Integral relations for the surface transfer coefficients.

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(Dated: July 27, 2009)

In this paper we derive relations between the local resistivities inside the interfacial region and the overall resistances of the surface between two phases for a mixture. These resistivities are the coefficients in the force-flux relations for the stationary heat and mass transfer through the interface. We have shown that interfacial resistances depend among other things on the enthalpy profile across the interface. Since this variation is substantial (the enthalpy of evaporation is one of the main differences between liquid and vapor phases) the interfacial resistivities are also substantial. Particularly, surface put up much more resistance to the heat and mass transfer then the homogeneous phase. This is the case not only for the pure heat conduction and diffusion but also for the cross effects like thermal diffusion.

I. INTRODUCTION

During evaporation and condensation heat and mass is transported through the interface. The common description of these phenomena uses certain assumptions which are debatable. For instance, one usually assumes equilibrium conditions at the interface [1] and neglects the coupling effects between the heat and mass transfer [2]. The first one is a zero approximation and it is desirable to extend it to a more accurate theory. This is done in [2] for instance. Neglecting the coupling coefficients was shown to violate the second law of thermodynamics for a one-component system [3]. The coupling is important since the corresponding transfer coefficients depend on the enthalpy of vaporization. The significance of this quantity in this context is due to the large difference between the liquid and the vapor values of the enthalpy.

The situation becomes even more complicated when one consider evaporation in mixtures. These processes happen in such industrial applications as distillation and therefore the precise description is important. Depending on conditions one can get the mass fluxes of components in the same or in the opposite directions.

There has been done a number of studies of the interfacial transport for one-component systems: experiments [4, 5, 6, 7], molecular dynamic simulations [8, 9, 10, 11, 12], kinetic theory [13, 14, 15, 16] and square gradient continuous description [17, 18]. All these works use different approaches, which allows one to investigate different aspects. Mainly one-component systems have been studied. One of the points of interest is the dependence of the overall interfacial resistances on the continuous profiles. Once we have a description which relates the resistance of the Gibbs surface [19] to the continuous profiles of, in particular, local resistivities, we can describe the surface separately from the adjacent bulk phases which is closely related to hypothesis of local equilibrium of a surface [2].

In this paper we extend the analysis done in [18] for one-component system. Here we do the analysis for mixtures. Using the square gradient theory for the non-equilibrium interface developed earlier [20] we derive the general relations for the case of the transport perpendicular to the surface. We show that, as in the case of a one-component system, one can obtain the interfacial resistances using the continuous profiles obtained for equilibrium. This simplifies analysis a lot since one does not need to consider a non-equilibrium solution in order to obtain these resistivities. This is in fact a requirement, which the interfacial resistances must satisfy: as being defined within the linear force-flux relations they should depend only on unperturbed quantities, i.e. equilibrium ones.

The evaporation and condensation often take place not only through planar interfaces, but also through curved ones, like the evaporation into a bubble. We do not restrict ourselves to the planar interfaces and give the expressions for the interfacial resistivities for curved surfaces.

In [21] we have obtained the overall interfacial resistivities $R^q$ and $R^f$ using three different methods: an experiment-like procedure, a perturbation cell method and kinetic theory (only $R^q$). Those methods were found to be in a good agreement. In this paper we compare them with the interfacial resistivities found using integral relations, which relates these quantities to the local resistivities directly. We show that the agreement is also good.

In this paper we will focus on the heat and mass transfer through the interface of a two-phase mixture. We will not consider non-equilibrium perturbation along the surface. We will also assume the fluid to be non-viscous. Furthermore we will focus on the stationary non-equilibrium perturbation. In Sec. [IV] we give the expressions for the local and the excess entropy production found in [20] and [21]. In Sec. [V] we derive the integral relations in general form. It is convenient to use measurable heat and mass fluxes and we therefore show how to translate general relations to the resistivities associated with the measurable fluxes in Sec. [V]. In Sec. [V] we give the explicit expressions for a
binary mixture and apply the analysis to the particular mixture of cyclohexane and \( n \)-hexane. Concluding remarks are given in Sec. [VI].

II. THE ENTROPY PRODUCTION.

A. Stationary states.

Consider the total energy flux \( \mathbf{J}_e \) and the mass fluxes \( \mathbf{J}_i \equiv \rho_i \mathbf{v}_i \) and \( \mathbf{J}_m \equiv \rho \mathbf{v} \), where \( \rho_i \) and \( \rho \) are the density of the \( i \)-th component and the overall density respectively, while \( \mathbf{v}_i \) and \( \mathbf{v} \equiv \sum_{i=1}^{n-1} \xi_i \mathbf{v}_i \) are the velocity of the \( i \)-th component and the barycentric velocity respectively. Furthermore \( \xi_i \) is the mass fraction of the \( i \)-th component and \( n \) is the total number of components. In the stationary states these fluxes satisfy the relations

\[
\nabla \cdot \mathbf{J}_e = 0, \quad \nabla \cdot \mathbf{J}_i = 0, \quad \nabla \cdot \mathbf{J}_m = 0
\]

As we are interested in transport through the surface we will restrict analysis to solutions of the form \( \mathbf{J}(x_1, x_\parallel) = (J(x_1), 0, 0) \), where \( \mathbf{J} \) is one of the above fluxes. Furthermore \( x_1 \) is the normal coordinate to the surface and \( x_\parallel \equiv (x_2, x_3) \) are the tangential coordinates. In the case of normal transport all the quantities depend only on \( x_1 \) but not on \( x_\parallel \). For these solutions

\[
\nabla \cdot \mathbf{J} = \nabla_\perp J = \frac{1}{h_1 h_2 h_3} \frac{d}{dx_1} (h_2 h_3 J) = 0
\]

where \( h_i \equiv h_i(x_1, x_\parallel) \) are Lame coefficients for curvilinear coordinates. It follows from Eq. (II.2) that

\[
h_2(x_1) h_3(x_1) J(x_1) = h_2(x^s) h_3(x^s) J(x^s) \equiv h_2^s h_3^s J^s
\]

where \( x^s \) is the chosen dividing surface and \( h_2^s \) and \( h_3^s \) are the Lame coefficients on that dividing surface. We will suppress the superscript \( s \) for the flux \( J \) as long as it does not lead to confusion.

B. Local entropy production.

Consider the local entropy production for the mixture interface found in [20], written for the case of transport in the direction through the interface

\[
\sigma_s = J_q \nabla_\perp \frac{1}{T} \sum_{i=1}^{n-1} J_i \nabla_\perp \frac{\psi_i}{T} = J_q \nabla_\perp \frac{1}{T} \sum_{i=1}^{n} J_i \nabla_\perp \frac{\mu_i}{T}
\]

where \( T \) is the temperature, \( J_q \) is the heat flux and \( J_i \equiv \rho_i (v_i - v) = J_{\xi_i} - \xi_i J_m \) is the diffusive mass flux, which satisfies the relation

\[
\sum_{i=1}^{n} J_i = 0
\]

Furthermore \( \psi_i = \mu_i - \mu_n \), where \( \mu_i \) is the chemical potential of the \( i \)-th component. The heat flux is related to the total energy flux and to the measurable heat flux \( J'_q \) as

\[
J_q = J_e - J_m (h + v^2/2 - \mathbf{g} \cdot \mathbf{r}) = J'_q + \sum_{i=1}^{n} h_i J_i
\]

Here \( h_i \) and \( h \) are the partial enthalpy of the \( i \)-th component and the specific enthalpy respectively, while \( \mathbf{g} \) is the gravitational acceleration and \( v^2/2 - \mathbf{g} \cdot \mathbf{r} \) is the sum of specific kinetic and potential energies of the mixture.

For the stationary transport through the interface the Gibbs-Duhem relation has the following form (see [21] for details):

\[
s \frac{\partial T}{\partial x_1} + \sum_{i=1}^{n} \xi_i \frac{\partial \mu_i}{\partial x_1} - v \frac{\partial \sigma_{11}}{\partial x_1} = 0
\]
where \( \sigma_{11} \) is an element of the thermodynamic pressure tensor \( \sigma_{\alpha\beta} \). Together with the equation of motion, \( \nabla_\perp \sigma_{11} + \rho \nabla_\perp (v^2/2 - g \cdot r) = 0 \), it gives

\[
\sum_{i=1}^{n} \xi_i \left( \nabla_\perp \frac{\mu_i}{T} - \tilde{h}_i \nabla_\perp \frac{1}{T} \right) = 0 \quad \text{(II.8)}
\]

where \( \mu_i \equiv \mu_i + v^2/2 - g \cdot r \) and \( \tilde{h}_i \equiv h_i + v^2/2 - g \cdot r \). Substituting Eq. (II.6) and \( J_i \) into Eq. (II.4) and using Eq. (II.8) one can express the local entropy production (II.4) in terms of the total energy flux:

\[
\sigma_s = J_e \nabla_\perp \frac{1}{T} - \sum_{i=1}^{n} J_i \left( \nabla_\perp \frac{\psi_i}{T} - \eta_i \nabla_\perp \frac{1}{T} \right) \quad \text{(II.9)}
\]

and in terms of the measurable heat flux:

\[
\sigma_s = J_q' \nabla_\perp \frac{1}{T} - \sum_{i=1}^{n-1} J_i \left( \nabla_\perp \psi_i - \eta_i \nabla_\perp \frac{1}{T} \right) \quad \text{(II.10)}
\]

where \( \eta_i \equiv \tilde{h}_i - \tilde{h}_n = h_i - h_n \). Note that the difference between partial enthalpies with a tilde is equal to the difference without the tilde. In stationary states Eq. (II.9), Eq. (II.10) and Eq. (II.4) are completely equivalent expressions.

### C. Excess entropy production.

We define the excess \( \tilde{\phi}(x^s) \) of a density \( \phi(x^s) \) per unit of volume in curvilinear coordinates as

\[
\tilde{\phi}(x^s) \equiv \frac{1}{b_2 b_3} \int_{x^{g,s}}^{x^{f,s}} dx_1 \, \frac{\phi^{ex}(x_1; x^s)}{b_1 b_2 b_3} \quad \text{(II.11)}
\]

where

\[
\phi^{ex}(x_1; x^s) \equiv \phi(x_1) - \phi^g(x_1) \Theta(x^s - x_1) - \phi^f(x_1) \Theta(x_1 - x^s) \quad \text{(II.12)}
\]

Here \( x^s \) indicates the position of the chosen dividing surface while \( x^{g,s} \) and \( x^{f,s} \) are the boundaries of the interfacial region at the gas and liquid side respectively. These boundaries are chosen such that \( \phi(x^{g,s}) = \phi^g(x^{g,s}) \) and \( \phi(x^{f,s}) = \phi^f(x^{f,s}) \) with a certain accuracy. Superscripts \( \ell \) and \( q \) indicate the function \( \phi \) extrapolated from the liquid and gas to the surface region. We refer to \cite{21} for more extensive discussion.

Taking the excess of the local entropy production given by Eq. (II.9) we obtain (see \cite{21} for details):

\[
\tilde{\sigma}_s = J_e \left( \frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^{n} J_i \left( \frac{\tilde{\mu}_i^\ell}{T^\ell} - \frac{\tilde{\mu}_i^g}{T^g} \right) \quad \text{(II.13)}
\]

Here \( T^\ell \equiv T^\ell(x^s) \) and \( T^g \equiv T^g(x^s) \) are the temperatures extrapolated from the liquid and gas to the dividing surface. The analogous meaning have \( \tilde{\mu}_i^\ell \) and \( \tilde{\mu}_i^g \). All the quantities, both the fluxes and the forces, are evaluated at the dividing surface \( x^s \).

Using Eq. (II.6) we obtain

\[
\tilde{\sigma}_s = J_{q'}^{\ell,g} \left( \frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^{n} J_i \left[ \left( \frac{\tilde{\mu}_i^\ell}{T^\ell} - \tilde{h}_i^\ell \right) - \left( \frac{\tilde{\mu}_i^g}{T^g} - \tilde{h}_i^g \right) \right] \quad \text{(II.14)}
\]

and

\[
\tilde{\sigma}_s = J_{q'}^{r}\left( \frac{1}{T^\ell} - \frac{1}{T^9} \right) - \sum_{i=1}^{n} J_i \left[ \left( \frac{\tilde{\mu}_i^\ell}{T^\ell} - \tilde{h}_i^\ell \right) - \left( \frac{\tilde{\mu}_i^g}{T^g} - \tilde{h}_i^g \right) \right] \quad \text{(II.15)}
\]

where \( J_{q'}^{\ell} \) and \( J_{q'}^{r,g} \) are the measurable heat fluxes on the liquid and gas side respectively. Again Eq. (II.14), Eq. (II.15) and Eq. (II.13) are completely equivalent in stationary states.
III. INTEGRAL RELATIONS.

Consider the entropy production Eq. (II.9), each term in which has a form \( J \nabla \phi \). Following the common procedure in non-equilibrium thermodynamics one can write the force-flux relations for those entropy productions. Since all the terms have the same form, it is sufficient to consider only one force-flux pair. The phenomenological relation for that pair then reads

\[
\nabla \phi(x_1) = \frac{1}{b_1} \frac{d\phi(x_1)}{dx_1} = r(x_1) J(x_1)
\]

for the local entropy production. The corresponding term in the excess entropy production in Eq. (II.13) has a form \( J(\phi - \phi') \). The phenomenological relation relation for this term reads

\[
\phi(x_s) - \phi(x_s) = R(x_s) J(x_s)
\]

For the general case \( \phi \) and \( J \) must be replaced by a set as well as \( R \) and \( r \) by the corresponding matrix.

Let us introduce excess operators \( \mathcal{E}_n \) and \( \mathcal{E}_r \) which we will apply to a quantity \( \phi \). Let

\[
\mathcal{E}_n \{ \phi \} = \int_{x_s}^{x_s} dx_1 b_1 \phi^{ex}(r; x_s)
\]

and

\[
\mathcal{E}_r \{ \phi \} = b_2 b_3 \int_{x_s}^{x_s} dx_1 b_1 b_2 b_3 \phi^{ex}(r; x_s)
\]

where \( \phi^{ex} \) is defined by Eq. (II.12). In cartesian coordinates the excess operators \( \mathcal{E}_n \), \( \mathcal{E}_r \) and the excess \( \nabla \), are given be the same expression when \( \phi \) is a density per unit of volume. One should not confuse them however, as these operators have different meanings. The excess \( \phi \) may be applied only to a volume density \( \phi \) and means the surface density. In contrast, neither \( \mathcal{E}_n \{ \phi \} \) nor \( \mathcal{E}_r \{ \phi \} \) need to be applied to a volume density. In Eq. (II.9) \( \phi \) can be the inverse temperature or a chemical potential divided by the temperature.

Applying \( \mathcal{E}_n \) operator to the both sides of Eq. (III.1) one can show that

\[
\phi(x_s) - \phi(x_s) = \mathcal{E}_r \{ r \} J(x_s)
\]

Comparing Eq. (III.5) with Eq. (III.2) we conclude that

\[
R = \mathcal{E}_r \{ r \}
\]

This is the general form of the integral relation for the resistivities \( r \) and \( R \). Eq. (III.5) together with Eq. (III.6) are the most important and fundamental results of the paper. The generalization to a set of \( \phi \) and \( J \) is straightforward and will be applied in the rest of the paper.

We then proceed to the explicit expressions for the phenomenological equations. The local entropy production (II.9) produces the following force-flux relations

\[
\nabla \phi = r_{qq} J_e - \sum_{i=1}^{n} r_{qi} J_{\xi_i}
\]

\[
\nabla \phi = r_{qq} J_e - \sum_{i=1}^{n} r_{qi} J_{\xi_i}
\]

and the excess entropy production (II.13) produces

\[
\frac{1}{T} T - \frac{1}{T} T = R_{qq} J_e - \sum_{i=1}^{n} R_{qi} J_{\xi_i}
\]

\[
\frac{1}{T} T - \frac{1}{T} T = R_{qq} J_e - \sum_{i=1}^{n} R_{qi} J_{\xi_i}
\]

where \( J_e \) and \( J_{\xi_i} \) as well as \( T \) and \( \mu_i \) are evaluated at the dividing surface \( x_s \). The off-diagonal coefficients of both sets satisfy the Onsager reciprocal relations.
Comparing Eq. (III.7) with Eq. (III.8) and using Eq. (III.5) together with Eq. (III.6) we may conclude that

\[
\begin{align*}
R_{qq}^e &= \mathcal{E}_r \{ r_{qq}^e \} \\
R_{qi}^e &= \mathcal{E}_r \{ r_{qi}^e \} = \mathcal{E}_r \{ r_{qi}^c \} = R_{qi}^c \\
R_{ji}^g &= \mathcal{E}_r \{ r_{ji}^g \} = \mathcal{E}_r \{ r_{ij}^e \} = R_{ij}^e
\end{align*}
\]  
(III.9)

Eq. (III.9) represents integral relations for the resistivity coefficients associated with the total energy flux.

IV. MEASURABLE HEAT FLUXES.

It is convenient to obtain the integral relations for the interface resistivities associated with the measurable heat fluxes rather than the total energy flux. We obtain the relations between resistivities, both local and for the whole surface.

First a note regarding the dependence of the resistivities on the reference state of for instance the enthalpy. Both \( R^c \) and \( r^e \) coefficients depend on the reference state, as they are the resistivities associated with the absolute fluxes. The resistivities \( R'^g \) and \( r'^c \), which will be defined below, are associated with the measurable fluxes and therefore independent of the reference state.

A. The whole surface.

In order to obtain the resistivities for the whole surface we consider Eq. (II.14) for the entropy production in terms of the measurable heat flux on the gas side of the surface. The analysis for the liquid side is completely equivalent to the one done for the gas side.

The entropy production (II.14) produces the following phenomenological equations

\[
\begin{align*}
\frac{1}{T^l} - \frac{1}{T^g} &= R'^g_{qq} J'_{q, q} - \sum_{i=1}^{n} R'^g_{qi} J_{q, i} \\
\left( \frac{\tilde{T}^l}{T^l} - \frac{\tilde{T}^g}{T^g} \right) - \tilde{h}^g_i \left( \frac{1}{T^l} - \frac{1}{T^g} \right) &= R'^g_{ji} J'_{j, i} - \sum_{i=1}^{n} R'^g_{ji} J_{j, i}
\end{align*}
\]  
(IV.1)

The resistivities from Eq. (IV.1) and Eq. (III.8) are related, using Eq. (III.6) by

\[
\begin{align*}
R_{qq}^e &= R'^g_{qq} \\
R_{qi}^e &= R'^g_{qi} + \tilde{h}^g_i R'^g_{qq} \\
R_{ji}^g &= R'^g_{ji} + \tilde{h}^g_i R'^g_{q, q} + \tilde{h}^g_j R'^g_{q, i} + \tilde{h}^g_i \tilde{h}^g_j R'^g_{q, q}
\end{align*}
\]  
(IV.2)

Eq. (IV.1) and Eq. (III.8) are linear relations between the forces and the fluxes. In Eq. (IV.2) we should therefore use coexistence values of the enthalpies.

Inverting Eq. (IV.2) and using the equilibrium enthalpies we obtain for the resistivities associated with the measurable heat flux

\[
\begin{align*}
R'^g_{qq} &= R_{qq}^c \\
R'^g_{qi} &= R_{qi}^c - \tilde{h}_{i, eq} R_{qq}^e \\
R'^g_{ji} &= R_{ji}^c - \tilde{h}_{i, eq} R_{q, q}^e - \tilde{h}_{j, eq} R_{q, i}^c + \tilde{h}_{i, eq} \tilde{h}_{j, eq} R_{qq}^e
\end{align*}
\]  
(IV.3)

where \( \tilde{h}_{i, eq} = h_{i, eq}(x^s) - \mathbf{g} \cdot \mathbf{r}^s \) and all the quantities are evaluated at the chosen dividing surface.
B. Local resistivities.

In order to write the linear laws for the local forces and fluxes we use Eq. (II.10) and Eq. (II.4). The entropy production (II.10) gives

$$\nabla \perp \frac{1}{T} = r_{qq}' J_q' - \sum_{i=1}^{n-1} r_{qi}' J_i$$

while the entropy production (II.4) gives

$$\nabla \perp \psi_i T - \eta_i \nabla \perp \frac{1}{T} = r_{iq}' J_q' - \sum_{i=1}^{n-1} r_{ji}' J_i$$

The local resistivities \(r\) and \(r'\) are related as follows

$$r_{qq}' = r_{qq}$$

$$r_{qi}' = r_{qi} - \eta_i r_{qq}$$

$$r_{ji}' = r_{ji} - \eta_i r_{jq} - \eta_j r_{qi} + \eta_i \eta_j r_{qq}$$

(IV.6)

Again, we should use the equilibrium profiles for \(\eta_i\).

We now relate the local resistivities associated with the measurable heat flux to the local resistivities associated with the total energy flux, similarly\(^1\) to how it was done for the overall surface resistivities. Comparing Eq. (IV.4) with Eq. (III.7) we obtain

$$r_{qq}^e = r_{qq}'$$

$$r_{qi}^e = r_{qq}' \tilde{h}_i - \sum_{k=1}^{n-1} r_{qk}' \xi_k + r_{qi}'$$, \(i = 1, n-1\)

$$r_{en}^e = r_{qq}' \tilde{h}_n - \sum_{k=1}^{n-1} r_{qk}' \xi_k$$

$$r_{ji}^e = r_{iq}' \tilde{h}_j - \sum_{k=1}^{n-1} \xi_k (r_{kq}' \tilde{h}_i + r_{qk}' \tilde{h}_j) + r_{jq}' \tilde{h}_i + r_{qi}' \tilde{h}_j +$$

$$+ r_{ji}' - \sum_{k=1}^{n-1} \xi_k (r_{ki}' + r_{jk}') + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl}' \xi_k \xi_l$$, \(i = 1, n-1\)

$$r_{ni}^e = r_{qj}' \tilde{h}_n h_n - \sum_{k=1}^{n-1} \xi_k (r_{kq}' \tilde{h}_i + r_{qk}' \tilde{h}_n) + r_{qj}' \tilde{h}_n - \sum_{k=1}^{n-1} \xi_k r_{ki}' + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl}' \xi_k \xi_l$$, \(i = 1, n-1\)

$$r_{nn}^e = r_{qj}' \tilde{h}_n^2 - \tilde{h}_n \sum_{k=1}^{n-1} \xi_k (r_{qk}' + r_{qk}') + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl}' \xi_k \xi_l$$

(IV.7)

\(^1\) The details of this procedure are given in Appendix A.
and comparing Eq. (IV.5) with Eq. (III.7) we obtain

\[ r_{qq}^e = r_{qq} \]
\[ r_{qi}^e = r_{qq} \tilde{h} - \sum_{k=1}^{n-1} r_{qk} \xi_k + r_{qi}, \quad i = 1, n-1 \]
\[ r_{en}^e = r_{qq} \tilde{h} - \sum_{k=1}^{n-1} r_{qk} \xi_k \]
\[ r_{ji}^e = r_{qq} \tilde{h}^2 - \tilde{h} \sum_{k=1}^{n-1} \xi_k (r_{ke} + r_{qk}) + \tilde{h} (r_{jq} + r_{qi}) + r_{ji} - \sum_{k=1}^{n-1} \xi_k (r_{ki} + r_{jk}) + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \xi_k \xi_l, \quad j, i = 1, n-1 \]
\[ r_{ni}^e = r_{qq} \tilde{h}^2 - \tilde{h} \sum_{k=1}^{n-1} \xi_k (r_{ke} + r_{qk}) + \tilde{h} r_{qi} - \sum_{k=1}^{n-1} r_{ki} \xi_k + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \xi_k \xi_l, \quad i = 1, n-1 \]
\[ r_{en}^e = r_{qq} \tilde{h}^2 - \tilde{h} \sum_{k=1}^{n-1} \xi_k (r_{ke} + r_{qk}) + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} r_{kl} \xi_k \xi_l \]

where \( \tilde{h} \equiv h + v^2/2 - \mathbf{g} \cdot \mathbf{r} \).

Again, as in Eq. (IV.2) we should use the enthalpy and the mass fraction profiles in Eq. (IV.7) and Eq. (IV.8) in equilibrium. This leads to the relation \( \tilde{h}_i = h_{i, eq} - \mathbf{g} \cdot \mathbf{r} \) and \( \tilde{h} = h_{eq} - \mathbf{g} \cdot \mathbf{r} \).

V. RESULTS FOR THE TWO COMPONENT MIXTURE.

In this section we derive the integral relations for a binary mixture. The formula given in this section is not restricted to a particular binary mixture however. We do that for the sake of convenience as well as because we will apply them to a particular two component mixture. For simplicity of notation we will not write subscript \( eq \) for enthalpies, keeping in mind that all of them should be evaluated at equilibrium.

The relations (IV.7), (IV.8) between resistivities in case of binary mixture take the following form

\[ r_{qq}^e = r_{qq}^', \]
\[ r_{q1}^e = r_{qq}^' \tilde{h}_1 + r_{q1}^' \xi_2 \]
\[ r_{q2}^e = r_{qq}^' \tilde{h}_2 - r_{q1}^' \xi_1 \]
\[ r_{11}^e = r_{qq}^' \tilde{h}_1^2 + 2 r_{q1}^' \xi_2 \tilde{h}_1 + r_{11}^' \xi_2^2 \]
\[ r_{21}^e = r_{qq}^' \tilde{h}_2 \tilde{h}_1 + r_{q1}^' (\xi_2 \tilde{h}_2 - \xi_1 \tilde{h}_1) - r_{11}^' \xi_1 \xi_2 \]
\[ r_{22}^e = r_{qq}^' \tilde{h}_2^2 - 2 r_{q1}^' \xi_1 \tilde{h}_2 + r_{11}^' \xi_1^2 \]

and

\[ r_{qq}^e = r_{qq} \]
\[ r_{q1}^e = r_{qq} \tilde{h} + r_{q1} \xi_2 \]
\[ r_{q2}^e = r_{qq} \tilde{h} - r_{q1} \xi_1 \]
\[ r_{11}^e = r_{qq} \tilde{h}_1^2 + 2 r_{q1} \xi_2 \tilde{h} + r_{11} \xi_2^2 \]
\[ r_{21}^e = r_{qq} \tilde{h}_2^2 + r_{q1} (\xi_2 \tilde{h}_2 - \xi_1 \tilde{h}) - r_{11} \xi_1 \xi_2 \]
\[ r_{22}^e = r_{qq} \tilde{h}_2^2 - 2 r_{q1} \xi_1 \tilde{h} + r_{11} \xi_1^2 \]
respectively. Using Eq. (III.9) and Eq. (IV.3) we therefore obtain

\[ R'_{qq} = \mathcal{E}_r \{ r'_{qq} \} \]
\[ R'_{q1} = \mathcal{E}_r \{ r'_{qq}(h_1 - \tilde{h}_1^q) + r'_q \xi_2 \} \]
\[ R'_{q2} = \mathcal{E}_r \{ r'_{qq}(h_2 - \tilde{h}_2^q) - r'_q \xi_1 \} \]
\[ R'_{11} = \mathcal{E}_r \{ r'_{qq}(h_1 - \tilde{h}_1^q)^2 + 2r'_q \xi_2 (h_1 - \tilde{h}_1^q) + r'_{11} \xi_2^2 \} \]
\[ R'_{12} = \mathcal{E}_r \{ r'_{qq}(h_1 - \tilde{h}_1^q)(h_2 - \tilde{h}_2^q) + r'_q (\xi_2 (h_2 - \tilde{h}_2^q) - \xi_1 (h_1 - \tilde{h}_1^q)) - r'_{11} \xi_1 \xi_2 \} \]
\[ R'_{22} = \mathcal{E}_r \{ r'_{qq}(h_2 - \tilde{h}_2^q)^2 - 2r'_q \xi_1 (h_2 - \tilde{h}_2^q) + r'_{11} \xi_1^2 \} \]

and

\[ R_{qq} = \mathcal{E}_r \{ r_{qq} \} \]
\[ R_{q1} = \mathcal{E}_r \{ r_{qq}(h - \tilde{h}_1^q) + r_{q1} \xi_2 \} \]
\[ R_{q2} = \mathcal{E}_r \{ r_{qq}(h - \tilde{h}_2^q) - r_{q1} \xi_1 \} \]
\[ R_{11} = \mathcal{E}_r \{ r_{qq}(h - \tilde{h}_1^q)^2 + 2r_{q1} \xi_2 (h - \tilde{h}_1^q) + r_{11} \xi_2^2 \} \]
\[ R_{12} = \mathcal{E}_r \{ r_{qq}(h - \tilde{h}_1^q)(h - \tilde{h}_2^q) + r_{q1} (\xi_2 (h - \tilde{h}_2^q) - \xi_1 (h - \tilde{h}_1^q)) - r_{11} \xi_1 \xi_2 \} \]
\[ R_{22} = \mathcal{E}_r \{ r_{qq}(h - \tilde{h}_2^q)^2 - 2r_{q1} \xi_1 (h - \tilde{h}_2^q) + r_{11} \xi_1^2 \} \]

Furthermore we used that \( \tilde{h}_1 - \tilde{h}_2^q = h_1 - h_2^q \) in both equations. Eq. (V.3) and Eq. (V.4) are the integral relations for the resistivities associated with the measurable heat flux for a binary mixture. They clearly do not depend on the reference chosen for the enthalpies.

We further need the values for the local resistivities. In [22] we developed a scheme which uses \( r \) coefficients in calculation. We therefore use the following expressions

\[ r_{qq}(x) = r_{qq}^g + (r_{qq}^f - r_{qq}^g) q_0(x) + \alpha_{qq}(r_{qq}^f + r_{qq}^g) q_1(x) \]
\[ r_{q1}(x) = r_{q1}^g + (r_{q1}^f - r_{q1}^g) q_0(x) + \alpha_{q1}(r_{q1}^f + r_{q1}^g) q_1(x) \]
\[ r_{11}(x) = r_{11}^f + (r_{11}^f - r_{11}^g) q_0(x) + \alpha_{11}(r_{11}^f + r_{11}^g) q_1(x) \]

where \( q_0(x) \) and \( q_1(x) \) for each resistivity are modulatory curves for the resistivity profiles: \( q_0(x) \) is a smooth arctan-like function which changes its value from 0 to 1 within the range \([x_0^g; x_0^f]\) and \( q_1(x) \) is zero on the boundaries of the \([x^g; x^f]\) interval and has a peak proportional to the square gradient of the density inside this interval. Thus, the first two terms in each expression for the resistivity represents a smooth transitions from the gas bulk resistivity to the liquid bulk resistivity, while the third term represents a peak in the resistivity proportional to the square gradient of the density.

The bulk values \( r^f \) and \( r^g \) are related to the measurable transport coefficients such as heat conductivity, the diffusion coefficient and the Soret coefficient. We refer for the details to [22].

Consider a binary mixture of cyclohexane and \( n \)-hexane, which is the same as in [22] and [21]. Furthermore we consider a planar interface between liquid and vapor. The mixture is in a box with gravity directed along axes \( x \) from left to right. The gas phase is therefore in the left part of the box and the liquid is in the right part.

We compare the resistivities found in [21] to the values obtained from Eq. (V.4). The relative difference between them is almost the same within the range of temperatures and chemical potential differences considered: \( T = \{325, \ldots, 335\} \) and \( \psi = \{400, \ldots, 1000\} \). In Table [I] we give the relative errors for gas and liquid side coefficients. The data are obtained for \( \alpha \)-amplitudes, values of which were found to fit best kinetic theory in [21].
The relative differences are not more then a few promille. It is larger only for $R_{12}^t$ which is discussed below. We also do a consistency check. Consider Eq. (IV.1) for two component mixture, which has a form

$$X_q = R_{qq}^t J_q^t - R_{q1}^t J_{1q} - R_{q2}^t J_{2q}$$

$$X_1 = R_{1q}^t J_q^t - R_{11}^t J_{11} - R_{12}^t J_{12}$$

$$X_2 = R_{2q}^t J_q^t - R_{21}^t J_{11} - R_{22}^t J_{22}$$

(V.6)

The left hand side of each equation must be equal to the right hand side. The difference therefore reflects the error. We give the relative error between the left an the right hand side of Eq. (V.6) in percent in Table [II]. As a testing perturbation we used one of those used in the perturbation cell method.

TABLE II: Relative error in percent between the left- and right-hand side of Eq. (V.6) for coefficients obtained by "perturbation cell" and "integral relations" methods at $T_{eq} = 330$ and $\psi_{eq} = 700$ for $\beta = 0.0002$ and $\alpha_{qq} = 9$, $\alpha_{1q} = 0$, $\alpha_{11} = 3$.

| phase | $X_q$ | $X_1$ | $X_2$ | $X_q$ | $X_1$ | $X_2$ |
|-------|-------|-------|-------|-------|-------|-------|
| gas   | 0.059489 | 0.037918 | 0.296959 | 0.046965 | 0.087411 | 0.867098 |
| liquid| 0.059489 | 0.172608 | 0.027275 | 0.046851 | 0.216819 | 6.233983 |

Again, the relative difference is not more then a few promille. Given that this is the case even for a few percent difference in one of the coefficients, we may conclude that the values of the forces are insensitive to the precise value of this resistivity coefficient. This also indicates that the value of this coefficient obtained in [21] has a 6% error. This does not necessarily affect, however, the accuracy of the integral relations.

VI. DISCUSSION AND CONCLUSIONS.

In this paper we have derived integral relations for the resistivities to the transport of heat and mass across the interface for mixtures. We have given relations between the local resistivity profiles and the overall interfacial resistivities.

The integral relations make it possible to calculate the interfacial resistivities in a relatively simple way, using only the equilibrium profiles of the system. This is important especially for mixtures, for which the computation of a non-equilibrium profiles is much more time consuming.

The integral relations give an insight in the origin of the interfacial resistances. According to Eq. (V.3) and Eq. (V.4) the interfacial resistivities depend on the variation of the enthalpy across the interface. The transport coefficients depend on the equilibrium enthalpies which vary a lot through the interface. One can see from the above formulae, that the dependence on the enthalpy of evaporation (the difference between the enthalpies of the liquid and gas phases) is crucial not only for the diagonal diffusion coefficient, but also for the off-diagonal coefficients. This is an important result since cross coefficients are usually neglected in the description of the interfacial phenomena.

Another factor which affects the overall interfacial resistivity is the local resistivity profile. For instance, for the heat resistivity this is the only factor. It is noticeable that the interfacial resistivity depends on the whole profile of the local resistivity, not only on its bulk values. It is therefore crucial to have complete information about the local resistivity profiles. We have used sums of a function that smoothly connects the liquid and the vapor values and a peak proportional to the square gradient of the density. In principle one can use any model for this and further investigation are required. We have shown in [21] by comparison with the predictions from kinetic theory, that the local resistivities do have a peak in their profile and that the overall resistivities therefore depend on the amplitudes of these peaks. Within the current theory these amplitudes are adjustable parameters.

The integral relations are in fact mathematical equalities. Given the local resistivities defined through the local force-flux relations, for instance $r^e$ from Eq. (III.7), Eq. (III.8) follows and one can consider Eq. (V.3) as a definition.
of the overall interfacial resistivities $R_e$ used in Eq. (III.8). It means that the force-flux relations (IV.1) for the whole surface follow from the local force-flux relations. One therefore does not need the excess entropy production Eq. (II.14) to obtain Eq. (III.8).

This allows us to use them as a test for the accuracy of the numerical solution of the non-equilibrium case. Given that both local and overall linear laws are true independently, the different methods to obtain the overall resistivities give information about the accuracy of the method. The discussion below Table [I] and Table [II] is based on this observation.

**APPENDIX A: LOCAL RESISTIVITIES.**

We need to relate the resistivities $r$ from Eq. (III.7) to the resistivities $p$ from Eq. (IV.4). This is done by comparing the coefficients at the same fluxes in these equations. To do this we need to translate the set of fluxes used in Eq. (IV.4), \{ $J'_q$, $J_1$, $\cdots$, $J_{n-1}$ \}, to the set of fluxes used in Eq. (III.7), \{ $J_e$, $J_{\xi_1}$, $\cdots$, $J_{\xi_n}$ \}. This is done with the help of the relation

\[
J_i = J_{\xi_i} - \xi_i \sum_{k=1}^n J_{\xi_k}
\]

Substituting $J'_q$ and $J_i$ into the first of Eq. (IV.4) we obtain

\[
\nabla_\perp \frac{1}{T} = r'_{qq} J_e - \sum_{i=1}^{n-1} J_{\xi_i} \left( r'_{qi} \tilde{h}_i + r'_{q'q} \sum_{k=1}^{n} r'_{q'k} \xi_k \right) - J_{\xi_n} \left( r'_{qn} \tilde{h}_n - \sum_{k=1}^{n-1} r'_{q'k} \xi_k \right)
\]

(A.2)

Comparing it with the first of Eq. (III.7) we obtain

\[
r'^e_{qq} = r'_{qq}
\]

\[
r'^e_{qi} = r'_{qi} \tilde{h}_i - \sum_{k=1}^{n-1} r'_{q'k} \xi_k + r'_{q'i}, \quad i = 1, n-1
\]

\[
r'^e_{en} = r'_{qn} \tilde{h}_n - \sum_{k=1}^{n-1} r'_{q'k} \xi_k
\]

(A.3)

which are the first 3 equations of Eq. (IV.7).

In order to obtain the remaining relations we consider the second of Eq. (III.7), which gives

\[
\sum_{j=1}^n \xi_j \nabla_\perp \tilde{\mu}_j = J_e \sum_{j=1}^n r'^e_{jj} \xi_j - \sum_{i=1}^n J_{\xi_i} \sum_{j=1}^n r'^e_{ji} \xi_j
\]

(A.4)

Furthermore we use Eq. (II.8) which in case of the transport in the direction only perpendicular to the surface becomes

\[
\sum_{i=1}^n \xi_i \left( \nabla_\perp \tilde{\mu}_i - \tilde{h}_i \nabla_\perp \frac{1}{T} \right) = 0
\]

(A.5)

Together with the second of Eq. (IV.3) it gives

\[
\sum_{i=1}^n \xi_i \nabla_\perp \tilde{\mu}_i = \sum_{i=1}^n \xi_i \tilde{h}_i \nabla_\perp \frac{1}{T},
\]

\[
\nabla_\perp \psi_i = \eta_i \nabla_\perp \frac{1}{T} + r'_{qi} J'_{q_i} - \sum_{i=1}^{n-1} r'_{q'i} J_i
\]

(A.6)
Substituting $\nabla_{\perp} (1/T)$ from Eq. (A.2) and $J'_e$ and $J'_r$ from Eq. (A.1) we obtain the left hand size of Eq. (A.6) expressed in terms of the fluxes $J'_e$ and $J'_r$ and the resistivities $r'$. Comparing the result with Eq. (A.4) we obtain the following equations sets

\[ \sum_{j=1}^{n} r'_{ej} \xi_j = r'_{ee} \sum_{k=1}^{n} \xi_k \eta_k \]
\[ r'_{ej} - r'_{ee} = r'_{eq} \eta_j + r'_{jq} \eta_q, \quad j = 1, n-1 \]  
(A.7a)

\[ \sum_{j=1}^{n} r'_{j\infty} \xi_j = (r'_{eq} \eta_n - \sum_{k=1}^{n-1} r'_{eq} \xi_k) \sum_{k=1}^{n} \xi_k \eta_k \]
\[ r'_{j\infty} - r'_{ee} = (r'_{eq} \eta_n + r'_{jq} \eta_q) \sum_{k=1}^{n-1} (r'_{eq} \xi_j + r'_{jq} \xi_k), \quad j = 1, n-1 \]  
(A.7b)

\[ \sum_{j=1}^{n} r'_{j\infty} \xi_j = (r'_{eq} \eta_i - \sum_{k=1}^{n-1} r'_{eq} \xi_k + r'_{eq}) \sum_{k=1}^{n} \xi_k \eta_k, \quad i = 1, n-1 \]
\[ r'_{j\infty} - r'_{ee} = (r'_{eq} \eta_i + r'_{jq} \eta_q) \sum_{k=1}^{n-1} (r'_{eq} \xi_j + r'_{jq} \xi_k), \quad j = 1, n-1, i = 1, n-1 \]  
(A.7c)

solving which we obtain the relations between the remaining resistivities

\[ r'_{j\infty} = r'_{eq} \eta_j - \sum_{k=1}^{n-1} r'_{eq} \xi_k + r'_{eq}, \quad j = 1, n-1 \]
\[ r'_{ee} = r'_{eq} \eta_n - \sum_{k=1}^{n-1} r'_{eq} \xi_k \]
\[ r'_{ji} = r'_{eq} \eta_j + \sum_{k=1}^{n-1} \xi_k (r'_{eq} \eta_i + r'_{eq} \eta_j) + r'_{jq} \eta_i + r'_{eq} \eta_j + 
\]
\[ + r'_{ji} - \sum_{k=1}^{n-1} r'_{eq} \xi_k + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} r'_{eq} \xi_k \xi_l, \quad j, i = 1, n-1 \]  
(A.8)

\[ r'_{jn} = r'_{eq} \eta_j \eta_n - \sum_{k=1}^{n-1} \xi_k (r'_{eq} \eta_n + r'_{eq} \eta_j) + r'_{jq} \eta_n - \sum_{j=1}^{n-1} r'_{eq} \xi_k + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} r'_{eq} \xi_k \xi_l, \quad j = 1, n-1 \]
\[ r'_{ni} = r'_{eq} \eta_n \eta_i - \sum_{k=1}^{n-1} \xi_k (r'_{eq} \eta_i + r'_{eq} \eta_n) + r'_{jq} \eta_n - \sum_{i=1}^{n-1} r'_{eq} \xi_k + \sum_{i=1}^{n-1} \sum_{k=1}^{n-1} r'_{eq} \xi_k \xi_l, \quad i = 1, n-1 \]
\[ r'_{nn} = r'_{eq} \eta_n \eta_n - \eta_n \sum_{k=1}^{n-1} \xi_k (r'_{eq} + r'_{eq}) + \sum_{k=1}^{n-1} \sum_{i=1}^{n-1} r'_{eq} \xi_k \xi_l \]

As one can confirm the symmetry of the $r'$-matrix leads to the symmetry of the $r$-matrix and vice versa. We therefore do not give the expressions for $r'_{jq}$, $r'_{ee}$ and $r'_{jn}$ in Eq. (IV.7).

The relations (IV.8) between the $r'$- and $r$- resistivities are derived in the similar manner.

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