*,l} + r_{qq}^{s,g} (q^{*,g} + \Delta_{l,g}H)J] \\ -\frac{\mu^g(T^s) - \mu^l(T^s)}{T^s} &= -[r_{qq}^{s,l} q^{*,l} + r_{qq}^{s,g} q^{*,g}] J_q^l + [r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g} + r_{qq}^{s,g} q^{*,g} \Delta_{l,g}H] J \end{aligned}$$

In order to eliminate T^s in Eq.(10b), we can use the definition of the difference in the chemical potential across the interface at the interfacial temperature in combination with the Gibbs-Helmholtz equation, for details, see [5]. We can then rewrite the equation set (10) as:

$$(11) \quad \begin{aligned} \frac{1}{T^g} - \frac{1}{T^l} &= (r_{qq}^{s,l} + r_{qq}^{s,g})J_q^l - [r_{qq}^{s,l} q^{*,l} + r_{qq}^{s,g} (q^{*,g} + \Delta_{l,g}H)J] \\ -\frac{\mu^g(T^l) - \mu^l(T^l)}{T^l} &= -[r_{qq}^{s,l} q^{*,l} + r_{qq}^{s,g} (q^{*,g} + \Delta_{l,g}H)] J_q^l \\ &\quad + [r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g} + r_{qq}^{s,g} \Delta_{l,g}H (2q^{*,g} + \Delta_{l,g}H)] J \end{aligned}$$

Equations (11) make it possible to calculate the jumps of the temperature and the chemical potential across the surface in terms of three unknown surface coefficients. These are $r_{qq}^{s,l}$, $r_{qq}^{s,g}$ and the sum $r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g}$. Again, we see that the coefficient matrix has Onsager symmetry. The forces and fluxes used in Eq.(11) are conjugate, a fact that can be verified by writing the entropy production in terms of these forces and fluxes. All together, this means that the second law of thermodynamics is always obeyed with the set. This set, derived with a

simple assumption of the surface (negligible coupling across the surface between the sets of Eqs.(2) and (3)), is now the basis for further examinations.

2.1. One-component phase transitions. Consider now the simplest case, evaporation and condensation in a one-component system. The heats of transfer in the homogeneous liquid and the homogeneous vapour phases (Eqs.4) are then zero. Equations (11) reduce to

$$(12) \quad \begin{aligned} \frac{1}{T^g} - \frac{1}{T^l} &= (r_{qq}^{s,l} + r_{qq}^{s,g}) J_q^l - r_{qq}^{s,g} \Delta_{1,g} H J \\ -\frac{\mu^g(T^l) - \mu^l(T^l)}{T^l} &= -r_{qq}^{s,g} \Delta_{1,g} H J_q^l + [r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g} + r_{qq}^{s,g} (\Delta_{1,g} H)^2] J \end{aligned}$$

Bedeaux et al. [5] considered isothermal mass transfer. Equation (12) then gives (for small driving forces)

$$(13) \quad -\frac{\mu^g(T^l) - \mu^l(T^l)}{T^l} = -R \ln \frac{p}{p^*(T^l)} = [r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g} + r_{qq}^{s,g} (\Delta_{1,g} H)^2] J$$

Here p is the pressure and $p^*(T^l)$ is the vapor pressure of the liquid at temperature T^l . The heat of transfer for the two sides the surface in this formulation becomes from Eqs.(8,9):

$$(14) \quad q^{*,s,l} = \left(\frac{J_q^l}{J^l} \right)_{\Delta_{1,s} T=0} = \frac{r_{qq}^{s,g} \Delta_{1,g} H}{r_{qq}^{s,l} + r_{qq}^{s,g}} \quad \text{and} \quad q^{*,s,g} = \left(\frac{J_q^g}{J^g} \right)_{\Delta_{s,g} T=0} = -\frac{r_{qq}^{s,l} \Delta_{1,g} H}{r_{qq}^{s,l} + r_{qq}^{s,g}}$$

The enthalpy of evaporation, $\Delta_{1,g} H$, is large, positive and in good approximation independent of the temperature. The resistivities to heat transfer are positive. This explains that the heat of transfer on the liquid side, $q^{*,s,l}$ is positive, while $q^{*,s,g}$ is negative on the vapor side. At least one heat of transfer has a large absolute value. Equations (4) had, for comparison, small heats of transfer in the homogeneous phases. The definitions of the various heats of transfer are important to understand the difference. In Eq. (14), the temperature difference across the surface is zero, while in Eq. (4) there is a zero difference in temperature between the surface and the homogeneous phase. It is important to realize that the temperature of the surface will be larger (or smaller) than the temperatures on both sides of the surface for condensation (evaporation) when $\Delta_{1,g} T = 0$.

In the one-component case a simple physical interpretation of Eq.(14) is possible. The phase transition gives a heat source (or sink) at the surface. The equations say that this heat is then conducted away from (or to) the surface, partly into the gas phase, partly into the liquid phase. The relative amount going into (or coming from) each phase is determined by the relative size of the thermal resistivities to the heat flux on both sides.

2.2. Multicomponent phase transitions, one volatile component. In multi-component cases with only one volatile component, Eq.(11a) gives the heats of transfer for the surface:

$$(15) \quad \begin{aligned} q^{*,s,l} &= \left(\frac{J_q^l}{J^l} \right)_{\Delta_{l,s}T=0} = \frac{r_{qq}^{s,l} q^{*,l} + r_{qq}^{s,g} (q^{*,g} + \Delta_{l,g}H)}{r_{qq}^{s,l} + r_{qq}^{s,g}} \\ q^{*,s,g} &= \left(\frac{J_q^g}{J^g} \right)_{\Delta_{s,g}T=0} = - \frac{r_{qq}^{s,l} (q^{*,l} - \Delta_{l,g}H) + r_{qq}^{s,g} q^{*,g}}{r_{qq}^{s,l} + r_{qq}^{s,g}} \end{aligned}$$

where we again used Eq.(7). Not only the enthalpy difference, but also the heats of transfer in the homogeneous phases contribute to the heats of transfer for the surface. The heats of transfer in the homogeneous phases give further contributions to the heats of transfer of the surface.

Again we may conclude that the heats of transfer or the coupling coefficients for the surface are large. The heats of transfer for the homogeneous phases are of the order of magnitude of 500 J/mol, while the absolute value of $\Delta_{l,g}H$ is of the order of 5 to 50 kJ/mol. The influence of the heats of transfer of the homogeneous phases on the surface heats of transfer is thus a second order effect. By neglecting the surface heats of transfer in the heat flux in a binary mixture, an error of 20-30% was found by Olivier [12], for temperature jumps of 20 K across the surface. We arrive at several conclusions:

- It is not enough to use Fourier's law to describe heat transfer across an interface when there is a simultaneous mass flux. A mass flux generates a large heat transport that must be included.
- Similarly, because of the symmetry relations, the mass flux, cannot be approximated by an equation with one driving force only (i.e. Fick's law) in the presence of a heat flux, using Eqs.(11). The mass flux is largely influenced by the heat flux.
- Models of interface transport, that use Fourier's and Fick's law in combination with the energy conservation equation, violate the second law, because these transport equations are setting heats of transfer across the surface in Eq.(16) equal to zero. The consequences are that the second law and the Onsager relations are not fulfilled at the surface! This can be seen by setting the heat of transfer in the homogeneous phases equal to zero in Eqs.(11). One might argue that Fourier's and Fick's laws can be used with Eqs.(2,3). Four coefficients of transport are then needed, plus information of the (unknown) surface temperature.
- From the energy balance we find a relation between the heats of transfer: $q^{*,s,g} = q^{*,s,l} - \Delta_{l,g}H$

This insight provides knowlegde on how to write proper flux equations for important industrial and natural phenomena like evaporation, condensation, or distillation. We proceed to look at coefficient values.

3. The heat of transfer for the vapour side of the interface

The resistivities to heat transfer in the absence of a mass flux, $r_{qq}^{s,l}$ and $r_{qq}^{s,g}$, and the total resistivity to mass transfer in the absence of a heat flux, $r_{\mu\mu}^{s,l} + r_{\mu\mu}^{s,g}$, are the more common transport coefficients (the resistivities to simple heat transfer and simple mass transfer), and shall not be discussed here. We continue to discuss the coupling coefficient as it appears though the heat of transfer.

3.1. Kinetic theory. Heats of transfer have since long been given by kinetic theory, not only for one- component fluids but also for two-component fluid mixtures (see e.g. Bedeaux et al. [2]). Bedeaux and Kjelstrup [3] gave the heat of transfer as a fraction of the enthalpy of evaporation, using

$$q^{*,s,g} = -k\Delta_{l,g}H$$

They found, using kinetic theory, that $k = 0.18$, independent of the value of the so-called condensation coefficient. The heat of transfer for the vapour side of the surface $q^{*,s,g}$ was calculated for argon, using kinetic theory. The results are shown in Fig.1 (open circles). We see that its value of roughly -350 J/mol does not depend much on the surface tension of the fluid, as we move from the triple point to the critical point. The value is 18 % of the enthalpy of evaporation. The negative sign agrees with Eq. (14). According to kinetic theory, and Eqs.(14), 18 % of the resistance to heat transfer is then located on the liquid side of the surface, while 82 % is located on the vapour side. This is a consequence of the boundary conditions used in kinetic theory.

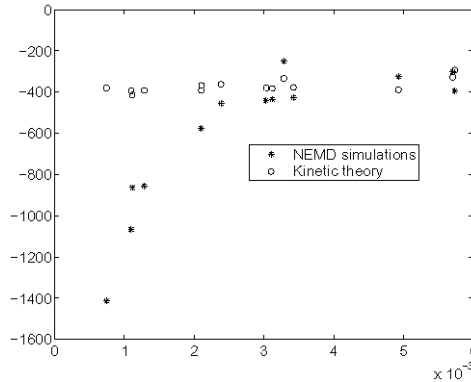


FIGURE 1. The heat of transfer for the vapour side of the surface, $q^{*,s,g}$, in J/mol for argon-like particles from kinetic theory and from NEMD simulations. Courtesy of Røsjorde [15]

In one-component systems, the surface temperature is a unique function of the surface tension [15]. It is therefore appropriate to give properties of the surface as a function of the surface tension.

3.2. Non-equilibrium molecular dynamics simulations. The first determination of heat of transfer for the vapour side of the surface by non-equilibrium molecular dynamics simulations (NEMD), was done by Røsjorde et al. [15] for a one component system of Lennard-Jones spline particles. The equation of state for such systems, is the surface tension as a function of the temperature of the surface. The results for the argon-like particles were also plotted in Fig. 1. It is interesting that the reported values agree with kinetic theory when the surface tension is high. This is expected because these particles are similar to hard spheres near the triple point. Away from the triple point, the results seemed to deviate from the kinetic theory value.

Kjelstrup et al. [7] investigated two pair-potentials for particle interactions, Lennard-Jones /spline and Lennard-Jones pair potentials. The spline potential gave a smaller coupling coefficient than the normal potential. The heat of transfer for the vapour side of the surface with the Lennard-Jones potential was, -9400 J/mol. Simon et al. [16] determined the same heat of transfer in an octane-like fluid. The molecular liquid had a heat of transfer that varied very much like the one in Fig.1. The internal degrees of freedom in the molecule lowered the thermal resistivity of the surface, and also the absolute value of the heat of transfer. At the critical and triple temperatures the values were - 6000 and -1000 J/mol, respectively.

Two-component systems are far more industrially relevant than one-component systems. A first attempt to find interface transport coefficients by NEMD in two-component systems was reported by Olivier et al.[13]. The coefficients for the isotope (ideal) mixture were clearly different from the coefficients for the non-ideal mixture. The obtained coefficients had a similar order of magnitude as above. No agreement with kinetic theory was established, probably because sets of data were combined that belong to conditions that were too far apart. (An incorrect statement was made in this article concerning the sign of the off-diagonal resistivities).

3.3. Analytical results. Using an extension of the van der Waals square gradient model applicable to non-equilibrium systems, Johannessen and Bedeaux [10] established that all common thermodynamic relations apply for the interface, when it is described by excess densities [9], also when it is exposed to a large temperature gradient. Johannessen and Bedeaux [11] proceeded on this basis to calculate all three surface transfer coefficients of Eqs.(11) using measured values of the thermal conductivity of the liquid and the vapour at coexistence, and one fitting parameter. This made it possible to study the dependence of these quantities on the surface tension. Their size depended largely on the fitting parameter. Such a parameter will have to be found using NEMD simulations or experiments.

3.4. Exerimental results. Ward and coworkers measured temperature jumps at interfaces for water, octane and cyclohexane [8]. The authors interpreted the jumps in terms of statistical rate theory, a theory that disregards coupling between heat and mass fluxes. The results were also interpreted using the equations given by non-equilibrium thermodynamics [3]. The surface was found to be very resistive, much more resistive than predicted by kinetic theory for all three components. In that way, the results for octane were at variance with the results found by NEMD by Simon et.al. [16] for this compound.

It has later been established that these experiments contained heat transferred by convection [17], which was not taken into account in the analysis using kinetic theory. It is therefore not surprising that the results were at variance with kinetic theory.

4. Conclusions

From the entropy production of the interface during evaporation or condensation, it is possible to show that the heat of transfer on the vapour side of a one-component fluid is always a fraction of the negative enthalpy of evaporation. Most likely the heat of transfer on the vapor side is also negative for a two-component system, where one component stays behind in the liquid. The sign can be explained by both vapor and liquid taking part

in the process of conducting the heat of evaporation away from or into the interface. The magnitude can be explained by the relative thermal resistivity of the vapor and liquid phases.

We have seen, that it is never justified to neglect the coupling between heat and mass transfer at interfaces when we describe transport across this layer (Eqs.11). The Onsager symmetry for the surface transport processes is then lost, and the second law is violated for the interface. We have therefore collected and discussed the data that are now available to estimate this important coupling effect. It is clear that there are relatively few data for one-component fluids, and that data for mixtures are almost non-existent. It is therefore clearly necessary to increase the work in this technically and otherwise important field. The results indicate that kinetic theory may work for the conditions it is developed for (hard spheres near the triple point), but that non-ideal fluids may have heats of transfer that are order(s) of magnitude away from the kinetic theory value. A systematic collection of thermal conductivities for the surface may give a basis for estimates of the coefficient in one-component fluids, according to Eqs.(15a and b).

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