



Green–Kubo relations for dynamic interfacial excess properties

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ABSTRACT

In this paper we analyze the fluctuations of the in-plane interfacial excess fluxes in multiphase systems, in the context of the extended irreversible thermodynamics formalism. We derive expressions for the time correlation functions of the surface extra stress tensor, the surface mass flux vector, and the surface energy flux vector, and use these expressions to derive Green–Kubo relations for the surface shear viscosity, the surface dilatational viscosity, the surface diffusion coefficient, and the surface thermal conductivity. These Green–Kubo relations can be used to compute these excess transport coefficients using for example molecular dynamics simulations.

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1. Introduction

Dynamic excess properties of interfaces can have an appreciable effect on the behavior of multiphase systems [1]. For example, surface rheological properties, such as the surface shear and surface dilatational viscosities, affect the breakup of droplets [2,3], coalescence in immiscible polymer blends [4], the stability of foam and emulsions [5–8], the wetting behavior of thin films on solid surfaces [9], or the dynamic behavior of vesicles, nanocapsules, and microcapsules [10]. For surface rheological properties a wide range of techniques exist to determine these parameters experimentally [1,11–14]. For the effective design of new multiphase materials with tailored dynamic properties it is essential to know how these surface excess properties are related to the microstructure of the interface, and in turn, how that microstructure is related to the molecular structure and properties of the constituents of the interface.

Unfortunately, this type of information is hard to obtain experimentally, since for most systems of practical interest the interfacial region has a thickness of at most a few nanometers. Structure resolution on such small length scales can often be obtained only using neutron or X-ray reflectometry experiments [15]. Molecular simulation techniques, such as molecular dynamics can provide an important contribution to establishing a link between molecular structure of surface active components and dynamic interfacial properties, since in these computational methods it is relatively easy to explore the effects of molecular architecture and molecular interactions on microstructural organization at an interface [16].

To compute interfacial dynamic properties, using molecular simulations, we need expressions that link these properties to the microstructure in the interfacial region. Here we derive Green–Kubo relations for the surface viscosities, surface thermal conductivity, and surface diffusion coefficient, in terms of the time correlation functions of their conjugate fluxes, i.e. the surface extra stress tensor, the surface energy flux vector, and the surface mass flux vector. We then show how these excess fluxes are related to the actual flux fields in the interfacial region. The Green–Kubo relations are derived from an analysis of the fluctuations around equilibrium for a multiphase system, in the context of extended irreversible thermodynamics (EIT) [17–19].

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In the next section we start with a short overview of the EIT formalism for multiphase systems. Then we proceed with a discussion of the necessary conditions for equilibrium in multiphase systems in Section 3. In Section 4 we analyze the fluctuations of a multiphase system around equilibrium, and the expressions we derive there for the time correlation functions of the excess fluxes we use in Section 5 to derive the Green–Kubo relations for the interfacial dynamic properties. In Section 6 we then express the excess fluxes in terms of the actual fields in the interfacial region.

2. EIT model for multiphase systems

In EIT the time rate of change of the surface entropy per unit mass \hat{S}^s is given by Sagis [19], de Groot and Mazur [20], Zielinska and Bedeaux [21] and Kjelstrup and Bedeaux [22]

$$\rho^s \frac{d_s \hat{S}^s}{dt} = -\nabla_s \cdot \mathbf{j}_s^s + \hat{\epsilon}^s - \left[\rho \left(\hat{S} - \hat{S}^s \right) (\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \mathbf{j}_s \cdot \boldsymbol{\xi} \right] \quad (1)$$

where the rate of surface entropy production per unit mass $\hat{\epsilon}^s \geq 0$. The variable ρ^s denotes the surface mass density, \mathbf{j}_s^s is the surface entropy flux vector, \mathbf{j}_s is the entropy flux vector in the bulk phase, ρ is the density in the bulk phase, \hat{S} is the entropy per unit mass of the bulk phase, \mathbf{v} is the bulk velocity field, \mathbf{v}^s is the surface velocity, $\boldsymbol{\xi}$ is the unit vector normal to the interface, and ∇_s denotes the surface gradient operator [13]. The boldface brackets in (1) are used to denote jump terms, and are defined as

$$[\psi \boldsymbol{\xi}] = \psi^{(m)} \boldsymbol{\xi}^{(m)} + \psi^{(n)} \boldsymbol{\xi}^{(n)} \quad (2)$$

where $\psi^{(m)}$ denotes the value of an arbitrary observable ψ in bulk phase m , and $\boldsymbol{\xi}^{(m)}$ is the unit vector normal to the interface separating phase m and n , and pointing in the direction of phase m . The surface material derivative in (1) is defined as

$$\frac{d_s \psi^s}{dt} = \frac{\partial \psi^s}{\partial t} + (\nabla_s \psi^s) \cdot (\mathbf{v}^s - \mathbf{u}) \quad (3)$$

where \mathbf{u} is the speed of displacement of the interface. The difference between surface velocity and speed of displacement, $\mathbf{v}^s - \mathbf{u} = \dot{\mathbf{y}}$, is referred to as the intrinsic surface velocity, and since this is a tangential vector field [13], we have $\mathbf{v}^s \cdot \boldsymbol{\xi} = \mathbf{u} \cdot \boldsymbol{\xi}$. It should be noted that other authors use alternative definitions of the surface material derivative. For example, without loss of generality, this derivative can also be expressed in terms of the surface velocity \mathbf{v}^s [11].

In EIT the surface entropy per unit mass is assumed to depend on the surface internal energy per unit mass \hat{U}^s , the surface area per unit mass $\hat{\mathcal{A}}$, the surface mass fraction of species A , $\omega_{(A)}^s$ ($A = 1, \dots, N$), the symmetric traceless part of the surface extra stress tensor, $\bar{\sigma}^s$, the trace of the surface extra stress tensor, $\text{tr} \sigma^s$, the surface energy flux vector, \mathbf{q}^s , and the surface mass flux vectors, $\mathbf{j}_{(A)}^s$ [17–19]:

$$\hat{S}^s = \hat{S}^s(\hat{U}^s, \hat{\mathcal{A}}, \omega_{(1)}^s, \dots, \omega_{(N-1)}^s, \bar{\sigma}^s, \text{tr} \sigma^s, \mathbf{q}^s, \mathbf{j}_{(1)}^s, \dots, \mathbf{j}_{(N)}^s). \quad (4)$$

The symmetric traceless part of the extra stress tensor is given by $\bar{\sigma}^s = \sigma^s - \frac{1}{2}(\text{tr} \sigma^s) \mathbf{P}$, where \mathbf{P} is the surface projection tensor [13]. Note that we have not included any dependencies of the surface entropy per unit mass on the bulk variables (the bulk internal energy per unit mass, the volume per unit mass, the bulk mass fractions, and the bulk fluxes), nor have we included an explicit dependence of the surface entropy on the curvature of the interface. As we will see in Section 6, the excess properties in Eq. (4) all implicitly depend on their generating bulk fields, and on the mean and Gaussian curvatures of the interface, so there is no need to explicitly account for this dependence.

This assumption for the functional dependence of the surface entropy per unit mass leads to the following expression for the rate of surface entropy production per unit mass [19]:

$$\begin{aligned} \hat{\epsilon}^s = & \frac{1}{T^s} \bar{\sigma}^s : \left[\bar{\mathbf{D}}^s - \alpha_\sigma \frac{d_s \bar{\sigma}^s}{dt} \right] + \frac{\text{tr} \sigma^s}{T^s} \left[\text{tr} \mathbf{D}^s - \alpha_{\text{tr} \sigma} \frac{d_s \text{tr} \sigma^s}{dt} \right] \\ & - \frac{1}{T^s} \sum_{A=1}^N \mathbf{j}_{(A)}^s \cdot \left(\mathbf{d}_{(A)}^s + \sum_{B=1}^N \alpha_{(BA)} \frac{d_s \mathbf{j}_{(B)}^s}{dt} + \alpha_{q(A)} \frac{d_s \mathbf{q}^s}{dt} \right) \\ & - \frac{1}{(T^s)^2} \left(\mathbf{q}^s - \sum_{A=1}^N \mu_{(A)}^s \mathbf{j}_{(A)}^s \right) \cdot \nabla_s T^s - \frac{1}{T^s} \mathbf{q}^s \cdot \left(\alpha_{q(A)} \sum_A \frac{d_s \mathbf{j}_{(A)}^s}{dt} + \alpha_{qq} \frac{d_s \mathbf{q}^s}{dt} \right) \\ & - \frac{1}{T^s} \left[\rho \left(\hat{U} - T^s \hat{S} - \sum_{A=1}^N \mu_{(A)}^s \omega_{(A)} + \frac{1}{2} |\mathbf{v} - \mathbf{v}^s|^2 \right) (\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} \right. \\ & \left. + \mathbf{q} \cdot \boldsymbol{\xi} - (\mathbf{v} - \mathbf{v}^s) \cdot \mathbf{T} \cdot \boldsymbol{\xi} - \sum_{A=1}^N \mu_{(A)}^s \mathbf{j}_{(A)} \cdot \boldsymbol{\xi} - T^s \mathbf{j}_s \cdot \boldsymbol{\xi} \right] \geq 0. \end{aligned} \quad (5)$$

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