diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Numerical Evidence for the Validity of the Local Equilibrium Hypothesis - The n-Octane Vapor-Liquid Interface

Jean-Marc Simon[ab], *Signe Kjelstrup*[b] *and Dick Bedeaux*[b]

[a] Laboratoire de Recherches sur la Réactivité des Solides, UMR 5613 du CNRS, Université de Bourgogne, 21000 Dijon, France, E-mail: jmsimon@u-bourgogne.fr
[b] Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

1. Introduction

The region between two phases, the surface, has physical properties that are different from those of the homogeneous phases. While methods and techniques for calculations of equilibrium properties of a surface are well established, such methods are hardly available for a surface in a system that is not in equilibrium.

The aim of this work is to contribute to definitions and quantifications of transport properties of the surface. In homogeneous systems such properties are expressed by a well known set of linear continuous flux/force equations following a procedure starting by the Gibbs relation and detailed in the book of de Groot and Mazur [1]. Applying the same procedure to the surface Gibbs relation, two of us obtained comparable discrete linear flux/force equations for the surface [2]. In both approaches the results are based on a fundamental assumption, the hypothesis of local equilibrium, the term local here being applied to the whole volume of the surface as Gibbs defined it. By simulating a liquid-vapour interface of a Lennard-Jones spline system under heat and mass fluxes, Røsjorde et al. [3], using non-equilibrium molecular dynamic simulations (NEMD), were able to validate this hypothesis at different temperatures. Additionally they could check the linearity of the transport equations and calculate surface transport coefficients. To study the influence of internal degrees of freedom, we applied the same procedure to a molecular liquid-vapour interface of n-octane submitted to heat fluxes. The surfaces were studied at equilibrium and out of global equilibrium. The applied heat fluxes ranged from 20 to 70 MW/m^2. The results agreed with the previous simulations, and were published in a recent article [4].

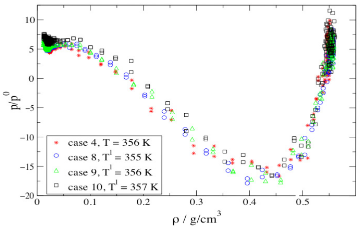

Fig. 1: Pressure parallel to the surface as a function of the local density in the surface, at equilibrium (case 4) and out of equilibrium (cases 8, 9 and 10), the cases mentioned referred to the situation of ref [4]. The calculated heat fluxes equaled, respectively, 27.0, 41.3 and 69.0 MW/m^2, for the cases 8, 9 and 10.

Here we verify for n-octane the validity of the local equilibrium hypothesis for the surface. We proceed to compare the two expressions for transport equations at the interface (continuous or discrete). The details of the simulations are given in the previous article [4].

2. Results

At surfaces, under stationary state, the thermodynamic forces for the heat and mass flux are defined as the difference of the local thermodynamic properties, the temperature and the chemical potential, of the liquid and of the gas in contact with the surface [2], whatever the properties inside the surface. As for the continuous equation of transport, authors defined two main excess resistivity coefficients through surfaces, for heat transfer and for mass transfer, and two coupling coefficients which are equal by symmetry. If the conditions are fulfilled to use continuous equations inside the surface, the two kinds of resistivity coefficients have to be directly related. In the following we focus on the heat transfer resistance, r^s_{qq} for the surface definition and r^*_{qq} the continuous local definition.

The component of the pressure that is parallel to the surface is plotted in Figure 1 under equilibrium and out of equilibrium as a function of local density through the surface. Surprisingly, the results from a surface in global equilibrium and from a surface with a temperature gradient are indistinguishable in this figure, within the accuracy of the calculation. This means that every part of the surface is in local equilibrium, the surface maintains its internal structure from the case of global equilibrium, even if a strong temperature gradient is applied to the surface. The direct consequence is that the continuous transport equations may be applied within the interface to get r^*_{qq}. On figure 2 the profile of r^*_{qq} is plotted through the surface. The figure shows constant values for the bulk phases and a peak in the surface that is close to the gas side. The integral under the curve gave the excess resistivity r^s_{qq} for the surface at temperature T^s, we got a value of 8.04 10^{-12} $m^2/W/K$ while the direct result from the flux equations was 9.4 10^{-12} $m^2/W/K$.

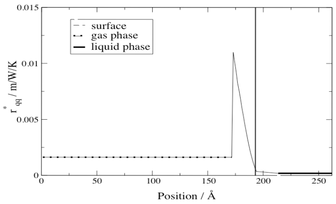

Fig. 2: Profile of the thermal resistivity across the surface for state 7 of ref [4], (the heat flux equal 23.9 MW/m^2). The values of the liquid and gas phases are shown as constants. The position of the equimolar surface is shown by a vertical line.

3. Conclusion

NEMD was used to study the liquid-vapour interface of n-octane under a stationary heat flux. The local equilibrium hypothesis was verified both for the whole surface as defined by Gibbs, and locally inside the surface. This defined two different ways to get the excess heat resistivity coefficients, which are equivalent. A similar analysis can be done for the mass resistivity and the coupling coefficients using that energy and mass fluxes are constant though the surface.

References

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