ON SOME HYDRODYNAMIC AND OPTICAL PROPERTIES OF A FLUCTUATING FLUID SURFACE

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INTRODUCTION

In this thesis we study the properties of a liquid-vapour interface. The densities (as e.g. the mass or energy density) vary in the interfacial region from their liquid to their vapour value. This can happen in various ways. The mass density for instance, varies gradually from its liquid into its vapour value, while the free energy density exhibits a sharp maximum in the interfacial region. In this case such a maximum manifests itself as surface tension. Far enough from the critical point the interfacial region between liquid and vapour is of the order of a moleculair diameter. In a thermo-hydrodynamic description one can in this case replace the interfacial region by a sharp dividing surface.[1,2,3]) On this surface the excess densities can be defined, e.g. the energy, entropy or mass density. The precise choice of the position of the dividing surface in the interfacial region is to some extent arbitrary. The choice of Gibbs, in which the excess mass density is set equal to zero, is most commonly used. Also the fluxes (as e.g. the momentum or energy flux) vary in the interfacial region. As a consequence they have surface components on the dividing surface. In this way one develops a model of a liquid-vapour system, which contains the usual densities and fluxes in the bulk phases as well as the densities on and the fluxes along the dividing surface.[4-8])

In recent years the thermodynamics of irreversible processes is applied to such a system.[5,8-11]) In section 1.2 an application of thermodynamics of irreversible processes to a system with surface densities and fluxes in an external gravitational potential is derived. First the conservation laws for surface densities are formulated and subsequently, using the Gibbs-Duhem relation for the surface, the entropy production is derived. From the entropy production follows the identification of thermodynamic forces and fluxes and the derivation of the linear laws. The linear laws for the surface fluxes are of the same form as the corresponding laws in a bulk fluid. This means that the surface thermodynamic fluxes are related through the dissipative coefficients to the thermodynamic forces. The other linear laws, however, have the form of boundary conditions for the bulk fluxes at the dividing surface. This means that the jumps of the normal components of the bulk fluxes are expressed in terms of surface and bulk thermodynamic forces. The Onsager relations for the dissipative coefficients, which appear in the linear laws, are given. Furthermore it is shown in this section that at both sides of the interface the normal velocities are equal in good approximation.12) This is due to the fact that the latent heat of condensation or evaporation in the interfacial region is generally very large.

In section 1.3 we describe the equilibrium fluctuations. The fluctuations of the total entropy of a two fluid system with a dividing surface are on the one hand due to the entropy fluctuations in the bulk phases and on the surface, and on the other hand due to the fluctuations in the location of the dividing surface around its equilibrium position. Subsequently, the entropy is expanded to the second order in the fluctuating quantities. As the fluctuating surface is generally curved, the description in terms of curvilinear coordinates13) turned out to be useful. The equilibrium correlation functions for the bulk and surface temperature, mass and velocity fields which follow from the entropy expansion are derived. In equilibrium there are no correlations between the bulk and the surface fields. The terms in the entropy expansion which depend on the distance d from the interface to its equilibrium position, are more complicated. The first of these terms is proportional to the square of d and is a consequence of gravitation. The second term contains the square of the gradient of d and is proportional to the surface tension. This term corresponds to the fact that the curvature of the surface brings about an increase of the size of the surface. The total surface energy then grows proportionally to this size. The resulting correlation function of d has the usual form, as found in the context of the capillary wave model14). The corresponding correlation length (the so-called capillary length) diverges in the limit of zero gravitation. As a consequence the mean square root of d exhibits a logarithmic divergence in the same limit14,15). This divergence corresponds to the fact that the position of the surface is a symmetry breaking collective coordinate16).

In order to obtain the stochastic equations of motion (the so-called Landau - Lifshitz equations)17) one should include random fluxes in the linear laws. The fluctuation-dissipation theorem relates these fluxes to the dissipative coefficients. The time dependent correlation functions of the fluctuating fluid fields can then be derived from the stochastic properties of the random fluxes. In section 1.4 the fluctuation-dissipation theorem for the surface is formulated. The resulting equations make it in principle possible to study the properties of the time dependent correlation functions of e.g.

the position of the interface.

The properties of the interface between two fluids can be studied using light[18-21]. If in such a system the dielectric constant is a step-function on the equilibrium surface, the amplitudes of the reflected and transmitted electro-magnetic field are the Fresnel amplitudes. Because of the fluctuations in the position of the interface, these amplitudes differ from the Fresnel value. This is on the one hand due to the fact that the average profile is no longer a step-function, and on the other hand due to the correlations between the local field and the fluctuations in the position of the interface. These differences can be measured in an optical experiment[18-21]. In chapters 2 and 3 two quantities are studied, which can be measured in such an experiment: the ellipsometric coefficient (the ratio of the amplitude of the reflected light, polarized parallel (p) to the plane of incidence and the amplitude of the reflected light, polarized perpendicular (s) to the plane of incidence) and the reflectivity (the square of the absolute value of the amplitude of the reflected (p) or (s) polarized light).

In section 2.4 the method of equivalent polarisation and magnetization density is discussed.[10,22,23]. This method replaces the boundary conditions for the electro-magnetic field on the curved, fluctuating interface by boundary conditions for this field on the plane, equilibrium surface. By this procedure some components of this field obtain fluctuating excess contributions. These contributions are subsequently expanded to the second order in a small parameter (the thickness of the average profile divided by the wavelength of the light). The averaging of the fluctuating polarization and magnetization is done (section 2.5) using the equilibrium autocorrelation function for the position of the interface derived in section 1.3. From the boundary conditions for the averaged fields the amplitudes of the (p) and (s) polarised light are obtained and subsequently the ellipsometric coefficient is derived, cf. section 2.2. The ellipsometric coefficient is linear in the cut-off wavevector, which is interpreted as being inversely proportional to the intrinsic thickness of the interface. Far from the critical point this thickness is of the order of the molecular diameter. Comparison with experiment[20)] confirms this interpretation (section 2.6). It shows that for fluids far from the critical point the intrinsic thickness is 50% larger than the molecular diameter. Furthermore in this chapter the conclusion is drawn, that the value of the ellipsometric coefficient practically does not depend on whether the light is incident from the liquid or from the vapour side.

Using the amplitudes of the reflected and transmitted e-m field, calculated in chapter 2, the reflectivity and transmittivity are derived in chapter 3. Compared to the older theories[18,19,24)], these formulae contain some new terms which are the consequence of the correlations along the interface. These terms include e.g. the total loss of energy due to scattering. The new terms depend in a complicated way on the frequency and the wavevector. In section 3.2 simple approximate relations for these terms are derived and compared with the values obtained from the numerical calculations of the exact expressions. Like the ellipsometric coefficient, the reflectivity and transmittivity also depend on the intrinsic thickness. In this case, however, the dependence is logarithmic, while it was linear in the case of the ellipsometric coefficient.

If one calculates the reflectivity on the basis of the average profile[25], as is usually done, the result differs from the one obtained in section 3.2. In section 3.3 a comparison between the two approaches is made and the conclusion is drawn, that the average profile method is less adequate, because it does not take the correlations along the interface into account. Also for the ellipsometric coefficient the results are different. In the average profile method the ellipsometric coefficient is proportional to the thickness of the average profile. As mentioned earlier, the method used in this thesis yields this coefficient proportional to the intrinsic thickness. In this method all effects due to correlations are taken into account, so that one may conclude that the result of the average profile method is not correct.

When a two fluid system approaches the critical point, two important phenomena appear. Firstly, the interface becomes more diffuse and secondly the correlation length in the fluid becomes larger. Very close to the critical point the thickness of the average profile becomes larger than the wavelength of light. In this case the method using equivalent surface polarization and magnetization densities is no longer correct. In this thesis we study the liquid-vapour system, but most results can also be applied to an interface between two fluids. In section 3.4 a comparison is made with an experiment[21] on a binary fluid mixture close to the critical mixing point. A detailed discussion of the various contributions to the ellipsometric coefficient and the (s) and (p) reflectivity is given.

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A HYDRODYNAMIC THEORY FOR FLUCTUATIONS AROUND EQUILIBRIUM OF A LIQUID–VAPOUR INTERFACE

1. Introduction

It has been shown in recent years that irreversible thermodynamics can be used to derive boundary conditions at, and expressions for currents along, an interface between two coexisting bulk phases[1–6]). In this analysis one allows the densities and currents describing the system to be singular at the dividing surface. As such this description is similar to the capillary wave model (see refs. 7 and 8 for recent reviews).

In a real system the densities and currents are not singular. Rather they vary continuously from one bulk phase to the other through the interfacial region. Such a continuous density profile may be studied using a theory due to van der Waals[9]). Far from the critical point the interface is very sharp and a description using singular densities and currents at a dividing surface seems to be preferable[10–13]). For a systematic way to define singular densities and currents after the choice of a dividing surface we refer to ref. 14.

In the present paper we shall consider fluctuations of the interfacial densities and currents as well as fluctuations in the location of the interface. We shall use the capillary-wave model like description with singular densities and currents on the dividing surface. The mean square fluctuation in the location of the Gibbs dividing surface has been calculated in this way, using the free energy associated with a distortion of the interface (e.g. ref. 7). The capillary-wave contribution to the surface tension may then be calculated. It was first pointed out by Buff et al.[16]) that the mean square dispacement exhibits logarithmic divergencies. We refer to Evans[10]) for a more extensive discussion of this point and further references. Modifications of these divergencies by curvature of the equilibrium dividing surface are discussed in this paper.

It is our aim to extend the capillary-wave model like analysis by considering also fluctuations of the velocity, temperature and excess density of the interface (for any choice of the dividing surface). Furthermore we shall formulate equations and fluctuation–dissipation theorems which can be used to calculate time dependent correlation functions for the interface. We restrict ourselves to a one component system consisting of a liquid and its vapour. The conservation laws describing this system in a gravitational potential ϕ are: the continuity equation for the density ρ

$$\frac{\partial}{\partial t}\rho = -\operatorname{div}\rho\boldsymbol{v}, \tag{1.1}$$

where $\boldsymbol{v}$ is the velocity field, and

$$\frac{\partial}{\partial t}\rho\boldsymbol{v} = -\operatorname{div}(\rho\boldsymbol{v}\boldsymbol{v} + \boldsymbol{P}) - \rho \operatorname{grad}\phi, \tag{1.2}$$

$$\frac{\partial}{\partial t}\rho e = -\operatorname{div}(\rho e\boldsymbol{v} + \boldsymbol{P}\cdot\boldsymbol{v} + \boldsymbol{J}_q), \tag{1.3}$$

for the momentum and total energy densities, $\rho\boldsymbol{v}$ and ρe respectively. Furthermore $\boldsymbol{P}$ is the pressure tensor and $\boldsymbol{J}_q$ the heat current. For the definition of the dividing surface it is convenient to use a set of time-dependent orthogonal curvilinear coordinates $\xi_i(\boldsymbol{r}, t)$, $i = 1, 2, 3$[17]). The time-dependent dividing surface is given by

$$\xi_1(\boldsymbol{r}, t) = 0. \tag{1.4}$$

Characteristic functions Θ^+ and Θ^- for the regions occupied by the liquid and the vapour phase respectively are defined by

$$\Theta^{\pm}(\boldsymbol{r}, t) \equiv \Theta(\pm\,\xi_1(\boldsymbol{r}, t)), \tag{1.5}$$

where Θ is the Heaviside function. The δ function, which reduces an integration over the volume to an integration over the dividing surface, is defined by

$$\delta^s(\boldsymbol{r}, t) \equiv |\operatorname{grad}\xi_1(\boldsymbol{r}, t)|\,\delta(\xi_1(\boldsymbol{r}, t)). \tag{1.6}$$

In our analysis the densities and currents have the following general form

$$\begin{aligned}
\rho(\boldsymbol{r}, t) &= \rho^-(\boldsymbol{r}, t)\Theta^-(\boldsymbol{r}, t) + \rho^s(\boldsymbol{r}, t)\delta^s(\boldsymbol{r}, t) + \rho^+(\boldsymbol{r}, t)\Theta^+(\boldsymbol{r}, t),\\
(\rho\boldsymbol{v})(\boldsymbol{r}, t) &= \rho^-(\boldsymbol{r}, t)\boldsymbol{v}(\boldsymbol{r}, t)\Theta^-(\boldsymbol{r}, t) + \rho^s(\boldsymbol{r}, t)\boldsymbol{v}^s(\boldsymbol{r}, t)\delta^s(\boldsymbol{r}, t)\\
&\quad + \rho^+(\boldsymbol{r}, t)\boldsymbol{v}(\boldsymbol{r}, t)\Theta^+(\boldsymbol{r}, t),\\
\boldsymbol{P}(\boldsymbol{r}, t) &= \boldsymbol{P}^-(\boldsymbol{r}, t)\Theta^-(\boldsymbol{r}, t) + \boldsymbol{P}^s(\boldsymbol{r}, t)\delta^s(\boldsymbol{r}, t) + \boldsymbol{P}^+(\boldsymbol{r}, t)\Theta^+(\boldsymbol{r}, t),
\end{aligned} \tag{1.7}$$

and similar expressions for $(\rho vv)(r,t)$, $(\rho e)(r,t)$, $(P \cdot v)(r,t)$ and $J_q(r,t)$. Upon substitution of these expressions in the conservation laws one also needs the gradient of the characteristic functions. Using eqs. (1.5) and (1.6) one has[2,14])

$$\text{grad}\, \Theta^{\pm}(r,t) = \pm\, n\delta^{s}(r,t), \tag{1.8}$$

where n is the normal on the dividing surface (n points into the liquid). The time derivative is given by

$$\frac{\partial}{\partial t}\Theta^{\pm}(r,t) = \mp\, v_n^{s}\delta^{s}(r,t), \tag{1.9}$$

where v_n^s is the normal component of the interfacial velocity field. One may show[2,14]) that the time and spatial derivatives of δ^s in eqs. (1.1)–(1.3) do not contribute if one uses the fact that the interfacial momentum and heat current are parallel to the dividing surface

$$n \cdot P^{s} = 0 \quad \text{and} \quad n \cdot J_q^{s} = 0. \tag{1.10}$$

In addition to the conservation laws one needs the following equation of motion for the normal on the dividing surface[15])

$$\frac{\partial}{\partial t} n = -(1 - nn)\cdot \nabla v_n^{s} = -\nabla_{\parallel} v_n^{s}. \tag{1.11}$$

Using irreversible thermodynamics[1,2]) one may now derive an explicit expression for the interfacial entropy production and give the resulting linear constitutive laws for the currents along, into and through the interfacial region for the system under consideration[4,5]). In section 2 we review this analysis. We also give the fully linearized equations of motion for the interfacial (excess) density, velocity and temperature.

In section 3 we derive the equilibrium (equal time) correlation functions for the interface. In the last section we formulate the Landau-Lifshitz equations, which are comparable to the Langevin equation for the velocity of a Brownian particle, for the interfacial densities. In these equations one has random contributions to the various currents for which fluctuation-dissipation theorems are given. We note that the constitutive equations for the currents into and through the interface give boundary conditions for the equations of motion of the bulk fields. These boundary conditions thus contain random contributions.

2. Conservation laws and constitutive relations

In this section we briefly review the conservation laws, entropy balance and the resulting linear constitutive relations for the currents in a one-component two-phase system[4,5]). This shall be done in particular for the currents into, through and along the interfacial region. The general form of a conservation law for the specific density of a certain quantity a is

$$\frac{\partial}{\partial t}\rho a = -\operatorname{div}(\rho a \boldsymbol{v} + \boldsymbol{J}_a), \tag{2.1}$$

where ρ is the mass density, $\boldsymbol{v}$ the velocity field and $\boldsymbol{J}_a$ the conductive flux of a. In this expression ρa, $\rho a \boldsymbol{v}$ and $\boldsymbol{J}_a$ have the form given in eq. (1.7), e.g.

$$\begin{aligned}\rho a = {} & \rho^-(\boldsymbol{r},t)a^-(\boldsymbol{r},t)\Theta^-(\boldsymbol{r},t) + \rho^s(\boldsymbol{r},t)a^s(\boldsymbol{r},t)\delta^s(\boldsymbol{r},t) \\ & + \rho^+(\boldsymbol{r},t)a^+(\boldsymbol{r},t)\Theta^+(\boldsymbol{r},t).\end{aligned} \tag{2.2}$$

We note that if the Gibb's dividing surface is used $\rho^s = 0$. In the general analysis it is somewhat more convenient to take $\rho^s \neq 0$ which makes it possible to define specific densities on the dividing surface. In the resulting equations one is then still free to choose the most convenient definition of the dividing surface. In the bulk regions eq. (2.1) gives the usual conservation laws

$$\frac{\partial}{\partial t}\rho^{\pm}a^{\pm} = -\operatorname{div}(\rho^{\pm}a^{\pm}\boldsymbol{v}^{\pm} + \boldsymbol{J}_a^{\pm}). \tag{2.3}$$

For the interfacial density one finds[2,14]) from eq. (2.1)

$$\frac{\partial}{\partial t}\rho^s a^s = -\operatorname{div}(\rho^s a^s \boldsymbol{v}^s + \boldsymbol{J}_a^s) - [\rho a(v_n - v_n^s) + J_{a,n}]_-. \tag{2.4}$$

The subindex $-$ indicates the jump $Q_- \equiv (Q^+ - Q^-)_{\xi_1=0}$ of Q at the interface. The last term in this expression describes the flow of a into the interfacial region from the bulk regions. Finally eq. (2.1) also gives a transversality condition for the interfacial conductive current[2,14])

$$J_{a,n}^s = 0. \tag{2.5}$$

Using a equal to one, one finds the following equation for the conservation of mass at the interface

$$\frac{\partial}{\partial t}\rho^s = -\operatorname{div}(\rho^s\boldsymbol{v}^s) - [\rho(v_n - v_n^s)]_-, \tag{2.6}$$

where we have also used the fact that the conductive mass current is zero. Introducing the total time derivative at the dividing surface as

$$\frac{\mathrm{d}^s}{\mathrm{d}t} \equiv \frac{\partial}{\partial t} + \boldsymbol{v}^s\cdot\operatorname{grad}, \tag{2.7}$$

one may then write eq. (2.4), using eq. (2.6) in the form

$$\rho^s\frac{\mathrm{d}^s}{\mathrm{d}t}a^s = -\operatorname{div}\boldsymbol{J}_a^s - [\rho(a - a^s)(v_n - v_n^s) + J_{a,n}]_-. \tag{2.8}$$

Conservation of momentum in a gravitational potential $\phi = -gz$ leads to the following equation on the interface (choose a equal to the three components of the velocity field)

$$\frac{\partial}{\partial t}\rho^{s}\boldsymbol{v}^{s} = -\operatorname{div}(\rho^{s}\boldsymbol{v}^{s}\boldsymbol{v}^{s} + \boldsymbol{P}^{s}) - [\rho\boldsymbol{v}(v_{n} - v_{n}^{s}) + \boldsymbol{n}\cdot\boldsymbol{P}]_{-} + \rho^{s}\mathbf{g}, \tag{2.9a}$$

where $\boldsymbol{P}$ is the pressure tensor and $\mathbf{g} = (0, 0, g)$ the gravitational acceleration. This equation may alternatively be written as

$$\rho^{s}\frac{\mathrm{d}^{s}}{\mathrm{d}t}\boldsymbol{v}^{s} = -\operatorname{div}\boldsymbol{P}^{s} - [\rho(\boldsymbol{v} - \boldsymbol{v}^{s})(v_{n} - v_{n}^{s}) + \boldsymbol{n}\cdot\boldsymbol{P}]_{-} + \rho^{s}\mathbf{g}. \tag{2.9b}$$

The transversality condition in this case becomes

$$\boldsymbol{n}\cdot\boldsymbol{P}^{s} = \boldsymbol{P}^{s}\cdot\boldsymbol{n} = 0, \tag{2.10}$$

where we used the fact that $\boldsymbol{P}^{s}$ is a symmetric tensor 1) just like $\boldsymbol{P}^{+}$ and $\boldsymbol{P}^{-}$.

Conservation of energy e similarly gives (using $a = e$)

$$\frac{\partial}{\partial t}\rho^{s}e^{s} = -\operatorname{div}(\rho^{s}e^{s}\boldsymbol{v}^{s} + \boldsymbol{P}^{s}\cdot\boldsymbol{v}_{\parallel}^{s} + \boldsymbol{J}_{q}^{s}) - [\rho e(v_{n} - v_{n}^{s}) + \boldsymbol{n}\cdot\boldsymbol{P}\cdot\boldsymbol{v} + J_{q,n}]_{-}, \tag{2.11a}$$

where $\boldsymbol{J}_{q}$ is the heat current. This equation may alternatively be written as

$$\rho^{s}\frac{\mathrm{d}^{s}}{\mathrm{d}t}e^{s} = -\operatorname{div}(\boldsymbol{P}^{s}\cdot\boldsymbol{v}_{\parallel}^{s} + \boldsymbol{J}_{q}^{s}) - [\rho(e - e^{s})(v_{n} - v_{n}^{s}) + \boldsymbol{n}\cdot\boldsymbol{P}\cdot\boldsymbol{v} + J_{q,n}]_{-}. \tag{2.11b}$$

The transversality condition gives, using also eq. (2.10),

$$J_{q,n}^{s} = 0. \tag{2.12}$$

From the above equations one finds for the internal interfacial energy

$$u^{s} = e^{s} - \tfrac{1}{2}|\mathbf{v}^{s}|^{2} - (-gz)^{s}, \tag{2.13}$$

where $(-gz)^{s}$ is the value of the gravitational potential $(-gz)$ on the surface, the following balance equation

$$\begin{aligned}\frac{\partial}{\partial t}\rho^{s}u^{s} = {}& -\operatorname{div}(\rho^{s}u^{s}\boldsymbol{v}^{s} + \boldsymbol{J}_{q}^{s}) - \boldsymbol{P}^{s}\colon \boldsymbol{\nabla}_{\parallel}\boldsymbol{v}_{\parallel}^{s}\\ & - [(\rho u + \tfrac{1}{2}|\boldsymbol{v} - \boldsymbol{v}^{s}|^{2})(v_{n} - v_{n}^{s}) + J_{q,n} + \boldsymbol{n}\cdot\boldsymbol{P}\cdot(\boldsymbol{v} - \boldsymbol{v}^{s})]_{-}.\end{aligned} \tag{2.14a}$$

This equation may also be written in the following form:

$$\begin{aligned}\rho^{s}\frac{\mathrm{d}^{s}}{\mathrm{d}t}u^{s} = {}& -\operatorname{div}\boldsymbol{J}_{q}^{s} - \boldsymbol{P}^{s}\colon \boldsymbol{\nabla}_{\parallel}\boldsymbol{v}_{\parallel}^{s} - [\rho(u - u^{s} + \tfrac{1}{2}|\boldsymbol{v} - \boldsymbol{v}^{s}|^{2})(v_{n} - v_{n}^{s})\\ & + J_{q,n} + \boldsymbol{n}\cdot\boldsymbol{P}\cdot(\boldsymbol{v} - \boldsymbol{v}^{s})]_{-}.\end{aligned} \tag{2.14b}$$

The Gibbs relation for the interface is

$$\frac{\mathrm{d}^s}{\mathrm{d}t} s^s = \frac{1}{T^s} \frac{\mathrm{d}^s}{\mathrm{d}t} u^s + \frac{p^s}{T^s} \frac{\mathrm{d}^s}{\mathrm{d}t} (1/\rho^s), \tag{2.15}$$

where s^s, T^s and p^s are the interfacial entropy density, temperature and pressure (minus the surface tension) respectively. Using furthermore the following expression for the interfacial chemical potential

$$\mu^s = u^s - T^s s^s + p^s/\rho^s, \tag{2.16}$$

one may derive an explicit expression for the entropy production σ^s in the interfacial region[5]). The viscous parts of the pressure tensor in the bulk and on the dividing surface are defined by

$$\boldsymbol{\Pi}^{\pm} \equiv \boldsymbol{P}^{\pm} - p^{\pm} \quad \text{and} \quad \boldsymbol{\Pi}^s \equiv \boldsymbol{P}^s - p^s(1 - \boldsymbol{nn}). \tag{2.17}$$

The expression for the entropy production is given by

$$\begin{aligned}
\sigma^s = & -\frac{1}{T^s} \overline{\boldsymbol{\Pi}}^s : \overline{\boldsymbol{\nabla}_{\|} \boldsymbol{v}_{\|}^s} \\
& - \left(\frac{1}{T^s}\right)^2 \boldsymbol{J}_q^s \cdot \boldsymbol{\nabla} T^s - \frac{1}{T^s} [(\boldsymbol{n} \cdot \boldsymbol{\Pi})_{\|} + \tfrac{1}{2}\rho(v_n - v_n^s)(\boldsymbol{v}_{\|} - \boldsymbol{v}_{\|}^s)]_+ \cdot \boldsymbol{v}_{\|-} \\
& - \frac{1}{T^s} [(\boldsymbol{n} \cdot \boldsymbol{\Pi})_{\|} + \tfrac{1}{2}\rho(v_n - v_n^s)(\boldsymbol{v}_{\|} - \boldsymbol{v}_{\|}^s)]_- \cdot (\boldsymbol{v}_{\|+} - \boldsymbol{v}_{\|}^s) \\
& - \frac{1}{T^s} \Pi^s \boldsymbol{\nabla} \cdot \boldsymbol{v}^s - (J_{q,n} + T\rho s(v_n - v_n^s))_- \left(\left(\frac{1}{T}\right)_+ - \frac{1}{T^s}\right) \\
& - [J_{q,n} + T\rho s(v_n - v_n^s)]_+ \left(\frac{1}{T}\right)_- \\
& - \frac{1}{T^s} [\Pi_{nn} + \tfrac{1}{2}\rho(v_n - v_n^s)^2 + \rho(\mu - \mu^s)]_- (v_{n+} - v_n^s) \\
& - \frac{1}{T^s} [\Pi_{nn} + \tfrac{1}{2}\rho(v_n - v_n^s)^2 + \rho(\mu - \mu^s)]_+ v_{n-}.
\end{aligned} \tag{2.18}$$

The subscript + indicated the average $Q_+ = \frac{1}{2}(Q^+ + Q^-)_{\xi_1 = 0}$ of a at the interface. Furthermore

$$\Pi^s \equiv \tfrac{1}{2} \boldsymbol{\Pi}^s \tag{2.19}$$

and the traceless symmetric part of $\boldsymbol{\Pi}^s$, which itself is already symmetric, is defined by

$$\overline{\boldsymbol{\Pi}}^s \equiv \boldsymbol{\Pi}^s - \Pi^s(1 - \boldsymbol{nn}). \tag{2.20}$$

The symmetric traceless gradient of $\boldsymbol{v}^s$ is defined by

$$(\overline{\boldsymbol{\nabla}_{\|} \boldsymbol{v}_{\|}^s})_{\alpha\beta} \equiv \tfrac{1}{2}(\nabla_{\|\alpha} v_{\|\beta}^s + \nabla_{\|\beta} v^s_{\|\alpha}) - \tfrac{1}{2}(\delta_{\alpha\beta} - n_\alpha n_\beta) \boldsymbol{\nabla}_{\|} \cdot \boldsymbol{v}_{\|}^s. \tag{2.21}$$

As is clear from eq. (2.18) there are one 2 × 2 tensorial, three vectorial (with 2 components) and five scalar force–flux pairs.

One thus finds the following linear constitutive relations:

$$\overline{\boldsymbol{\Pi}}^{s} = -2\eta^{s}\overline{\nabla_{\|}\boldsymbol{v}_{\|}^{s}}. \tag{2.22}$$

Here η^s is in the interfacial shear viscosity.

$$\begin{aligned}
\boldsymbol{J}_q^s &= -\lambda^s\nabla_{\|}T^s - \alpha_{12}\boldsymbol{v}_{\|-} - \alpha_{13}(\boldsymbol{v}_{\|+} - \boldsymbol{v}_{\|}^s)\\
[(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\|} + \tfrac{1}{2}\rho(v_n - v_n^s)(\boldsymbol{v}_{\|} - \boldsymbol{v}_{\|}^s)]_+ &= -\alpha_{21}\nabla_{\|}T^s - \beta\boldsymbol{v}_{\|-} - \alpha_{23}(\boldsymbol{v}_{\|+} - \boldsymbol{v}_{\|}^s)\\
[(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\|} + \tfrac{1}{2}\rho(v_n - v_n^s)(\boldsymbol{v}_{\|} - \boldsymbol{v}_{\|}^s)]_- &= -\alpha_{31}\nabla_{\|}T^s - \alpha_{32}\boldsymbol{v}_{\|-} - \alpha_{33}(\boldsymbol{v}_{\|+} - \boldsymbol{v}_{\|}^s).
\end{aligned} \tag{2.23}$$

Here λ^s is the interfacial heat conductivity and β the coefficient of sliding friction. The coefficient α_{21} describes the phenomena of thermal slip.

$$\begin{aligned}
\Pi^s &= -\eta_s^s\nabla_{\|}\cdot\boldsymbol{v}_{\|}^s - L_{12}(T_+ - T^s) - L_{13}T_- - L_{14}(v_{n+} - v_n^s) - L_{15}v_{n-},\\
[J_{q,n} + T\rho s(v_n - v_n^s)]_- &= -L_{21}\nabla_{\|}\cdot\boldsymbol{v}_{\|}^s - L_{22}(T_+ - T^s) - L_{23}T_- - L_{24}(v_n - v_n^s) - L_{25}v_{n-},\\
[J_{q,n} + T\rho s(v_n - v_n^s)]_+ &= -L_{31}\nabla_{\|}\cdot\boldsymbol{v}_{\|}^s - L_{32}(T_+ - T^s) - L_{33}T_- - L_{34}(v_{n+} - v_n^s) - L_{35}v_{n-},\\
&[\Pi_{nn} + \tfrac{1}{2}\rho(v_n - v_n^s)^2 + \rho(\mu - \mu^s)]_-\\
&\quad = -L_{41}\nabla\cdot\boldsymbol{v}_{\|}^s - L_{42}(T_+ - T^s) - L_{43}T_- - L_{44}(v_{n+} - v_n^s) - L_{45}v_{n-},\\
&[\Pi_{nn} + \tfrac{1}{2}\rho(v_n - v_n^s)^2 + \rho(\mu - \mu^s)]_+\\
&\quad = -L_{51}\nabla_{\|}\cdot\boldsymbol{v}_{\|}^s - L_{52}(T_+ - T^s) - L_{53}T_- - L_{54}(v_{n+} - v_n^s) - L_{55}v_{n-}.
\end{aligned} \tag{2.24}$$

Here η_s^s is an interfacial viscosity analogous to the bulk viscosity. The Onsager relations are

$$\begin{aligned}
&\alpha_{21} = -\alpha_{12}, \quad \alpha_{31} = -\alpha_{13} \quad \text{and} \quad \alpha_{32} = \alpha_{23},\\
&L_{21} = -L_{12}, \quad L_{31} = -L_{13}, \quad L_{41} = L_{14}, \quad L_{51} = L_{15},\\
&L_{32} = L_{23}, \quad L_{42} = -L_{24}, \quad L_{52} = -L_{25}, \quad L_{43} = -L_{34},\\
&L_{53} = -L_{35}, \quad L_{54} = L_{45}.
\end{aligned} \tag{2.25}$$

Consequently there are 22 independent constitutive coefficients.

Substituting the constitutive relations into eqs. (2.9) and (2.14) one obtains equations of motion for the interfacial velocity field and the internal energy density. Furthermore the constitutive relations provide boundary conditions for the equations of motion for the bulk variables.

If one studies fluctuations around equilibrium one usually linearizes the equations of motion around equlibrium. In equilibrium one has in the bulk

$$\begin{aligned}
&P_{\text{eq},\alpha\beta}^{\pm} = p_{\text{eq}}^{\pm}\delta_{\alpha\beta}, \quad \boldsymbol{J}_{q,\text{eq}}^{\pm} = 0, \quad \boldsymbol{v}^{\pm} = 0, \quad T_{\text{eq}}^{\pm}(\boldsymbol{r}) = T_{\text{eq}}^{\pm},\\
&\text{grad}\, p_{\text{eq}}^{\pm} = \rho^{\pm}\boldsymbol{g} \quad \text{and} \quad \mu_{\text{eq}}^{\pm}(\boldsymbol{r}) = gz + (\text{const})^{\pm}.
\end{aligned} \tag{2.26}$$

The equilibrium dividing surface is assumed to be planar and is chosen to coincide with the x–y plane. On this surface we then have in equilibrium

$$\begin{aligned} &\boldsymbol{P}^s_{eq}(x, y) = p^s_{eq}(1 - \boldsymbol{n}_{eq}\boldsymbol{n}_{eq}), \quad \text{with } \boldsymbol{n}_{eq} = (0, 0, 1), \\ &\boldsymbol{J}^s_{q,eq} = 0, \quad \boldsymbol{v}^s = 0, \quad T^+_{eq} = T^-_{eq} = T^s_{eq} = T_{eq}, \\ &P_{eq,-} = \rho^s_{eq} g \quad \text{and} \quad \mu^+_{eq} = \mu^s_{eq} = \mu^-_{eq}. \end{aligned} \tag{2.27}$$

Using eq. (2.26) and (2.27) it follows together with eqs. (2.15) and (2.16) that $\mathrm{grad}(\mu_{eq} + \phi) = 0$ and consequently

$$\mu_{eq}(\boldsymbol{r}) = -\phi(\boldsymbol{r}) + \mu_0 = gz + \mu_0, \tag{2.28}$$

where μ_0 is the chemical potential for $z = 0$. Linearizing eq. (2.6) one obtains for the variation of the interfacial density around equilibrium

$$\frac{\partial}{\partial t} \Delta\rho^s = -\rho^s_{eq} \operatorname{div} \boldsymbol{v}^s - [\rho_{eq}(v_n - v^s_n)]_-. \tag{2.29}$$

A deviation from the equilibrium value will be indicated by a prefactor Δ. Similarly one finds for the velocity field

$$\rho^s_{eq} \frac{\partial}{\partial t} \boldsymbol{v}^s = -\operatorname{div}(\Delta\boldsymbol{P}^s) - \boldsymbol{n} \cdot (\Delta\boldsymbol{P}_-) - \boldsymbol{n}d\left(\frac{\partial}{\partial z} p_{eq}\right)_- + \Delta\rho^s \boldsymbol{g}. \tag{2.30}$$

Here $d(x, y)$ is the position along the z axis of the moving interface. The reason that the term proportional to d appears is that the term $\boldsymbol{n} \cdot \boldsymbol{P}_-$ in eq. (2.9) is evaluated at the moving interface. The variation of $\boldsymbol{n} \cdot \boldsymbol{P}_-$ around equilibrium is due on the one hand to the variation of $\boldsymbol{P}$ around equilibrium but on the other hand due to the difference between p_{eq} at the moving and p_{eq} at the equilibrium position of the interface. Using eq. (2.26) one may write eq. (2.30) in the form

$$\rho^s_{eq} \frac{\partial}{\partial t} \boldsymbol{v}^s = -\operatorname{div}(\Delta\boldsymbol{P}^s) - \boldsymbol{n} \cdot (\Delta\boldsymbol{P}_-) - \boldsymbol{n}d\rho_{eq,-}g + \boldsymbol{n}\Delta\rho^s g. \tag{2.31}$$

It should be emphasized that the jumps in eqs. (2.29)–(2.31) are now calculated in $z = 0$. The linearized version of eq. (2.14a) for the internal energy becomes

$$\begin{aligned} \frac{\partial}{\partial t} \Delta(\rho u)^s = &-[T_{eq}(\rho s)^s_{eq} + \mu^s_{eq}\rho^s_{eq}]\boldsymbol{\nabla}_\parallel \cdot \boldsymbol{v}^s_\parallel - \operatorname{div} \boldsymbol{J}^s_q - T_{eq}s_{eq,-}[\rho_{eq}(v_n - v^s_n)]_+ \\ &- (T_{eq}s_{eq,+} + \mu^s_{eq})[\rho_{eq}(v_n - v^s_n)]_- - J_{q,n-}, \end{aligned} \tag{2.32}$$

where we have used eq. (2.16) and the analogous equation in the bulk*. In

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* When Gibb's choice of the dividing surface is used $\rho^s = 0$ and furthermore $(\rho\boldsymbol{v})^s = 0$. The interfacial energy density $(\rho u)^s$ is, however, in general unequal to zero. This is the reason why we write $\partial\Delta(\rho u)^s/\partial t$ rather than $\rho^s\partial\Delta u^s/\partial t$ on the left hand side of eq. (2.32).

order to obtain an equation of motion for the interfacial temperature we write

$$\frac{\partial}{\partial t}\Delta(\rho u)^{s} = \left(\frac{\partial(\rho u)^{s}}{\partial T^{s}}\right)_{\rho^{s}} \frac{\partial \Delta T^{s}}{\partial t} + \left(\frac{\partial(\rho u)^{s}}{\partial \rho^{s}}\right)_{T^{s}} \frac{\partial \Delta \rho^{s}}{\partial t}$$

$$= c^{s}\frac{\partial}{\partial t}\Delta T^{s} + \left[\mu^{s} + T^{s}\left(\frac{\partial(\rho s)^{s}}{\partial \rho^{s}}\right)_{T^{s}}\right]\frac{\partial}{\partial t}\Delta\rho^{s}, \tag{2.33}$$

where we used eqs. (2.15) and (2.16). Furthermore

$$c^{s} \equiv \left(\frac{\partial(\rho u)^{s}}{\partial T^{s}}\right)_{\rho^{s}} \tag{2.34}$$

is the interfacial specific heat. Substituting eq. (2.33) into eq. (2.32) and using eq. (2.29) one finds

$$c^{s}\frac{\partial}{\partial t}\Delta T^{s} = -\operatorname{div}\boldsymbol{J}_{q}^{s} - J_{qn-} + T_{eq}[s_{eq,+}\rho_{eq}^{s} - (\rho s)_{eq}^{s}]\boldsymbol{\nabla}_{\parallel}\cdot \boldsymbol{v}_{\parallel}^{s}$$

$$- T_{eq}s_{eq,-}[\rho_{eq}(v_{n} - v_{n}^{s})]_{+} + T_{eq}\left[s_{eq,+} - \left(\frac{\partial(\rho s)^{s}}{\partial \rho^{s}}\right)_{T^{s}}\right]\frac{\partial}{\partial t}\Delta\rho^{s} \tag{2.35}$$

as the linearized equation for the interfacial temperature.

While it is convenient for the general formulation of the fluctuation-dissipation theorem for the random currents to take $\rho^{s} \neq 0$, one is free to use Gibb's definition of the dividing surface in which case $\rho^{s} = \rho_{eq}^{s} = \Delta\rho^{s} = 0$. The linearised equations, eqs. (2.29), (2.31) and (2.35), then reduce to

$$[\rho_{eq}(v_{n} - v_{n}^{s})]_{-} = 0 \Leftrightarrow v_{n}^{s} = (\rho_{eq}v_{n})_{-}/\rho_{eq,-}, \tag{2.36}$$

$$\boldsymbol{n}\cdot\Delta\boldsymbol{P}_{-} = -\operatorname{div}(\Delta\boldsymbol{P}^{s}) - \boldsymbol{n}d\rho_{eq,-}g, \tag{2.37}$$

$$c^{s}\frac{\partial}{\partial t}\Delta T^{s} = -\operatorname{div}\boldsymbol{J}_{q}^{s} - J_{qn-} - T_{eq}(\rho s)_{eq}^{s}\boldsymbol{\nabla}_{\parallel}\cdot\boldsymbol{v}_{\parallel}^{s} - T_{eq}s_{eq,-}[\rho_{eq}(v_{n} - v_{n}^{s})]_{+}. \tag{2.38}$$

The first equation expresses the normal component of the velocity of the interface in v_{n}^{+} and v_{n}^{-}. The second is related to the capillarity condition. The last equation describes the behaviour of the interfacial temperature. The last term on the right hand side of this equation describes the cooling or heating of the interface due to condensation or evaporation. $T_{eq}s_{eq,-}$ is the latent heat. As the latent heat is generally very large, the rate of condensation (or minus the evaporation), which is given by $[\rho_{eq}(v_{n} - v_{n}^{s})]_{+} = \rho_{eq}^{-}(v_{n}^{-} - v_{n}^{s}) = \rho_{eq}^{+}(v_{n}^{+} - v_{n}^{s})$, will be small. The normal velocities of and near the interface are thus equal in good approximation[18]).

3. Equilibrium fluctuations

The probability of thermal fluctuations around equilibrium of a closed system is given in terms of the total entropy S of the system by

$$W = W_{n}\exp(S/k_{B}), \tag{3.1}$$

where W_n normalizeds the distribution and k_B is Boltzmann's constant. The entropy of the two phase systems is the sum of the entropy of the two phases and the interfacial entropy. In our description the entropy density is written as

$$s_v(\boldsymbol{r}, t) = s_v^-(\boldsymbol{r}, t)\Theta^-(\boldsymbol{r}, t) + s_v^s(\boldsymbol{r}, t)\delta^s(\boldsymbol{r}, t) + s_v^+(\boldsymbol{r}, t)\Theta^+(\boldsymbol{r}, t). \tag{3.2}$$

Here $s_v^\pm \equiv \rho^\pm s^\pm$ are the entropy densities per unit of volume in the two phases, while $s_v^s \equiv (\rho s)^s$ is the interfacial entropy density per unit of surface. The total entropy of the system may now be written as

$$\begin{aligned} S = \int \mathrm{d}\boldsymbol{r} s_v &= \int \mathrm{d}\boldsymbol{r}(s_v^-\theta^- + s_v^s\delta^s + s_v^+\theta^+) \\ &= \int_{(-)\text{ phase}} s_v^- \,\mathrm{d}\boldsymbol{r} + \int_{\substack{\text{dividing}\\ \text{surface}}} s_v^s \,\mathrm{d}0 + \int_{(+)\text{ phase}} s_v^+ \,\mathrm{d}\boldsymbol{r}. \end{aligned} \tag{3.3}$$

The fluctuations ΔS of the total entropy S in this system are on the one hand due to the fluctuations of $s_v^\pm$ and s_v^s around their equilibrium value and on the other hand due to fluctuations in the location of the interface around its equilibrium position. We thus have

$$\begin{aligned} \Delta S = &\int \mathrm{d}\boldsymbol{r}[(\Delta s_v^-)\Theta_{eq}^- + (\Delta s_v^s)\delta_{eq}^s + (\Delta s_v^+)\Theta_{eq}^+] \\ &+ \int \mathrm{d}\boldsymbol{r}[s_v^-\Delta\Theta^- + s_v^s\Delta\delta^s + s_v^+\Delta\Theta^+]. \end{aligned} \tag{3.4}$$

It is convenient to write this equation in the following form

$$\Delta S = \sum_{\nu = -, s, +} \int \mathrm{d}\boldsymbol{r}[(\Delta s_v^\nu)\Theta_{eq}^\nu + s_v^\nu\Delta\Theta^\nu], \tag{3.5}$$

where $\Theta^s \equiv \delta^s$. We shall first expand Δs_v^ν to second order in the fluctuations of the density and the internal energy ($u_v \equiv \rho u$). This gives

$$\begin{aligned} \Delta S = \sum_\nu \int \mathrm{d}\boldsymbol{r}\Big\{&\Big[\Big(\frac{\partial s_v}{\partial \rho}\Big)_{eq}^\nu \Delta\rho^\nu + \Big(\frac{\partial s_v}{\partial u_v}\Big)_{eq}^\nu \Delta u_v^\nu\Big]\Theta_{eq}^\nu \\ &+ \frac{1}{2}\Big[\Big(\frac{\partial s_v}{\partial \rho^2}\Big)_{eq}^\nu (\Delta\rho^\nu)^2 + 2\Big(\frac{\partial^2 s_v}{\partial\rho\partial u_v}\Big)_{eq}^\nu \Delta\rho^\nu\Delta u_v^\nu + \Big(\frac{\partial^2 s_v}{\partial u_v^2}\Big)(\Delta u_v^\nu)^2\Big]\Theta_{eq}^\nu + s_v^\nu\Delta\Theta^\nu\Big\}. \end{aligned} \tag{3.6}$$

As usual we shall now use the conservation of the total energy and mass in order to eliminate the linear contributions to this expression. For the energy we have

$$\begin{aligned} 0 &= \Delta \int \mathrm{d}\boldsymbol{r}(u_v + \tfrac{1}{2}\rho|\boldsymbol{v}|^2 + \rho\phi) \\ &= \sum_\nu \int \mathrm{d}\boldsymbol{r}\{[\Delta u_v^\nu + \tfrac{1}{2}\rho_{eq}^\nu|\boldsymbol{v}^s|^2 + \Delta\rho^\nu\phi]\Theta_{eq}^\nu + [u_v^\nu + \rho^\nu\phi]\Delta\Theta^\nu\}, \end{aligned} \tag{3.7}$$

where $\phi(r) \equiv -gz$ is the gravitational potential. In the second equality we used the fact that $\boldsymbol{v}$ is zero in equilibrium. As a consequence $|\boldsymbol{v}|^2$ is already quadratic in the fluctuations. Furthermore we use the following thermodynamic relations

$$\left(\frac{\partial s_{\mathrm{v}}}{\partial u_{\mathrm{v}}}\right)_{\mathrm{eq}}^{\nu} = \frac{1}{T_{\mathrm{eq}}} \quad \text{and} \quad \left(\frac{\partial s_{\mathrm{v}}}{\partial \rho}\right)_{\mathrm{eq}}^{\nu} = -\frac{\mu_{\mathrm{eq}}}{T_{\mathrm{eq}}}. \tag{3.8}$$

Using eqs. (3.7), (3.8) and (2.28), the expression for ΔS becomes

$$\begin{aligned}\Delta S = \sum_{\nu} \int \mathrm{d}\boldsymbol{r} \Big\{ &-(\mu_0/T_{\mathrm{eq}})\Delta\rho^{\nu}\Theta_{\mathrm{eq}}^{\nu} \\ &+ \frac{1}{2}\Big[-(\rho_{\mathrm{eq}}^{\nu}/T_{\mathrm{eq}})|\boldsymbol{v}^{\nu}|^2 + \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial \rho^2}\right)_{\mathrm{eq}}^{\nu}(\Delta\rho^{\nu})^2 + 2\left(\frac{\partial^2 s_{\mathrm{v}}}{\partial\rho\partial u_{\mathrm{v}}}\right)_{\mathrm{eq}}^{\nu}\nabla\rho^{\nu}\Delta_{\mathrm{v}}^{\nu} \\ &+ \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial u_{\mathrm{v}}^2}\right)_{\mathrm{eq}}^{\nu}(\Delta u_{\mathrm{v}}^{\nu})^2\Big]\Theta_{\mathrm{eq}}^{\nu} - \frac{1}{T_{\mathrm{eq}}}(u_{\mathrm{v}}^{\nu} + \rho^{\nu}\phi - T_{\mathrm{eq}}s_{\mathrm{v}}^{\nu})\Delta\Theta^{\nu}\Big\}.\end{aligned} \tag{3.9}$$

Using conservation of mass we have

$$0 = \Delta\int \mathrm{d}\boldsymbol{r}\rho = \sum_{\nu}\int \mathrm{d}\boldsymbol{r}(\Delta\rho^{\nu}\Theta_{\mathrm{eq}}^{\nu} + \rho^{\nu}\Delta\Theta^{\nu}). \tag{3.10}$$

Substituting this relation in eq. (3.9) one obtains

$$\begin{aligned}\Delta S = \sum_{\nu}\int \mathrm{d}\boldsymbol{r}\Big\{&\frac{1}{2}\Big[-(\rho_{\mathrm{eq}}^{\nu}/T_{\mathrm{eq}})|\boldsymbol{v}^{\nu}|^2 + \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial\rho^2}\right)_{\mathrm{eq}}^{\nu}(\Delta\rho^{\nu})^2 + 2\left(\frac{\partial^2 s_{\mathrm{v}}}{\partial\rho\partial u_{\mathrm{v}}}\right)_{\mathrm{eq}}^{\nu}\Delta\rho^{\nu}\Delta u_{\mathrm{v}}^{\nu} \\ &+ \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial u_{\mathrm{v}}^2}\right)_{\mathrm{eq}}^{\nu}(\Delta u_{\mathrm{v}}^{\nu})^2\Big]\Theta_{\mathrm{eq}}^{\nu} - \frac{1}{T_{\mathrm{eq}}}[u_{\mathrm{v}}^{\nu} - (\mu_0 - \phi)\rho^{\nu} - T_{\mathrm{eq}}s_{\mathrm{v}}^{\nu}]\Delta\Theta^{\nu}\Big\}.\end{aligned} \tag{3.11}$$

With the help of the following thermodynamic relations

$$u_{\mathrm{v,eq}}^{\nu} = \mu_{\mathrm{eq}}\rho_{\mathrm{eq}}^{\nu} + T_{\mathrm{eq}}s_{\mathrm{v,eq}}^{\nu} - p_{\mathrm{eq}}^{\nu} \quad \text{and} \quad \Delta s_{\mathrm{v}}^{\nu} = \frac{1}{T_{\mathrm{eq}}}\Delta u_{\mathrm{v}}^{\nu} - \frac{\mu_{\mathrm{eq}}}{T_{\mathrm{eq}}}\Delta\rho^{\nu} \tag{3.12}$$

and $\mu_{\mathrm{eq}} = \mu_0 - \phi$, eq. (2.28), the fluctuations of the entropy becomes

$$\begin{aligned}\Delta S = \sum_{\nu}\int \mathrm{d}\boldsymbol{r}\Big\{&\frac{1}{2}\Big[-(\rho_{\mathrm{eq}}^{\nu}/T_{\mathrm{eq}})|\boldsymbol{v}^{\nu}|^2 + \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial\rho^2}\right)_{\mathrm{eq}}^{\nu}(\Delta\rho^{\nu})^2 + 2\left(\frac{\partial^2 s_{\mathrm{v}}}{\partial\rho\partial u_{\mathrm{v}}}\right)_{\mathrm{eq}}^{\nu}\Delta\rho^{\nu}\Delta u_{\mathrm{v}}^{\nu} \\ &+ \left(\frac{\partial^2 s_{\mathrm{v}}}{\partial u_{\mathrm{v}}^2}\right)_{\mathrm{eq}}^{\nu}(\Delta u_{\mathrm{v}}^{\nu})^2\Big]\Theta_{\mathrm{eq}}^{\nu} + \frac{1}{T_{\mathrm{eq}}}p_{\mathrm{eq}}^{\nu}\Delta\Theta^{\nu}\Big\} - \int \mathrm{d}\boldsymbol{r}(\rho_{\mathrm{eq}}^{\mathrm{s}}/T_{\mathrm{eq}})(\phi - \phi_{\mathrm{s}})\Delta\Theta^{\mathrm{s}}.\end{aligned} \tag{3.13}$$

ϕ_{s} is the value of ϕ on the dividing surface. The last term on the right hand side of this equation should be taken along because of the fact that $\Delta\Theta^{\mathrm{s}}$ contains terms proportional to $\boldsymbol{n}_{\mathrm{eq}} \cdot \nabla\delta_{\mathrm{eq}}^{\mathrm{s}}$. One may therefore not replace ϕ by ϕ_{s} in eq. (3.11) for the $\nu = \mathrm{s}$ contribution.

It is convenient to write ΔS in terms of fluctuations of the density and the temperature. One then obtains

$$\Delta S = -\frac{1}{2T_{\mathrm{eq}}}\Big\{\sum_{\nu}\int \mathrm{d}\boldsymbol{r}[(c_{\mathrm{v}}^{\nu}/T_{\mathrm{eq}})(\Delta T^{\nu})^2 + (\rho_{\mathrm{eq}}^{\nu})^{-2}(\kappa_T^{\nu})^{-1}(\Delta\rho^{\nu})^2 + \rho_{\mathrm{eq}}^{\nu}|\boldsymbol{v}^{\nu}|^2]\Theta_{\mathrm{eq}}^{\nu}$$
$$-2\int \mathrm{d}\boldsymbol{r}\Big[\sum_{\nu} p_{\mathrm{eq}}^{\nu}\Delta\Theta^{\nu} - \rho_{\mathrm{eq}}^{s}(\phi - \phi_s)\Delta\Theta^{s}\Big]\Big\}, \tag{3.14}$$

where we use the equilibrium values of

$$c_{\mathrm{v}}^{\nu} \equiv \left(\frac{\partial u_{\mathrm{v}}^{\nu}}{\partial T}\right)_{\rho} \quad \text{and} \quad \kappa_T^{\nu} \equiv \frac{1}{\rho^{\nu}}\left(\frac{\partial \rho^{\nu}}{\partial p^{\nu}}\right)_T, \tag{3.15}$$

which are the specific heat at constant volume (or surface area) per unit of volume (or surface area) and the isothermal compressibility respectively.

Finally we need expressions for $\Delta\Theta^{\nu}$ to second order in the fluctuations of the interface. One has

$$\Delta\Theta^{\pm}(\boldsymbol{r}) = \Theta(\pm\xi_1) - \Theta(\pm\xi_{1,\mathrm{eq}}) = \pm\Delta\xi_1\left(1 + \frac{1}{2}\Delta\xi_1\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\right)\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\Theta(\xi_{1,\mathrm{eq}})$$
$$= \pm\Delta\xi_1\left(1 + \frac{1}{2}\Delta\xi_1\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\right)\delta(\xi_{1,\mathrm{eq}}). \tag{3.16}$$

Here $\Delta\xi_1$ is the fluctuation of the first curvilinear coordinate around its equilibrium value

$$\Delta\xi_1(\boldsymbol{r}) \equiv \xi_1(\boldsymbol{r}) - \xi_{1,\mathrm{eq}}(\boldsymbol{r}). \tag{3.17}$$

The distance of the fluctuating dividing surface to the equilibrium dividing surface along a line of constant $\xi_{2,\mathrm{eq}}$ and $\xi_{3,\mathrm{eq}}$ is to linear order in $\Delta\xi_1$ given by

$$d(\xi_{2,\mathrm{eq}}, \xi_{3,\mathrm{eq}}) = -\int_0^{\Delta\xi_1(0,\,\xi_{2,\mathrm{eq}},\,\xi_{3,\mathrm{eq}})}\left|\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\boldsymbol{r}\right|\mathrm{d}\xi_{1,\mathrm{eq}}$$
$$= -h_{1,\mathrm{eq}}(0, \xi_{2,\mathrm{eq}}, \xi_{3,\mathrm{eq}})\Delta\xi_1(0, \xi_{2,\mathrm{eq}}, \xi_{3,\mathrm{eq}}), \tag{3.18}$$

where the scale factor for the *i*th coordinate is defined by[17])

$$h_i \equiv |\nabla\xi_i|^{-1} = \left|\frac{\partial}{\partial\xi_i}\boldsymbol{r}\right|. \tag{3.19}$$

In the special case that the equilibrium dividing surface is the x–y plane, cf. previous section, one has

$$\xi_{1,\mathrm{eq}} = z, \quad \xi_{2,\mathrm{eq}} = x, \quad \xi_{3,\mathrm{eq}} = y, \tag{3.20}$$

$$\Theta_{\mathrm{eq}}^{\pm}(\boldsymbol{r}) = \Theta(\pm z), \tag{3.21}$$

$$\Delta\Theta^{\pm}(\boldsymbol{r}) = \mp d(x, y)\left(1 - \frac{1}{2}d(x, y)\frac{\partial}{\partial z}\right)\delta(z). \tag{3.22}$$

In the appendix we show furthermore that

$$\Delta\Theta^{s}(\boldsymbol{r}) \equiv \Delta\delta^{s}(\boldsymbol{r}) \equiv \delta^{s}(\boldsymbol{r}) - \delta^{s}_{eq}(\boldsymbol{r})$$

$$= h^{-1}_{1,eq}\left[\frac{1}{2}|\Delta \boldsymbol{n}|^{2} + \frac{\partial}{\partial\xi_{1,eq}}\Delta\xi_{1}\left(1+\frac{1}{2}\Delta\xi_{1}\frac{\partial}{\partial\xi_{1,eq}}\right)\right]\delta(\xi_{1,eq}). \tag{3.23}$$

In the case that the equilibrium dividing surface is the x–y plane one thus has

$$\Theta^{s}_{eq} = \delta^{s}_{eq} = \delta(z), \tag{3.24}$$

$$\Delta\Theta^{s}(\boldsymbol{r}) = \Delta\delta^{s}(\boldsymbol{r}) = \left[\frac{1}{2}|\nabla d(x,y)|^{2} - d(x,y)\frac{\partial}{\partial z}\left(1-\frac{1}{2}d(x,y)\frac{\partial}{\partial z}\right)\right]\delta(z). \tag{3.25}$$

Using eqs. (3.16) and (3.23) one has

$$\int \mathrm{d}\boldsymbol{r}\left[\sum_{\nu} p^{\nu}_{eq}\Delta\Theta^{\nu} - \rho^{s}_{eq}(\phi-\phi_{s})\Delta\Theta^{s}\right]$$

$$= \int \mathrm{d}\xi_{1,eq}\,\mathrm{d}\xi_{2,eq}\,\mathrm{d}\xi_{3,eq}h_{1,eq}h_{2,eq}h_{3,eq}\Big[(p^{+}_{eq}-p^{-}_{eq})\Delta\Theta^{+}$$

$$+ (p^{s}_{eq} - \rho^{s}_{eq}(\phi-\phi_{s}))\Delta\delta^{s}]$$

$$= \int \mathrm{d}\xi_{2,eq}\,\mathrm{d}\xi_{3,eq}\Big[\frac{1}{2}h_{2,eq}h_{3,eq}p^{s}_{eq}|\Delta \boldsymbol{n}|^{2} + \left(1-\frac{1}{2}\frac{\partial}{\partial\xi_{1,eq}}\Delta\xi_{1}\right)\Delta\xi_{1}h_{1,eq}h_{2,eq}h_{3,eq}$$

$$\times\left(p^{+}_{eq}-p^{-}_{eq}+p^{s}_{eq}C+\rho^{s}_{eq}h^{-1}_{1,eq}\frac{\partial}{\partial\xi_{1,eq}}\phi-\rho^{s}_{eq}C(\phi-\phi_{s})\right)\Big]_{s}. \tag{3.26}$$

Here C is the curvature of a ξ_1 is constant surface$^{17)}$ in equilibrium

$$C = -\left[h_{1}^{-1}\frac{\partial}{\partial\xi_{1}}\ln(h_{2}h_{3})\right]_{eq} = -\nabla\cdot\boldsymbol{n}_{eq}. \tag{3.27}$$

Using the capillarity condition

$$\left[p^{+}_{eq}-p^{-}_{eq}+p^{s}_{eq}C+\rho^{s}_{eq}h^{-1}_{1,eq}\frac{\partial}{\partial\xi_{1,eq}}\phi\right]_{s} = 0, \tag{3.28}$$

which follows from eq. (2.9) (cf. ref. 2 for the $\phi = 0$ case), eq. (2.26), eq. (3.18) and $\phi = -gz$ one obtains from eq. (3.26)

$$\int \mathrm{d}\boldsymbol{r}\left[\sum_{\nu} p^{\nu}_{eq}\Delta\Theta^{\nu} - \rho^{s}_{eq}(\phi-\phi_{s})\Delta\Theta^{s}\right]$$

$$= \frac{1}{2}\int \mathrm{d}S\{p^{s}_{eq}|\Delta \boldsymbol{n}|^{2} - d^{2}[g(n_{z}\rho_{-} - (\boldsymbol{n}\cdot\nabla a_{1,z} - Cn_{z})_{s}\rho^{s})_{eq} + p^{s}_{eq}R_{c}^{-2}]\}, \tag{3.29}$$

where the unit vectors in the direction of increasing ξ_i are defined by

$$\boldsymbol{a}_{i} \equiv h_{i}\nabla\xi_{i}, \quad \text{with } \boldsymbol{a}_{i}\cdot\boldsymbol{a}_{j} = \delta_{ij}. \tag{3.30}$$

Note the fact that

$$n(\xi_2, \xi_3) = a_1(0, \xi_2, \xi_3). \tag{3.31}$$

Furthermore R_c is defined in terms of the normal derivative of the curvature of the $\xi_{1,\mathrm{eq}}$ is constant surfaces by

$$R_c^{-2} \equiv \left(h_{1,\mathrm{eq}}^{-1} \frac{\partial}{\partial \xi_{1,\mathrm{eq}}} C\right)_s = n_{\mathrm{eq}} \cdot (\nabla C)_s. \tag{3.32}$$

R_c is of the same order of magnitude as the radii of curvature (equal to $R/\sqrt{2}$ for a sphere for instance). The integration on the right-hand side of the equation is over the equilibrium dividing surface,

$$\mathrm{d}S \equiv \mathrm{d}\xi_{2,\mathrm{eq}}\, \mathrm{d}\xi_{3,\mathrm{eq}} h_{2,\mathrm{eq}} h_{3,\mathrm{eq}}. \tag{3.33}$$

Substituting eq. (3.29) into eq. (3.14) and introducing the surface tension $\sigma \equiv -p^s$, one obtains the following expression for the variation of the entropy around equilibrium

$$\begin{aligned}\Delta S = &-\frac{1}{2} T_{\mathrm{eq}}^{-1} \int_{\xi_{1,\mathrm{eq}}<0} \mathrm{d}\boldsymbol{r}[(c_{\mathrm{v}}^{-}/T_{\mathrm{eq}})(\Delta T^{-})^2 + (\rho_{\mathrm{eq}}^{-})^{-2}(\kappa_T^{-})^{-1}(\Delta\rho^{-})^2 + \rho_{\mathrm{eq}}^{-}|\boldsymbol{v}^{-}|^2]\\ &-\frac{1}{2} T_{\mathrm{eq}}^{-1} \int_{\xi_{1,\mathrm{eq}}>0} \mathrm{d}\boldsymbol{r}[(c_{\mathrm{v}}^{+}/T_{\mathrm{eq}})(\Delta T^{+})^2 + (\rho_{\mathrm{eq}}^{+})^{-2}(\kappa_T^{+})^{-1}(\Delta\rho^{+})^2 + \rho_{\mathrm{eq}}^{+}|\boldsymbol{v}^{+}|^2]\\ &-\frac{1}{2} T_{\mathrm{eq}}^{-1} \int \mathrm{d}S\{(c_{\mathrm{v}}^{s}/T_{\mathrm{eq}})(\Delta T^{s})^2 + (\rho_{\mathrm{eq}}^{s})^{-2}(\kappa_T^{s})^{-1}(\Delta\rho^{s}) + \rho_{\mathrm{eq}}^{s}|\boldsymbol{v}^{s}|^2\\ &+ \sigma_{\mathrm{eq}}(|\Delta \boldsymbol{n}|^2 - d^2/R_c^2) + g[n_z\rho_{-} - (\boldsymbol{n} \cdot \nabla a_{1,z} - Cn_z)_s\rho^s]_{\mathrm{eq}} d^2\}.\end{aligned} \tag{3.34}$$

The first two integrals in this expression contain the contributions of respectively the minus and the plus phases which have their usual form. The last integral is an integral over the equilibrium dividing surface and gives the contribution due to fluctuations of the interface. This contribution contains terms due to the fluctuations of the interfacial temperature, density and velocity, which are similar to those in the bulk, as well as terms due to fluctuations in the position of the interface. The last terms are the ones commonly used in the context of the capillary-wave model for the study of fluctuations around a planar equilibirum dividing surface (see e.g. ref. 10). As is clear one finds additional contributions proportional to d^2 if the equilibrium interface is not planar. One of these terms will clearly be important in the $g \to 0$ limit. See also the end of this section.

The probability of a fluctuation is now given by eq. (3.1), together with eq. (3.18). Using these formulae one may calculate the equilibrium correlation functions of the various quantities. It follows that the equilibrium correlation functions of the temperature, density and velocity fields in the bulk and on the surface are given by

$$\left.\begin{aligned} &\langle \Delta T^{-}(\boldsymbol{r})\Delta T^{-}(\boldsymbol{r}')\rangle = (k_B T_{\mathrm{eq}}^2/c_v^{-})\delta(\boldsymbol{r}-\boldsymbol{r}'),\\ &\langle \Delta\rho^{-}(\boldsymbol{r})\Delta\rho(\boldsymbol{r}')\rangle = k_B T_{\mathrm{eq}}(\rho_{\mathrm{eq}}^{-})^2\kappa_T^{-}\delta(\boldsymbol{r}-\boldsymbol{r}'),\\ &\langle \boldsymbol{v}^{-}(\boldsymbol{r})\boldsymbol{v}^{-}(\boldsymbol{r}')\rangle = (k_B T_{\mathrm{eq}}/\rho_{\mathrm{eq}}^{-})\delta(\boldsymbol{r}-\boldsymbol{r}'),\end{aligned}\right|\quad \text{for the } \xi_{1,\mathrm{eq}} < 0 \text{ phase}$$

$$\left.\begin{aligned} &\langle \Delta T^{s}(\xi_{2,\mathrm{eq}},\xi_{3,\mathrm{eq}})\Delta T^{s}(\xi'_{2,\mathrm{eq}},\xi'_{3,\mathrm{eq}})\rangle\\ &\quad = (k_B T_{\mathrm{eq}}^2/c_v^{s})h_{2,\mathrm{eq}}^{-1}h_{3,\mathrm{eq}}^{-1}\delta(\xi_{2,\mathrm{eq}}-\xi'_{2,\mathrm{eq}})\delta(\xi_{3,\mathrm{eq}}-\xi'_{3,\mathrm{eq}}),\\ &\langle \Delta\rho^{s}(\xi_{2,\mathrm{eq}},\xi_{3,\mathrm{eq}})\Delta\rho^{s}(\xi'_{2},{}_{\mathrm{eq}},\xi'_{3,\mathrm{eq}})\rangle\\ &\quad = k_B T_{\mathrm{eq}}(\rho_{\mathrm{eq}}^{s})^2\kappa_T^{s}h_{2,\mathrm{eq}}^{-1}h_{3,\mathrm{eq}}^{-1}\delta(\xi_{2,\mathrm{eq}}-\xi'_{2},{}_{\mathrm{eq}})\delta(\xi_{3,\mathrm{eq}}-\xi'_{3,\mathrm{eq}}),\\ &\langle \boldsymbol{v}^{s}(\xi_{2,\mathrm{eq}},\xi_{3,\mathrm{eq}})\boldsymbol{v}^{s}(\xi'_{2,\mathrm{eq}},\xi'_{3,\mathrm{eq}})\rangle\\ &\quad = (k_B T_{\mathrm{eq}}/\rho_{\mathrm{eq}}^{s})h_{2,\mathrm{eq}}^{-1}h_{3,\mathrm{eq}}^{-1}\delta(\xi_{2,\mathrm{eq}}-\xi'_{2,\mathrm{eq}})\delta(\xi_{3,\mathrm{eq}}-\xi'_{3,\mathrm{eq}});\end{aligned}\right|\quad \text{for the interface} \qquad (3.35)$$

$$\left.\begin{aligned} &\langle \Delta T^{+}(\boldsymbol{r})\Delta T^{+}(\boldsymbol{r}')\rangle = (k_B T_{\mathrm{eq}}^2/c_v^{+})\delta(\boldsymbol{r}-\boldsymbol{r}'),\\ &\langle \Delta\rho^{+}(\boldsymbol{r})\Delta\rho^{+}(\boldsymbol{r}')\rangle = k_B T_{\mathrm{eq}}(\rho_{\mathrm{eq}}^{+})^2\kappa_T^{+}\delta(\boldsymbol{r}-\boldsymbol{r}'),\\ &\langle \boldsymbol{v}^{+}(\boldsymbol{r})\boldsymbol{v}^{+}(\boldsymbol{r}')\rangle = (k_B T_{\mathrm{eq}}/\rho_{\mathrm{eq}}^{+})\delta(\boldsymbol{r}-\boldsymbol{r}').\end{aligned}\right|\quad \text{for the } \xi_{1,\mathrm{eq}} > 0 \text{ phase}$$

All cross correlations as for instance between the temperature and the density are zero. Also there are no correlations between the two phases and the interface. In the case of the x–y plane being the interface, one has x and y rather than $\xi_{2,\mathrm{eq}}$ and $\xi_{3,\mathrm{eq}}$ while $h_{2,\mathrm{eq}} = h_{3,\mathrm{eq}} = 1$.

Similarly, the equilibrium fluctuations of the position d of the dividing surface are not correlated to the temperature density and velocity fluctuations. The auto-correlation of d in equilibrium is more complicated because of the appearance of the gradient of d in the entropy, cf. eq. (3.34). We shall therefore first discuss the case that the equilibrium dividing surface is the x–y plane. Introducing the two-dimensional Fourier transform

$$d(k_x, k_y) \equiv \int \mathrm{d}x\,\mathrm{d}y\,\mathrm{e}^{-\mathrm{i}k_x x-\mathrm{i}k_y y}d(x, y), \tag{3.36}$$

we may write

$$\int \mathrm{d}x\,\mathrm{d}y[-\rho_{\mathrm{eq},-}gd^2 + \sigma_{\mathrm{eq}}|\nabla d|^2] = -\rho_{\mathrm{eq},-}g(2\pi)^{-2}\int \mathrm{d}k_x\,\mathrm{d}k_y(1 + l^2k^2)d^2, \tag{3.37}$$

where the capillary length is defined by

$$l \equiv \sqrt{\sigma_{\mathrm{eq}}/g\rho_{\mathrm{eq},-}}. \tag{3.38}$$

The equilibrium auto-correlation function of d thus becomes, $k^2 \equiv k_x^2 + k_y^2$,

$$\langle d(k_x, k_y) d(k_x', k_y') \rangle = (k_B T_{\mathrm{eq}} / g\rho_{\mathrm{eq},-})(1 + l^2 k^2)^{-1} \delta(k_x + k_x') \delta(k_y + k_y')(2\pi)^2. \tag{3.39}$$

This is the usual result found in the context of the capillary wave model (see e.g. ref. 16). As a function of the position one finds upon Fourier transformation, $r_\parallel \equiv \sqrt{(x - x')^2 + (y - y')^2}$,

$$\langle d(x, y) d(x', y') \rangle = \frac{k_B T_{\mathrm{eq}}}{2\pi\sigma_{\mathrm{eq}}} K_0(r_\parallel / l), \tag{3.40}$$

where K_0 is a Bessel function of imaginary argument[19]).

For distances small compared to the capillary length one has in good approximation[19])

$$\langle d(x, y) d(x', y') \rangle = \frac{k_B T_{\mathrm{eq}}}{2\sigma_{\mathrm{eq}}} \ln(2l / r_\parallel), \quad \text{for } r_\parallel \ll l, \tag{3.41}$$

while one has for large distances[19])

$$\langle d(x, y) d(x', y') \rangle = \frac{k_B T_{\mathrm{eq}}}{2\sigma_{\mathrm{eq}}} \sqrt{\frac{l}{2\pi r_\parallel}} \exp(-r_\parallel / l), \quad \text{for } r_\parallel \gg l. \tag{3.42}$$

In the limit of zero gravity the capillary length goes to infinity. In that case the auto-correlation function of d as a function of position diverges logarithmically as can easily be seen from eq. (3.41). This is related to the fact that $d(x, y)$, which characterizes the displacement of the dividing surface, is a symmetry breaking collective coordinate. The long-range collective motion (Goldstone mode) of this coordinate are capillary waves or ripples[20]).

We note that in the zero gravity limit and a planar equilibrium dividing surface one can use the normal on the dividing surface $\boldsymbol{n}(x, y)$ as a collective variable rather than the displacement. These two variables are related by

$$\boldsymbol{n}(x, y) \equiv \left(-\frac{\partial d(x, y)}{\partial x}, -\frac{\partial d(x, y)}{\partial y}, 1 \right) \Big/ \sqrt{1 + \left(\frac{\partial d(x, y)}{\partial x} \right)^2 + \left(\frac{\partial d(x, y)}{\partial y} \right)^2}. \tag{3.43}$$

In equilibrium we have $\boldsymbol{n}_{\mathrm{eq}} = (0, 0, 1)$ for the planar case to which we restrict ourselves here. For the more general case we refer to the appendix. To linear order the variation of $\boldsymbol{n}$ around the equilibrium value is given by

$$\Delta\boldsymbol{n}(x, y) \equiv \boldsymbol{n}(x, y) - \boldsymbol{n}_{\mathrm{eq}} = -\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, 0 \right) d(x, y) = -\nabla d(x, y). \tag{3.44}$$

The contribution to ΔS, cf. eq. (3.34), due to the displacement of the dividing surface, may thus be written, if the equilibrium interface is planar, as

$$-\frac{\sigma_{eq}}{2T_{eq}}\int dx\, dy|\Delta \boldsymbol{n}|^2 = -\frac{\sigma_{eq}}{2T_{eq}}\int dx\, dy(\Delta n_x^2 + \Delta n_y^2) \tag{3.45}$$

if $g = 0$. The equilibrium auto-correlation function of $\boldsymbol{n}$ then becomes

$$\begin{aligned}\langle \Delta n_x(x, y)\Delta n_x(x', y')\rangle &= \langle \Delta n_y(x, y)\Delta n_y(x', y')\rangle \\ &= (2k_B T_{eq}/\sigma_{eq})\delta(x - x')\delta(y - y'),\end{aligned} \tag{3.46}$$

while $\langle \Delta n_x \Delta n_y\rangle = 0$. This expression is perfectly well defined whereas the limit of eq. (3.40) for the auto-correlation function of d does not exist in the $g = 0$ limit.*

In the more general case of a curved equilibrium interface the above analysis of the auto-correlation function for $d(x, y)$ may in principle be extended using eq. (3.34) for ΔS. The additional terms containing $(\boldsymbol{n} \cdot \nabla a_{1,2} - Cn_z)$ and R_c complicate the analysis. This in particular because they will usually depend on the position along the interface. In general one may say that, if the radii of curvature are large compared to l, or more precisely $R_c \gg l$, the term containing R_c is unimportant. In the zero gravity limit, however, this term becomes important. For instance, a translation of a spherical droplet corresponds to $|\Delta \boldsymbol{n}|^2 - d^2/R_c^2 = 0$ and therefore the entropy remains the same in the $g = 0$ case. The behaviour of the auto-correlation function of d becomes interesting in particular when the radius of the droplet is of the same order of magnitude as the capillary length. Eq. (3.34) for S *seems* to suggest that the system is unstable for a parallel (i.e. $\nabla d = 0$) displacement of the interface. It should be emphasized that such a displacement is only possible in a finite and closed system if also ΔT and $\Delta \rho$ are finite and well in such a way that the total energy and mass are conserved. The sum of all these terms in fact determines the equilibrium shape of the droplet and the constant d displacement around this equilibrium will decrease the entropy.

Finally we note that in the interfacial region the density changes over a few molecular diameters from the liquid to the vapor density. For any choice of the dividing surface in this region the excess mass will therefore be small. For Gibb's definition of the dividing surface $\rho^s = \Delta\rho^s = \rho^s_{eq} = 0$. One may, however, argue that also for other choices, as e.g. for the surface of tension, ρ^s is sufficiently small to be neglected. If ρ^s is neglected, the contributions to ΔS in eq. (3.34) proportional to $(\Delta\rho^s)^2$ and $|\boldsymbol{v}^s|^2$ disappear. Similarly, one finds no

---

* If one would describe the fluctuations of a bulk fluid using Lagrange coordinates rather than the more usual Euler variables, one encounters similar problems. The equilibrium auto-correlation functions for the Lagrange coordinates do not exist, while those for the Euler variables do exist.

equilibrium auto-correlation functions for ρ^s and v^s. The term proportional to $(\boldsymbol{n} \cdot \nabla a_{1,z} - C n_z)$ also disappears and will in fact generally not be very important for a liquid vapour interface.

4. The Landau–Lifshitz equations

In order to calculate the (unequal) time correlation functions one must extend the equations of motion for the two phase system by the addition of random "currents". Following Landau–Lifshitz[21]) one writes the fluxes in the bulk media as the sum of the usual "systematic" part and a random contribution:

$$\boldsymbol{\Pi}^{\pm} = -2\eta^{\pm}\overline{\nabla \boldsymbol{v}}^{\pm} - \eta_{v}^{\pm}\nabla \cdot \boldsymbol{v}^{\pm} + \boldsymbol{\Pi}_{\mathrm{R}}^{\pm} = \boldsymbol{\Pi}_{\mathrm{S}}^{\pm} + \boldsymbol{\Pi}_{\mathrm{R}}^{\pm}, \tag{4.1}$$

$$\boldsymbol{J}_{q}^{\pm} = -\lambda^{\pm}\nabla T^{\pm} + \boldsymbol{J}_{q,\mathrm{R}}^{\pm} = \boldsymbol{J}_{q,\mathrm{S}}^{\pm} + \boldsymbol{J}_{q,\mathrm{R}}^{\pm}. \tag{4.2}$$

Substituting these equations in the conservation laws for momentum and energy one obtains the so-called Landau–Lifshitz equations for the fluctuating bulk fields. The random currents are Gaussian and white. Their averages are zero

$$\langle \boldsymbol{\Pi}_{\mathrm{R}}^{\pm} \rangle = 0 \quad \text{and} \quad \langle \boldsymbol{J}_{q,\mathrm{R}}^{\pm} \rangle = 0. \tag{4.3}$$

The fluctuation–dissipation theorem for the random currents is

$$\begin{aligned} \langle \Pi_{\mathrm{R},\alpha\beta}^{\pm}(\boldsymbol{r},t)\Pi_{\mathrm{R},\gamma\delta}^{\pm}(\boldsymbol{r}',t')\rangle &= 2k_{\mathrm{B}}T_{\mathrm{eq}}[\eta^{\pm}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}) \\ &\quad + \eta_{v}^{\pm}\delta_{\alpha\beta}\delta_{\gamma\delta}]\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t'), \\ \langle J_{q,\mathrm{R},\alpha}^{\pm}(\boldsymbol{r},t)J_{q,\mathrm{R},\beta}^{\pm}(\boldsymbol{r}',t')\rangle &= 2k_{\mathrm{B}}T_{\mathrm{eq}}^{2}\lambda^{\pm}\delta_{\alpha\beta}\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t') \\ &\quad \text{with } \boldsymbol{r} \text{ and } \boldsymbol{r}' \text{ in the } \pm \text{ region} \\ &\quad \text{and not on the dividing surface.} \end{aligned} \tag{4.4}$$

All other correlation functions of the bulk random currents in the bulk regions are zero. In particular there are no correlations of the random currents in the + region with those in the − region if $\boldsymbol{r}$ and $\boldsymbol{r}'$ are not on the dividing surface. On the dividing surface such correlations do exist as will become clear below.

Analogous to eqs. (4.1) and (4.2) we write the fluxes along, into and through the interface as a sum of a systematic and a random contribution:

$$\overline{\boldsymbol{\Pi}}^{s} = \overline{\boldsymbol{\Pi}}_{\mathrm{S}}^{s} + \overline{\boldsymbol{\Pi}}_{\mathrm{R}}^{s} \tag{4.5}$$

for the tensorial flux,

$$
\begin{aligned}
\boldsymbol{J}^{s}_{q} &= \boldsymbol{J}^{s}_{q,S} && + \boldsymbol{J}^{s}_{q,R},\\
[(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\parallel}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})(\boldsymbol{v}_{\parallel}-\boldsymbol{v}^{s}_{\parallel})]_{+} &= [(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\parallel}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})(\boldsymbol{v}_{\parallel}=\boldsymbol{v}^{s}_{\parallel})]_{+,S} \\
& && + (\boldsymbol{n}\cdot\boldsymbol{\Pi}_{R})_{\parallel+},\\
[(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\parallel}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})(\boldsymbol{v}_{\parallel}-\boldsymbol{v}^{s}_{\parallel})]_{-} &= [(\boldsymbol{n}\cdot\boldsymbol{\Pi})_{\parallel}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})(\boldsymbol{v}_{\parallel}-\boldsymbol{v}^{s}_{\parallel})]_{-,S} \\
& && + (\boldsymbol{n}\cdot\boldsymbol{\Pi}_{R})_{\parallel-},
\end{aligned}
\tag{4.6}
$$

for the vectorial fluxes and

$$
\begin{aligned}
\Pi^{s} &= \Pi^{s}_{S} && + \Pi^{s}_{R},\\
[J_{q,n}+T\rho s(v_{n}-v^{s}_{n})]_{-} &= [J_{q,n}+T\rho s(v_{n}-v^{s}_{n})]_{-,S} && + J_{q,R,n-},\\
[J_{q,n}+T\rho s(v_{n}-v^{s}_{n})]_{+} &= [J_{q,n}+T\rho s(v_{n}-v^{s}_{n})]_{+,S} && + J_{q,R,n+},\\
[\Pi_{nn}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})^{2}+\rho(\mu-\mu^{s})]_{-} &= [\Pi_{nn}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})^{2}+\rho(\mu-\mu^{s})]_{-,S} \\
& && + \Pi_{R,nn-},\\
[\Pi_{nn}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})^{2}+\rho(\mu-\mu^{s})]_{+} &= [\Pi_{nn}+\tfrac{1}{2}\rho(v_{n}-v^{s}_{n})^{2}+\rho(\mu-\mu^{s})]_{+,S} \\
& && + \Pi_{R,nn+},
\end{aligned}
\tag{4.7}
$$

for the scalar fluxes. The systematic parts of these fluxes are given by the usual linear constitutive equations, eqs. (2.22)–(2.24). The averages of the interfacial random fluxes are again zero

$$
\begin{aligned}
&\langle \boldsymbol{\Pi}^{s}_{R}\rangle = 0, \quad \langle \boldsymbol{J}^{s}_{q,R}\rangle = \langle(\boldsymbol{n}\cdot\boldsymbol{\Pi}_{R})_{\parallel+}\rangle = \langle(\boldsymbol{n}\cdot\boldsymbol{\Pi}_{R})_{\parallel-}\rangle = 0,\\
&\langle J_{q,R,n-}\rangle = \langle J_{q,R,n+}\rangle = \langle \Pi_{R,nn-}\rangle = \langle \Pi_{R,nn+}\rangle = 0.
\end{aligned}
\tag{4.8}
$$

The fluctuation–dissipation theorem for the random currents, which for the sake of simplicity will first be given for the special case that the equilibrium dividing surface is the x–y plane, is

$$
\begin{aligned}
\langle \Pi^{S}_{R,\alpha\beta}(x,y,t)\Pi^{s}_{R,\gamma\delta}(x',y',t')\rangle = 2k_{B}T_{eq}[\eta^{s}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}-\delta_{\alpha\beta}\delta_{\gamma\delta})\\
+\eta^{s}_{s}\delta_{\alpha\beta}\delta_{\gamma\delta}]\delta(x-x')\delta(y-y')\delta(t-t'),\\
\text{where } \alpha,\ \beta,\ \gamma \text{ and } \delta \text{ are either } x \text{ or } y;
\end{aligned}
\tag{4.9}
$$

$$
\begin{aligned}
&\langle J^{s}_{q,R,\alpha}(x,y,t)J^{s}_{q,R,\beta}(x',y',t')\rangle = 2k_{B}T^{2}_{eq}\lambda^{s}\delta_{\alpha\beta}\delta(x-x')\delta(y-y')\delta(t-t'),\\
&\langle \Pi_{R,n\alpha,\nu}(x,y,t)\Pi_{R,n\beta,\nu'}(x',y',t')\rangle = 2k_{B}T_{eq}\alpha_{\nu\nu'}\delta_{\alpha\beta}\delta(x-x')\delta(y-y')\delta(t-t'),\\
&\qquad \text{where } \alpha,\beta \text{ are either } x \text{ or } y \text{ and where}\\
&\qquad \nu,\nu' \text{ are either } + \text{ or } -. \text{ Furthermore}
\end{aligned}
\tag{4.10}
$$

$\alpha_{++}\equiv\beta,\quad \alpha_{+-}=\alpha_{-+}\equiv\alpha_{23}=\alpha_{32}\quad$ and $\quad\alpha_{--}\equiv\alpha_{33};$

$$
\begin{aligned}
&\langle J_{q,\mathrm{R},n,\nu}(x,y,t)J_{q,\mathrm{R},n,\nu'}(x',y',t')\rangle = 2k_{\mathrm{B}}T_{\mathrm{eq}}^{2}L^{q}_{\nu\nu'}\,\delta(x-x')\delta(y-y')\delta(t-t'),\\
&\langle \Pi_{\mathrm{R,nn},\nu}(x,y,t)\Pi_{\mathrm{R,nn},\nu'}(x',y',t')\rangle = 2k_{\mathrm{B}}T_{\mathrm{eq}}L_{\nu\nu'}\,\delta(x-x')\delta(y-y')\delta(t-t'),\\
&\langle \Pi^{\mathrm{s}}_{\mathrm{R}}(x,y,t)\Pi^{\mathrm{s}}_{\mathrm{R,nn},\nu}(x',y',t)\rangle = 2k_{\mathrm{B}}T_{\mathrm{eq}}L_{1\nu}\,\delta(x-x')\delta(y-y')\delta(t-t'),
\end{aligned}
$$

where ν, ν' are either + or −. Furthermore (4.11)

$$
\begin{aligned}
&L^{q}_{--} = L_{22},\ L^{q}_{+-} = L^{q}_{-+} = L_{23} = L_{32} \quad \text{and} \quad L^{q}_{++} = L_{33},\\
&L_{--} = L_{44},\quad L_{+-} = L_{-+} = L_{45} = L_{54} \quad \text{and} \quad L_{++} = L_{55},\\
&L_{1-} = L_{14} = L_{41} \quad \text{and} \quad L_{1+} = L_{15} = L_{51}.
\end{aligned}
$$

All other correlation functions of random fluxes at the interface are zero. In writing the prefactors of the δ functions in the above equations we follow Landau and Lifshitz[21]) for the present case, using the explicit expression for the entropy production eq. (2.18).

In the more general case that the equilibrium interface is not planar, the above fluctuation–dissipation theorems should be given, using the equilibrium curvilinear coordinates $\xi_{2,\mathrm{eq}}$ and $\xi_{3,\mathrm{eq}}$ rather than x and y. Furthermore, the right-hand side should be divided by $h_{2,\mathrm{eq}}h_{3,\mathrm{eq}}$ (compare with eq. (3.33) for the equal-time equilibrium correlation functions in the non-planar case).

The general equations describing the fluctuations of ρ^{s}, $\boldsymbol{v}^{\mathrm{s}}$ and u^{s} are found by substitution of eqs. (4.5)–(4.7) into eqs. (2.6), (2.9) and (2.14), while using eqs. (2.22)–(2.24) for the systematic parts of the fluxes together with the properties given in this section for the random parts. The various properties of the time dependent correlation functions may in this way be analysed. This may in particular also be done for the autocorrelation function of the location of (or the normal on) the dividing surface. The analysis will obviously only be possible in a closed form in the fully linearised case.

Appendix A

One has

$$
\Delta\delta(\xi_1) = \delta(\xi_1) - \delta(\xi_{1,\mathrm{eq}}) = \Delta\xi_1\left(1 + \frac{1}{2}\,\Delta\xi_1\,\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\right)\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\,\delta(\xi_{1,\mathrm{eq}}). \tag{A.1}
$$

Furthermore

$$
\begin{aligned}
\Delta|\mathrm{grad}\ \xi_1| &= [|\boldsymbol{\nabla}\xi_{1,\mathrm{eq}}|^2 + 2((\boldsymbol{\nabla}\xi_{1,\mathrm{eq}})\cdot(\boldsymbol{\nabla}\Delta\xi_1)) + |\boldsymbol{\nabla}\Delta\xi_1|^2]^{1/2} - |\boldsymbol{\nabla}\xi_{1,\mathrm{eq}}|\\
&= |\boldsymbol{\nabla}\xi_{1,\mathrm{eq}}|^{-1}\left\{(\boldsymbol{\nabla}\xi_{1,\mathrm{eq}})\cdot(\boldsymbol{\nabla}\Delta\xi_1) + \tfrac{1}{2}(\boldsymbol{\nabla}\Delta\xi_1)\cdot\left[1 - \frac{(\boldsymbol{\nabla}\xi_{1,\mathrm{eq}})(\boldsymbol{\nabla}\xi_{1,\mathrm{eq}})}{|\boldsymbol{\nabla}\xi_{1,\mathrm{eq}}|^2}\right](\boldsymbol{\nabla}\Delta\xi_1)\right\}\\
&= \boldsymbol{a}_{1,\mathrm{eq}}\cdot\boldsymbol{\nabla}\Delta\xi_1 + \tfrac{1}{2}h_{1,\mathrm{eq}}(\boldsymbol{\nabla}\Delta\xi_1)\cdot(1 - \boldsymbol{a}_{1,\mathrm{eq}}\boldsymbol{a}_{1,\mathrm{eq}})\cdot(\boldsymbol{\nabla}\Delta\xi_1).
\end{aligned} \tag{A.2}
$$

Combining eqs. (A.1) and (A.2) one finds for the fluctuation of the surface δ function

$$\begin{aligned}\Delta\delta^{s} &= \Delta(|\nabla\xi_1|\delta(\xi_1))\\ &= \Big[\boldsymbol{a}_{1,\mathrm{eq}}\cdot(\nabla\Delta\xi_1)+\tfrac{1}{2}\boldsymbol{h}_{1,\mathrm{eq}}(\nabla\Delta\xi_1)\cdot(\mathbf{1}-\boldsymbol{a}_{1,\mathrm{eq}}\boldsymbol{a}_{1,\mathrm{eq}})\cdot(\nabla\Delta\xi_1)\\ &\quad+(\boldsymbol{a}_{1,\mathrm{eq}}\cdot\nabla\Delta\xi_1)\Delta\xi_1\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}+h^{-1}_{1,\mathrm{eq}}\Delta\xi_1\Big(1+\tfrac{1}{2}\Delta\xi_1\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\Big)\frac{\partial}{\partial\xi_{1,\mathrm{eq}}}\Big]\delta(\xi_{1,\mathrm{eq}}).\end{aligned}\tag{A.3}$$

For the variation of $\boldsymbol{a}_1$ to linear order we write

$$\begin{aligned}\Delta\boldsymbol{a}_1 &= (\nabla\xi_1/|\nabla\xi_1|)-(\nabla\xi_{1,\mathrm{eq}}/|\nabla\xi_{1,\mathrm{eq}}|)\\ &= (\nabla\Delta\xi_1)/|\nabla\xi_{1,\mathrm{eq}}|)-|\nabla\xi_{1,\mathrm{eq}}|^{-3}(\nabla\xi_{1,\mathrm{eq}})\nabla\xi_{1,\mathrm{eq}}\cdot\nabla\Delta\xi_1\\ &= \boldsymbol{h}_{1,\mathrm{eq}}(\mathbf{1}-\boldsymbol{a}_{1,\mathrm{eq}}\boldsymbol{a}_{1,\mathrm{eq}})\cdot(\nabla\Delta\xi_1),\end{aligned}\tag{A.4}$$

where we used eq. (3.30). On the dividing surface this gives

$$\Delta\boldsymbol{n} = \boldsymbol{h}_{1,\mathrm{eq},s}(\mathbf{1}-\boldsymbol{n}_{\mathrm{eq}}\boldsymbol{n}_{\mathrm{eq}})\cdot(\nabla\Delta\xi_1)_s = -\nabla d - d(\boldsymbol{n}_{\mathrm{eq}}\cdot\nabla\boldsymbol{a}_{1,\mathrm{eq}})_s \tag{A.5}$$

for the variation of the normal. Eq. (A.3) together with eq. (A.5) then yields eq. (3.23).

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ELECTRIC AND MAGNETIC SUSCEPTIBILITIES FOR A FLUID–FLUID INTERFACE; THE ELLIPSOMETRIC COEFFICIENT

1. Introduction

The properties of a fluid–fluid interface may be investigated using light. In particular ellipsometry is sensitive to the properties of the interfacial region. In ellipsometry one studies the difference between the reflected amplitudes and the Fresnel amplitudes. The Fresnel amplitudes are found if one uses a step discontinuity in the dielectric constant at the dividing surface. Contamination of the liquid surface is one source of such differences. In this paper we will consider fluid interfaces which are not contaminated. In this case the difference with the Fresnel amplitudes is caused by thermal fluctuations of the interface around the equilibrium position. Vice versa one may use ellipsometry to study these fluctuations.

Recently such measurements were done by Beaglehole[1]* on the surface of liquid argon, which is a simple liquid, as well as on the surface of carbon tetrachloride, which may be expected to behave like a simple liquid. In both cases the surfaces were practically not contaminated.

It is the aim of this paper to calculate the ellipsometric coefficient for a non-contaminated fluid–fluid interface in terms of the interfacial position autocorrelation function. The equilibrium position of the dividing surface is assumed to be flat and the x–y plane is chosen along this surface. In our analysis we find that the equilibrium averages of the interfacial excess polarization and magnetization, $\boldsymbol{P}^s$ and $\boldsymbol{M}^s$ respectively, are unequal to zero. They are found to be given in terms of the electro-magnetic fields on both

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*For references to earlier ellipsometric measurements of liquid surfaces see ref. 1.

sides of the dividing surface by

$$\boldsymbol{P}^s(x, y, t) = \tfrac{1}{2}\begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \beta \end{pmatrix} \cdot [(E_x^-, E_y^-, D_z^-)(x, y, 0, t) + (E_x^+, E_y^+, D_z^+)(x, y, 0, t)]$$

$$- (\tau/2c)\hat{z} \wedge \frac{\partial}{\partial t}[\boldsymbol{H}^-(x, y, 0, t) + \boldsymbol{H}^+(x, y, 0, t)],$$

$$\boldsymbol{M}^s(x, y, t) = -(\tau/2c)\hat{z} \wedge \frac{\partial}{\partial t}[\boldsymbol{E}^-(x, y, 0, t) + \boldsymbol{E}^+(x, y, 0, t)]. \tag{1.1}$$

The coefficients γ and β can be interpreted as the dielectric parallel and orthogonal susceptibilities of the interface[2]). τ is a constitutive coefficient which couples $\boldsymbol{P}^s$ and $\boldsymbol{M}^s$ to the time derivatives of $\boldsymbol{H}$ and $\boldsymbol{E}$, respectively. This effect is also important in the study of rough solid surfaces[3]). The normal on the equilibrium dividing surface is given by $\hat{z} = (0, 0, 1)$. The super indices $+$ and $-$ indicate the corresponding fields in respectively the $z > 0$ and the $z < 0$ regions. Finally $\boldsymbol{E}$ and $\boldsymbol{B}$ are the electric and magnetic fields while $\boldsymbol{D}$ and $\boldsymbol{H}$ are the displacement fields; c is the velocity of light.

In sections 3 through 5 we derive formulae for the constitutive coefficients γ, β and τ in terms of the interfacial position autocorrelation function. The following explicit expressions are found

$$\gamma = -\tfrac{1}{2}\epsilon^-\epsilon^+\beta = -\left(\frac{k_B T}{\sigma}\right)\frac{(\epsilon^+ - \epsilon^-)^2}{(\epsilon^+ + \epsilon^-)}\frac{k_m}{4\pi},$$

$$\tau = \left(\frac{k_B T}{\sigma}\right)(\epsilon^+ - \epsilon^-)(4\pi)^{-1}\ln(lk_m), \tag{1.2}$$

where ϵ^+ and ϵ^- are the dielectric constants in the two bulk fluids in the $z > 0$ and $z < 0$ regions, k_B is Boltzmann's constant, T the temperature and σ the surface tension. The capillary length is given by $l = \sqrt{\sigma/g|\rho^+ - \rho^-|}$ where g is the gravitational acceleration and ρ^+ and ρ^- are the densities of the two fluids. The maximum wavevector k_m is a cut-off at molecular wavevectors and is of the order of 2π divided by the molecular diameter. Beaglehole[1]) used similar expressions for γ and β in his analysis.

In the next section we first discuss how the amplitudes and consequently the ellipsometric coefficient is affected by the constitutive coefficients γ, β and τ. A comparison with the experimental results is made in the discussion.

2. The coefficient of ellipsometry

In this section we shall express the coefficient of ellipsometry in terms of the interfacial susceptibilities γ, β and τ. In ref. 2 we showed, using Maxwell's equations, that the discontinuities of the electromagnetic fields at the interface, $z = 0$, are given in terms of the interfacial polarization and magnetization densities by*

$$\begin{aligned}
E^{+}_{x}(\boldsymbol{r}_{\|}, 0, t) - E^{-}_{x}(\boldsymbol{r}_{\|}, 0, t) &= -\frac{1}{c}\frac{\partial}{\partial t} M^{s}_{y}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial x} P^{s}_{z}(\boldsymbol{r}_{\|}, t), \\
E^{+}_{y}(\boldsymbol{r}_{\|}, 0, t) - E^{-}_{y}(\boldsymbol{r}_{\|}, 0, t) &= \frac{1}{c}\frac{\partial}{\partial t} M^{s}_{x}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial y} P^{s}_{z}(\boldsymbol{r}_{\|}, t), \\
D^{+}_{z}(\boldsymbol{r}_{\|}, 0, t) - D^{-}_{z}(\boldsymbol{r}_{\|}, 0, t) &= -\frac{\partial}{\partial x} P^{s}_{x}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial y} P^{s}_{y}(\boldsymbol{r}_{\|}, t), \\
H^{+}_{x}(\boldsymbol{r}_{\|}, 0, t) - H^{-}_{x}(\boldsymbol{r}_{\|}, 0, t) &= \frac{1}{c}\frac{\partial}{\partial t} P^{s}_{y}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial x} M^{s}_{z}(\boldsymbol{r}_{\|}, t), \\
H^{+}_{y}(\boldsymbol{r}_{\|}, 0, t) - H^{-}_{y}(\boldsymbol{r}_{\|}, 0, t) &= -\frac{1}{c}\frac{\partial}{\partial t} P^{s}_{x}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial y} M^{s}_{z}(\boldsymbol{r}_{\|}, t), \\
B^{+}_{z}(\boldsymbol{r}_{\|}, 0, t) - B^{-}_{z}(\boldsymbol{r}_{\|}, 0, t) &= -\frac{\partial}{\partial x} M^{s}_{x}(\boldsymbol{r}_{\|}, t) - \frac{\partial}{\partial y} M^{s}_{y}(\boldsymbol{r}_{\|}, t).
\end{aligned} \tag{2.1}$$

$\boldsymbol{P}^{s}$ and $\boldsymbol{M}^{s}$ are given in terms of the value of the fields at the interface by the constitutive equations (1.1). In the gas and liquid regions, $z \neq 0$, one has $\boldsymbol{D}^{-} = \epsilon^{-}\boldsymbol{E}^{-}$, $\boldsymbol{D}^{+} = \epsilon^{+}\boldsymbol{E}^{+}$ and $\boldsymbol{H} = \boldsymbol{B}$.

We shall first consider the case where the polarization of the incident beam is normal to the plane of incidence, which is chosen to be the x–z plane. The incident field is given by

$$\begin{aligned}
&\boldsymbol{E}_{i}(\boldsymbol{r}, t) = (0, 1, 0) e^{i\boldsymbol{k}_{i}\cdot\boldsymbol{r} - i\omega t}, \\
&\boldsymbol{B}_{i}(\boldsymbol{r}, t) = n^{-}(-\cos\theta_{i}, 0, \sin\theta_{i})\, e^{i\boldsymbol{k}_{i}\cdot\boldsymbol{r} - i\omega t}, \quad \text{for } z < 0,
\end{aligned} \tag{2.2}$$

where $n^{-} = \sqrt{\epsilon^{-}}$ is the refractive index, ω the frequency, $\boldsymbol{k}_{i} = (n^{-}\omega/c)(\sin\theta_{i}, 0, \cos\theta_{i})$ the wavevector of the incident light and θ_{i} the angle of incidence. The amplitude has been set equal to unity, which obviously does not affect the value of the coefficient of ellipsometry. The reflected field is given by

$$\begin{aligned}
&\boldsymbol{E}_{r}(\boldsymbol{r}, t) = r_{s}(0, 1, 0)\, e^{i\boldsymbol{k}_{r}\cdot\boldsymbol{r} - i\omega t}, \\
&\boldsymbol{B}_{r}(\boldsymbol{r}, t) = n^{-} r_{s}(\cos\theta_{r}, 0, \sin\theta_{r})\, e^{i\boldsymbol{k}_{r}\cdot\boldsymbol{r} - i\omega t}, \quad \text{for } z > 0,
\end{aligned} \tag{2.3}$$

where $\boldsymbol{k}_{r} = (n^{-}\omega/c)(\sin\theta_{r}, 0, -\cos\theta_{r})$ is the wavevector and θ_{r} the angle of reflection. The transmitted field is given by

$$\begin{aligned}
&\boldsymbol{E}_{t}(\boldsymbol{r}, t) = t_{s}(0, 1, 0)\, e^{i\boldsymbol{k}_{t}\cdot\boldsymbol{r} - i\omega t}, \\
&\boldsymbol{B}_{t}(\boldsymbol{r}, t) = n^{+} t_{s}(-\cos\theta_{t}, 0, \sin\theta_{t})\, e^{i\boldsymbol{k}_{t}\cdot\boldsymbol{r} - i\omega t} \quad \text{for } z > 0,
\end{aligned} \tag{2.4}$$

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*Note that the surface polarization and magnetization densities are related to the singularities in the fields by $\boldsymbol{P}^{s} = (D^{s}_{x}, D^{s}_{y}, -E^{s}_{z})$ and $\boldsymbol{M}^{s} = (B^{s}_{x}, B^{s}_{y}, -H^{s}_{z})$ which is a consequence of eq. (2.5) in ref. 2.

where $n^+ = \sqrt{\epsilon^+}$, $k_t = (n^+\omega/c)(\sin\theta_t, 0, \cos\theta_t)$ and θ_t the angle of transmission.

Upon substitution of eqs. (2.2)–(2.4) into the constitutive equations (1.1), one obtains the surface polarisation and magnetisation densities. These may then be substituted into eq. (2.1) for the discontinuities of the fields at the interface. Using again eqs. (2.2)–(2.4), one then obtains a set of two independent equations to determine r_s, t_s, θ_r and θ_t. It then follows that θ_r and θ_t are given as usual by Snell's law

$$\theta_r = \theta_i \equiv \theta \quad \text{and} \quad n^+ \sin\theta_t = n^- \sin\theta_i, \tag{2.5}$$

and are consequently not affected by β, γ and τ. Furthermore, one finds for r_s and t_s up to linear order in β, γ and τ

$$\begin{aligned} r_s &= r_s^0 + (\omega/c)^2\tau(1-(r_s^0)^2) + \tfrac{1}{2}\mathrm{i}\,\gamma(\omega/cn^- \cos\theta)(t_s^0)^2, \\ t_s &= t_s^0 - (\omega/c)^2\tau r_s^0 t_s^0 + \tfrac{1}{2}\mathrm{i}\,\gamma(\omega/cn^- \cos\theta)(t_s^0)^2. \end{aligned} \tag{2.6}$$

Here r_s^0 and t_s^0 are given by the Fresnel formulae for the amplitudes if γ and τ are zero.

$$\begin{aligned} r_s^0 &= (n^-\cos\theta - n^+\cos\theta_t)(n^-\cos\theta + n^+\cos\theta_t)^{-1}, \\ t_s^0 &= 2n^-\cos\theta(n^-\cos\theta + n^+\cos\theta_t)^{-1} = r_s^0 + 1. \end{aligned} \tag{2.7}$$

As will be discussed in more detail in the next section, β, γ and τ are, for the system under consideration, small compared to the wavelength of the incident light. Consequently it is sufficient to consider only linear contributions to eq. (2.6).

If the polarisation of the incident light is parallel to the plane of incidence, one finds by a similar analysis that Snell's law is again valid while r_p and t_p are given by

$$\begin{aligned} r_p &= r_p^0 - (\omega/c)^2\tau(1-(r_p^0)^2) - \tfrac{1}{2}\mathrm{i}(\gamma\cos^2\theta_t - \beta\epsilon^-\epsilon^+\sin^2\theta)(\omega/cn^-\cos\theta)(t_p^0)^2, \\ t_p &= t_p^0 + (\omega/c)^2\tau r_p^0 t_p^0 + \tfrac{1}{2}\mathrm{i}(\gamma\cos\theta\cos\theta_t + \beta\epsilon^-\epsilon^+\sin\theta\sin\theta_t)(\omega/cn^-\cos\theta)(t_p^0)^2. \end{aligned} \tag{2.8}$$

Here the Fresnel amplitudes are given by

$$\begin{aligned} r_p^0 &= (n^+\cos\theta - n^-\cos\theta_t)(n^+\cos\theta + n^-\cos\theta_t)^{-1}, \\ t_p^0 &= 2n^-\cos\theta(n^+\cos\theta + n^-\cos\theta_t)^{-1} = (n^-/n^+)(r_p^0 + 1). \end{aligned} \tag{2.9}$$

The coefficients of ellipsometry is defined as

$$r \equiv r_p/r_s \equiv \rho\, \mathrm{e}^{\mathrm{i}\Delta}. \tag{2.10}$$

Using eqs. (2.6) and (2.8) one has up to linear order in τ,γ and β

$$\begin{aligned} r = {} & r_p^0/r_s^0 - (\omega/c)^2\tau(r_s^0)^{-1}\{1 + r_p^0[(r_s^0)^{-1} - r_p^0 - r_s^0]\} \\ & - \tfrac{1}{2}\mathrm{i}(\omega/cn^-\cos\theta)[((t_p^0)^2/r_s^0)(\gamma\cos^2\theta_t - \beta\epsilon^-\epsilon^+\sin^2\theta) + r_p^0(t_s^0/r_s^0)^2\gamma]. \end{aligned} \tag{2.11}$$

The Brewster angle θ_B is defined by

$$\operatorname{Re} r(\theta_B) = [r_p^0/r_s^0 - (\omega/c)^2\tau(r_s^0)^{-1}\{1 + r_p^0[(r_s^0)^{-1} - r_p^0 - r_s^0]\}]_{\theta=\theta_B} = 0. \tag{2.12}$$

Neglecting τ one obtains the usual value θ_B^0 given by

$$r_p^0(\theta_B^0) = 0 \Rightarrow \theta_B^0 = \arccos[(\epsilon^-/(\epsilon^- + \epsilon^+))^{1/2}]. \tag{2.13}$$

Up to linear order in τ one obtains from eq. (2.12)

$$\theta_B = \theta_B^0 - 2(\omega/c)^2\tau\epsilon^+ n^+ n^-(\epsilon^{+2} - \epsilon^{-2})^{-1}. \tag{2.14}$$

If $\theta = \theta_B$ one has $\Delta = \pi/2$ and consequently

$$\begin{aligned}\rho(\theta_B) = & -\tfrac{1}{2}(\omega/cn^- \cos\theta)[((t_p^0)^2/r_s^0)(\gamma\cos^2\theta_t - \beta\epsilon^-\epsilon^+\sin^2\theta) \\ & + r_p^0(t_s^0/r_s^0)^2\gamma]\,|_{\theta=\theta_B}.\end{aligned} \tag{2.15}$$

In view of the fact that the right hand side of this equation is linear in γ and β, one may use (up to linear order) θ_B^0 rather than θ_B on this side. This yields, using eqs. (2.7), (2.9) and (2.13),

$$\rho(\theta_B) = \tfrac{1}{2}(\omega/c)(\gamma - \epsilon^+\epsilon^-\beta)(\epsilon^+ + \epsilon^-)^{1/2}(\epsilon^+ - \epsilon^-)^{-1}. \tag{2.16}$$

This expression was first given by Beaglehole[1]) on the basis of amplitudes given in ref. 2 for the special case that $\tau = 0$. Up to linear order this result is therefore not affected by the finite value of τ. In particular eq. (2.16) remains antisymmetric for the interchange of ϵ^+ and ϵ^-. If one goes to higher than linear order in γ, β and τ, one obtains contributions which break the antisymmetry. This effect may be estimated to be in the order of 1 part in 10^4 and is therefore in general unimportant. We refer to the discussion for a further analysis of this point.

3. Maxwell theory in the presence of induced interfacial polarization and magnetization densities

In the following sections we shall discuss how the thermal fluctuations of the location of the interface between the liquid and the gas affect the electromagnetic fields, using equivalent fluctuating polarization and magnetization densities at the equilibrium position of the interface. We shall assume that in equilibrium the interface is flat and we choose the x–y plane to coincide with it. The fluctuating electric and magnetic fields $\boldsymbol{e}$ and $\boldsymbol{b}$ and the displacement fields $\boldsymbol{d}$ and $\boldsymbol{h}$ satisfy Maxwell's equations

$$\begin{aligned}&\operatorname{rot} \boldsymbol{e} = -\frac{\partial}{\partial t}\boldsymbol{b}, \quad \operatorname{div} \boldsymbol{d} = 0, \\ &\operatorname{rot} \boldsymbol{h} = \frac{\partial}{\partial t}\boldsymbol{d}, \quad \operatorname{div} \boldsymbol{b} = 0.\end{aligned} \tag{3.1}$$

In sections 3–5 *units shall be used such that* $c = 1$. The induced polarization and magnetization densities satisfy

$$\boldsymbol{p} = \boldsymbol{d} - \boldsymbol{e} \quad \text{and} \quad \boldsymbol{m} = \boldsymbol{b} - \boldsymbol{h}. \tag{3.2}$$

The wave equations for $\boldsymbol{e}$ and $\boldsymbol{h}$ are

$$\begin{aligned} \left(\operatorname{rot}\operatorname{rot} + \frac{\partial^2}{\partial t^2}\right)\boldsymbol{e} &= -\frac{\partial^2}{\partial t^2}\boldsymbol{p} - \frac{\partial}{\partial t}\operatorname{rot}\boldsymbol{m}, \\ \left(\operatorname{rot}\operatorname{rot} + \frac{\partial^2}{\partial t^2}\right)\boldsymbol{h} &= -\frac{\partial^2}{\partial t^2}\boldsymbol{m} + \frac{\partial}{\partial t}\operatorname{rot}\boldsymbol{p}. \end{aligned} \tag{3.3}$$

Defining the Fourier transform of a field $a(\boldsymbol{r}, t)$ by

$$a(\boldsymbol{k}, \omega) = \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\, a(\boldsymbol{r}, t), \tag{3.4}$$

the wave equations may be written as

$$\begin{aligned} (\boldsymbol{kk} - k^2 + \omega^2)\boldsymbol{e} &= -\omega^2\boldsymbol{p} + \omega\boldsymbol{k} \wedge \boldsymbol{m}, \\ (\boldsymbol{kk} - k^2 + \omega^2)\boldsymbol{h} &= -\omega^2\boldsymbol{m} - \omega\boldsymbol{k} \wedge \boldsymbol{p}. \end{aligned} \tag{3.5}$$

The formal retarded solution of these wave equations is

$$\begin{aligned} \boldsymbol{e} &= \boldsymbol{E}_\mathrm{v} - \boldsymbol{F}\cdot(\boldsymbol{p} - \omega^{-1}\boldsymbol{k} \wedge \boldsymbol{m}), \\ \boldsymbol{h} &= \boldsymbol{H}_\mathrm{v} - \boldsymbol{F}\cdot(\boldsymbol{m} + \omega^{-1}\boldsymbol{k} \wedge \boldsymbol{p}). \end{aligned} \tag{3.6}$$

Here $\boldsymbol{E}_\mathrm{v}$ and $\boldsymbol{H}_\mathrm{v}$ are the vacuum fields. $\boldsymbol{F}$ is the retarded dipole propagator which is diagonal in $\boldsymbol{k}, \omega$ representation and is given by

$$\boldsymbol{F}(\boldsymbol{k}, \omega) \equiv (\boldsymbol{kk} - k^2 + (\omega + \mathrm{i}0)^2)^{-1}\omega^2 = (k^2 - (\omega + \mathrm{i}0)^2)^{-1}(\boldsymbol{kk} - \omega^2). \tag{3.7}$$

Here i0 is an infinitesimally small positive imaginary number.

In the regions occupied by the liquid and the gas, indicated as + and − regions respectively, one has

$$\boldsymbol{p}^{\pm}(\boldsymbol{r}, t) = (\epsilon^{\pm} - 1)\boldsymbol{e}^{\pm}(\boldsymbol{r}, t) \quad \text{and} \quad \boldsymbol{m}^{\pm}(\boldsymbol{r}, t) = 0. \tag{3.8}$$

Here we have taken the magnetic permeability of both fluids equal to unity. Due to the deviation of the fluctuating position of the interface from the equilibrium position one has a fluctuating excess polarization density in this region. This excess polarization density $\boldsymbol{p}^\mathrm{s}$ can be located at the equilibrium position of the interface[4]). The polarization density then has the general form

$$\boldsymbol{p}(\boldsymbol{r}, t) = \boldsymbol{p}^{-}(\boldsymbol{r}, t)\theta(-z) + \boldsymbol{p}^\mathrm{s}(\boldsymbol{r}_\parallel, t)\delta(z) + \boldsymbol{p}^{+}(\boldsymbol{r}, t)\theta(z), \tag{3.9}$$

where θ is the Heaviside function and $\boldsymbol{r}_\parallel \equiv (x, y, 0)$. In the next section we will derive an explicit expression for $\boldsymbol{p}^\mathrm{s}$ in terms of the fluctuating position of the interface. It is also found in this section that one needs an excess magnetization density $\boldsymbol{m}^s$ at the interface. Consequently one has, analogous to eq. (3.9) and using the fact that $\boldsymbol{m}^{\pm} = 0$,

$$\boldsymbol{m}(\boldsymbol{r}, t) = \boldsymbol{m}^s(\boldsymbol{r}_\parallel, t)\delta(z). \tag{3.10}$$

As was discussed in refs. 2 and 4, the singular nature of $\boldsymbol{p}$ and $\boldsymbol{m}$ implies that d_x, d_y, e_z, b_x, b_y and h_z are also singular at the $z = 0$ equilibrium interface. Furthermore, e_x, e_y, d_z, h_x, h_y and b_z are not singular in $z = 0$. These fields have discontinuities at $z = 0$ which are given in terms of $\boldsymbol{p}^s$ and $\boldsymbol{m}^s$, cf. eq. (2.1). In our analysis it is most convenient to use the non-singular fields. We therefore define

$$\boldsymbol{n}_e \equiv (e_x, e_y, d_z) \quad \text{and} \quad \boldsymbol{n}_m \equiv (h_x, h_y, b_z). \tag{3.11}$$

In order to write the formal solution of Maxwell's equations in terms of these non-singular fields we define

$$\boldsymbol{F}(\boldsymbol{k}, \omega) \equiv \boldsymbol{K}(\boldsymbol{k}, \omega) - \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{3.12}$$

$$\boldsymbol{L}(\boldsymbol{k}, \omega) \equiv \omega^{-1}\boldsymbol{F}(\boldsymbol{k}, \omega) \cdot \begin{pmatrix} 0 & -k_z & k_y \\ k_z & 0 & -k_x \\ -k_y & k_x & 0 \end{pmatrix}. \tag{3.13}$$

Eq. (3.6) then yields

$$\boldsymbol{n}_e = \boldsymbol{E}_v - \boldsymbol{K} \cdot \boldsymbol{p} + \boldsymbol{L} \cdot \boldsymbol{m}, \quad \boldsymbol{n}_m = \boldsymbol{H}_v - \boldsymbol{K} \cdot \boldsymbol{m} - \boldsymbol{L} \cdot \boldsymbol{p}. \tag{3.14}$$

Neglecting fluctuations one finds from this equation the fields reflected and transmitted by the equilibrium interface

$$\boldsymbol{N}_e^{(0)} = \boldsymbol{E}_v - \boldsymbol{K} \cdot \boldsymbol{P}_0, \quad \boldsymbol{N}_m^{(0)} = \boldsymbol{H}_v - \boldsymbol{L} \cdot \boldsymbol{P}_0, \tag{3.15}$$

where

$$\boldsymbol{P}_0(\boldsymbol{r}, t) = \boldsymbol{\xi}_0(z) \cdot \boldsymbol{N}_e^{(0)}(\boldsymbol{r}, t) \tag{3.16}$$

and

$$\boldsymbol{\xi}_0(z) = \boldsymbol{\xi}^- \theta(-z) + \boldsymbol{\xi}^+ \theta(z), \quad \text{with } \boldsymbol{\xi}^\nu = (\epsilon^\nu - 1) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (\epsilon^\nu)^{-1} \end{pmatrix}. \tag{3.17}$$

Substituting eq. (3.16) into eq. (3.15) one finds

$$\boldsymbol{N}_e^{(0)} = (1 + \boldsymbol{K} \cdot \boldsymbol{\xi}_0)^{-1} \cdot \boldsymbol{E}_v, \quad \boldsymbol{N}_m^{(0)} = \boldsymbol{H}_v - \boldsymbol{L} \cdot \boldsymbol{\xi}_0 \cdot (1 + \boldsymbol{K} \cdot \boldsymbol{\xi}_0)^{-1} \cdot \boldsymbol{E}_v. \tag{3.18}$$

In order to take the contributions due to fluctuations of the interface into account we write the polarization density in the following form:

$$p(r, t) = \xi_0(z) \cdot n_e(r, t) + p^s(r_\parallel, t)\delta(z). \qquad (3.19)$$

Using this equation together with eqs. (3.10) and (3.18) one may write eq. (3.14) in the following form:

$$\begin{aligned} n_e &= N_e^{(0)} - K_0 \cdot p^s\delta(z) + L_0 \cdot m^s\delta(z), \\ n_m &= N_m^{(0)} - L \cdot (1 - \xi_0 \cdot K_0) \cdot p^s\delta(z) - (K + L \cdot \xi_0 \cdot L_0) \cdot m^s\delta(z). \end{aligned} \qquad (3.20)$$

Here we defined the following propagators:

$$K_0 \equiv (1 + K \cdot \xi_0)^{-1} \cdot K, \quad L_0 \equiv (1 + K \cdot \xi_0)^{-1} \cdot L. \qquad (3.21)$$

These equations give the n_e and n_m fields due to the excess polarization and magnetization densities.

4. The fluctuating interfacial polarization and magnetization densities

The instantaneous position of the interface is characterized by

$$z = f(r_\parallel, t). \qquad (4.1)$$

The equilibrium position is given by $z = 0$ and consequently

$$\langle f(r_\parallel, t)\rangle = 0. \qquad (4.2)$$

Here $\langle \cdots \rangle$ indicates an average over the equilibrium ensemble. The excess interfacial polarization and magnetization densities are given by[14])

$$\begin{aligned} p^s(r_\parallel, t) &= \int_0^{f(r_\parallel, t)} [(d_x^-, d_y^-, -e_z^-)(r, t) - (d_x^+, d_y^+, -e_z^+)(r, t)]\,\mathrm{d}z, \\ m^s(r_\parallel, t) &= \int_0^{f(r_\parallel, t)} [(b_x^-, b_y^-, -h_z^-)(r, t) - (b_x^+, b_y^+, -h_z^+)(r, t)]\,\mathrm{d}z. \end{aligned} \qquad (4.3)$$

As f is small we may expand eq. (4.3) to second order in f. This gives

$$\begin{aligned} p_x^s(r_\parallel, t) = {} & [d_x^-(x, y, 0, t) - d_x^+(x, y, 0, t)]f(r_\parallel, t) \\ & + \tfrac{1}{2}\frac{\partial}{\partial z}[d_x^-(r, t) - d_x^+(r, t)]\,|_{z=0}\, f^2(r_\parallel, t) \end{aligned} \qquad (4.4)$$

and analogous formulae for the other fields. Using Maxwell's equations we may e.g. write

$$\frac{\partial}{\partial z} d_x^- = \epsilon^- \frac{\partial}{\partial z} e_x^- = \epsilon^- \left[(\mathrm{rot}\, e)_y + \frac{\partial}{\partial x} e_z^-\right] = -\epsilon^- \frac{\partial}{\partial t} b_y^- + \frac{\partial}{\partial x} d_z^-.$$

Eq. (4.4) may therefore be written, using also eq. (3.8), as

$$\begin{aligned} p^{\mathrm{s}}_{x}(\boldsymbol{r}_{\|}, t) &= f(\boldsymbol{r}_{\|}, t)[\epsilon^{-} n^{-}_{\mathrm{e},x}(\boldsymbol{r}_{\|}, t) - \epsilon^{+} n^{+}_{\mathrm{e},x}(\boldsymbol{r}_{\|}, t)] \\ &\quad - \tfrac{1}{2} f^{2}(\boldsymbol{r}_{\|}, t) \frac{\partial}{\partial t} [\epsilon^{-} n^{-}_{\mathrm{m},y}(\boldsymbol{r}_{\|}, t) - \epsilon^{+} n^{+}_{\mathrm{m},y}(\boldsymbol{r}_{\|}, t)] \\ &\quad + \tfrac{1}{2} f^{2}(\boldsymbol{r}_{\|}, t) \frac{\partial}{\partial x} [n^{-}_{\mathrm{e},z}(\boldsymbol{r}_{\|}, t) - n^{+}_{\mathrm{e},z}(\boldsymbol{r}_{\|}, t)]. \end{aligned} \tag{4.5}$$

If $f = 0$, the excess polarization and magnetization are zero. In that case the $\boldsymbol{n}_{\mathrm{e}}$ and the $\boldsymbol{n}_{\mathrm{m}}$ fields are continuous for $z = 0$, cf. eq. (2.1). In view of this the discontinuity in $\boldsymbol{n}_{\mathrm{e}}$ and $\boldsymbol{n}_{\mathrm{m}}$ in $z = 0$ is at least linear in f. Consequently the last term in eq. (4.5) is of third order in f and should be neglected. For the other components of $\boldsymbol{p}^{\mathrm{s}}$ and for $\boldsymbol{m}^{\mathrm{s}}$ a similar analysis can be made.

In this way one obtains the following expressions:

$$\begin{aligned} \boldsymbol{p}^{\mathrm{s}} &= \boldsymbol{\xi}^{(1)-}_{\mathrm{b}} \cdot \boldsymbol{n}^{-}_{\mathrm{e}} + \boldsymbol{\xi}^{(1)+}_{\mathrm{b}} \cdot \boldsymbol{n}^{+}_{\mathrm{e}} + \boldsymbol{\xi}^{(2)-}_{\mathrm{b}} \cdot \frac{\partial}{\partial t} \boldsymbol{n}^{-}_{\mathrm{m}} + \boldsymbol{\xi}^{(2)+}_{\mathrm{b}} \cdot \frac{\partial}{\partial t} \boldsymbol{n}^{+}_{\mathrm{m}}, \\ \boldsymbol{m}^{\mathrm{s}} &= \boldsymbol{\xi}^{(2)-}_{\mathrm{b}} \cdot \frac{\partial}{\partial t} \boldsymbol{n}^{-}_{\mathrm{e}} + \boldsymbol{\xi}^{(2)+}_{\mathrm{b}} \cdot \frac{\partial}{\partial t} \boldsymbol{n}^{+}_{\mathrm{e}}, \end{aligned} \tag{4.6}$$

where, $\nu = +$ or $-$,

$$\begin{aligned} \boldsymbol{\xi}^{(1)\nu}_{\mathrm{b}}(\boldsymbol{r}_{\|}, t) &= -\nu f(\boldsymbol{r}_{\|}, t) \begin{pmatrix} \epsilon^{\nu} & 0 & 0 \\ 0 & \epsilon^{\nu} & 0 \\ 0 & 0 & -1/\epsilon^{\nu} \end{pmatrix} \equiv -\nu f(\boldsymbol{r}_{\|}, t) \boldsymbol{\Pi}^{\nu}, \\ \boldsymbol{\xi}^{(2)}_{\mathrm{b}}(\boldsymbol{r}_{\|}, t) &= \tfrac{1}{2} \nu \epsilon^{\nu} f^{2}(\boldsymbol{r}_{\|}, t) \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{4.7}$$

As is clear from these expressions $\boldsymbol{p}^{\mathrm{s}}$ is of the first and higher order in f while $\boldsymbol{m}^{\mathrm{s}}$ is of second and higher order.

5. The interfacial constitutive coefficients for the averaged fields

Averaging eq. (3.20) one obtains for the averaged fields

$$\begin{aligned} \boldsymbol{N}_{\mathrm{e}} &= \boldsymbol{N}^{(0)}_{\mathrm{e}} - \boldsymbol{K}_{0} \cdot \boldsymbol{P}^{\mathrm{s}} \delta(z) + \boldsymbol{L}_{0} \cdot \boldsymbol{M}^{\mathrm{s}} \delta(z), \\ \boldsymbol{N}_{\mathrm{m}} &= \boldsymbol{N}^{(0)}_{\mathrm{m}} - \boldsymbol{L} \cdot (1 - \boldsymbol{\xi}_{0} \cdot \boldsymbol{K}_{0}) \cdot \boldsymbol{P}^{\mathrm{s}} \delta(z) - (\boldsymbol{K} + \boldsymbol{L} \cdot \boldsymbol{\xi}_{0} \cdot \boldsymbol{L}_{0}) \cdot \boldsymbol{M}^{\mathrm{s}} \delta(z), \end{aligned} \tag{5.1}$$

where

$$\boldsymbol{N}_{\mathrm{e}} = \langle \boldsymbol{n}_{\mathrm{e}} \rangle, \quad \boldsymbol{N}_{\mathrm{m}} = \langle \boldsymbol{n}_{\mathrm{m}} \rangle, \quad \boldsymbol{P}^{\mathrm{s}} = \langle \boldsymbol{p}^{\mathrm{s}} \rangle \quad \text{and} \quad \boldsymbol{M}^{\mathrm{s}} = \langle \boldsymbol{m}^{\mathrm{s}} \rangle. \tag{5.2}$$

Eq. (5.1) simply reflects the fact that the average fields again satisfy Maxwell's equations. In order to calculate the constitutive coefficients we shall now evaluate $\boldsymbol{P}^{\mathrm{s}}$ and $\boldsymbol{M}^{\mathrm{s}}$ to second order in f. Averaging eq. (4.6) one has

$$\boldsymbol{P}^{\mathrm{s}} = \sum_{\nu} [\langle \boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu} \cdot \boldsymbol{n}_{\mathrm{e}}^{\nu} \rangle + \langle \boldsymbol{\xi}_{\mathrm{b}}^{(2)\nu} \cdot \frac{\partial}{\partial t} \boldsymbol{n}_{\mathrm{m}} \rangle]. \tag{5.3}$$

In the last term we may replace $\boldsymbol{n}_{\mathrm{m}}^{\nu}$ by $\boldsymbol{N}_{\mathrm{m}}^{(0)\nu}$ in view of the fact that $\boldsymbol{\xi}_{\mathrm{b}}^{(2)\nu}$ is already of second order in f. In the first term $\boldsymbol{n}_{\mathrm{e}}^{\nu}$ must be used to linear order, as $\boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu}$ is linear. Using eqs. (3.20), (4.2) and (4.6) one therefore obtains

$$\boldsymbol{P}^{\mathrm{s}} = -\sum_{\nu,\nu'} \langle \boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu'} \cdot \boldsymbol{K}_0 \cdot \boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu} \rangle \cdot \boldsymbol{N}_{\mathrm{e}}^{(0)\nu} + \sum_{\nu} \langle \boldsymbol{\xi}_{\mathrm{b}}^{(2)\nu} \rangle \cdot \frac{\partial}{\partial t} \boldsymbol{N}_{\mathrm{m}}^{(0)\nu}. \tag{5.4}$$

Using the fact that the differences $(\boldsymbol{N}_{\mathrm{em}}^{\nu} - \boldsymbol{N}_{\mathrm{em}}^{(0)\nu})$ are of second order in f we may write this equation in the form

$$\boldsymbol{P}^{\mathrm{s}} = \sum_{\nu} (\boldsymbol{\xi}_{\mathrm{e}}^{\nu} \cdot \boldsymbol{N}_{\mathrm{e}}^{\nu} + \boldsymbol{\xi}_{\mathrm{m}}^{\nu} \cdot \frac{\partial}{\partial t} \boldsymbol{N}_{\mathrm{m}}^{\nu}), \tag{5.5}$$

where

$$\boldsymbol{\xi}_{\mathrm{e}}^{\nu} \equiv -\sum_{\nu'} \langle \boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu'} \cdot \boldsymbol{K}_0 \cdot \boldsymbol{\xi}_{\mathrm{b}}^{(1)\nu} \rangle, \quad \boldsymbol{\xi}_{\mathrm{m}}^{\nu} \equiv \langle \boldsymbol{\xi}_{\mathrm{b}}^{(2)\nu} \rangle. \tag{5.6}$$

In the same way one finds

$$\boldsymbol{M}^{\mathrm{s}} = \sum_{\nu} \boldsymbol{\xi}_{\mathrm{m}}^{\nu} \cdot \frac{\partial}{\partial t} \boldsymbol{N}_{\mathrm{e}}^{\nu}. \tag{5.7}$$

Using eq. (4.7) the interfacial constitutive coefficients, as given by eq. (5.6), become as a function of wavevector and frequency

$$\begin{aligned}
\boldsymbol{\xi}_{\mathrm{e}}^{\nu}(\boldsymbol{k}_{\parallel}, \omega \,|\, \boldsymbol{k}_{\parallel}', \omega') = {} & -\sum_{\nu'} \nu\nu' \boldsymbol{\Pi}^{\nu'} \cdot (2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}_{\parallel}'' \, \mathrm{d}\omega'' \langle f(\boldsymbol{k}_{\parallel} - \boldsymbol{k}_{\parallel}'', \omega - \omega'') \\
& \boldsymbol{K}_0(\boldsymbol{k}_{\parallel}'', z = 0, \omega'' \,|\, z' = 0) f(\boldsymbol{k}_{\parallel}'' - \boldsymbol{k}_{\parallel}', \omega'' - \omega') \rangle \cdot \boldsymbol{\Pi}^{\nu}, \\
\boldsymbol{\xi}_{\mathrm{m}}^{\nu}(\boldsymbol{k}_{\parallel}, \omega \,|\, \boldsymbol{k}_{\parallel}', \omega') = {} & \tfrac{1}{2}\nu\epsilon^{\nu}(2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}_{\parallel}'' \, \mathrm{d}\omega'' \langle f(\boldsymbol{k}_{\parallel} - \boldsymbol{k}_{\parallel}'', \omega - \omega'') \\
& f(\boldsymbol{k}_{\parallel}'' - \boldsymbol{k}_{\parallel}', \omega'' - \omega') \rangle \quad \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\end{aligned} \tag{5.8}$$

We now define the following correlation function for the position of the interface

$$S(\boldsymbol{r}_{\parallel} - \boldsymbol{r}_{\parallel}', t - t') \equiv \langle f(\boldsymbol{r}_{\parallel}, t) f(\boldsymbol{r}_{\parallel}', t') \rangle, \tag{5.9}$$

where we have used translational invariance in the x–y plane and stationarity.

After Fourier transformation one has

$$\langle f(\boldsymbol{k}_\parallel, \omega) f(\boldsymbol{k}'_\parallel, \omega')\rangle = S(\boldsymbol{k}_\parallel, \omega)(2\pi)^3 \delta(\boldsymbol{k}_\parallel + \boldsymbol{k}'_\parallel)\delta(\omega + \omega'). \tag{5.10}$$

Substituting this expression into eq. (5.8) one finds

$$\boldsymbol{\xi}^{\nu}_{e,m}(\boldsymbol{k}_\parallel, \omega \,|\, \boldsymbol{k}'_\parallel, \omega') = \boldsymbol{\xi}^{\nu}_{e,m}(\boldsymbol{k}_\parallel, \omega)(2\pi)^3 \delta(\boldsymbol{k}_\parallel - \boldsymbol{k}'_\parallel)\delta(\omega - \omega'), \tag{5.11}$$

with

$$\begin{aligned}\boldsymbol{\xi}^{\nu}_{e}(\boldsymbol{k}_\parallel, \omega) &= -\nu \sum_{\nu'} \nu' \boldsymbol{\Pi}^{\nu'} \cdot (2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}'_\parallel \,\mathrm{d}\omega' \, S(\boldsymbol{k}_\parallel - \boldsymbol{k}'_\parallel, \omega - \omega') \\ &\quad \times \boldsymbol{K}_0(\boldsymbol{k}'_\parallel, 0, \omega' | 0) \cdot \boldsymbol{\Pi}^{\nu}, \\ \boldsymbol{\xi}^{\nu}_{m}(\boldsymbol{k}_\parallel, \omega) &= \boldsymbol{\xi}^{\nu}_{m} = \tfrac{1}{2}\nu\epsilon^{\nu} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} (2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}'_\parallel \,\mathrm{d}\omega' \, S(\boldsymbol{k}'_\parallel, \omega').\end{aligned} \tag{5.12}$$

The typical velocity of the interface is much smaller than the speed of light. Consequently we may use the equilibrium correlation function. Replacing $S(\boldsymbol{k}_\parallel, \omega)$ by $S_{\mathrm{eq}}(\boldsymbol{k}_\parallel)(2\pi)\delta(\omega)$ in eq. (5.12), one then obtains

$$\begin{aligned}\boldsymbol{\xi}^{\nu}_{e}(\boldsymbol{k}_\parallel, \omega) &= -\nu \sum_{\nu'} \nu' \boldsymbol{\Pi}^{\nu'} \cdot (2\pi)^{-2} \int \mathrm{d}\boldsymbol{k}'_\parallel \, S_{\mathrm{eq}}(\boldsymbol{k}_\parallel - \boldsymbol{k}'_\parallel) \boldsymbol{K}_0(\boldsymbol{k}'_\parallel, 0, \omega | 0) \cdot \boldsymbol{\Pi}^{\nu}, \\ \boldsymbol{\xi}^{\nu}_{m} &= \tfrac{1}{2}\nu\epsilon^{\nu} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} (2\pi)^{-2} \int \mathrm{d}\boldsymbol{k}'_\parallel \, S_{\mathrm{eq}}(\boldsymbol{k}'_\parallel).\end{aligned} \tag{5.13}$$

The position autocorrelation function for the interface is given in equilibrium by[5])

$$S_{\mathrm{eq}}(\boldsymbol{k}_\parallel) = k_{\mathrm{B}} T (\sigma k_\parallel^2 + g|\rho^+ - \rho^-|)^{-1} \equiv (k_{\mathrm{B}} T / g |\rho^+ - \rho^-|)(1 + k_\parallel^2 l^2)^{-1}, \tag{5.14}$$

where k_{B} is Boltzmann's constant, T the temperature, σ the surface tension, g the gravitational acceleration, $\rho^{\pm}$ the mass densities of the two fluids and l is the capillary length. Using this correlation function and the explicit expression for the propagator $\boldsymbol{K}_0$ one may evaluate $\boldsymbol{\xi}^{\nu}_{e}$ and $\boldsymbol{\xi}^{\nu}_{m}$, using eq. (5.13). We shall restrict ourselves to the zero frequency and wavevector value of $\boldsymbol{\xi}^{\nu}_{e}$ as the dependence on $\boldsymbol{k}_\parallel$ and ω may be shown to be unimportant for this case. Then the propagator becomes for zero frequency* (and $z = z' = 0$)

$$\boldsymbol{K}_0(\boldsymbol{k}_\parallel, z = 0, \omega = 0 | z' = 0) = (\epsilon^- + \epsilon^+)^{-1} k_\parallel (\hat{\boldsymbol{k}}_\parallel \hat{\boldsymbol{k}}_\parallel - \epsilon^- \epsilon^+ \hat{z}\hat{z}). \tag{5.15}$$

Substituting eqs. (5.14) and (5.15) into eq. (5.13) one obtains

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*In fact the propagator given in ref. 6 also contains terms proportional to sign $(z - z')(\hat{\boldsymbol{k}}_\parallel \hat{z} + \hat{z}\hat{\boldsymbol{k}}_\parallel)$. As these terms give zero upon integration we did not give them explicitly.

$$\boldsymbol{\xi}^{\nu}_{\mathrm{e}}(\boldsymbol{k}_\parallel = 0, \omega = 0) = -\frac{\nu(\epsilon^+ - \epsilon^-)k_{\mathrm{B}}T}{4\pi^2 g\,|\rho^+ - \rho^-|(\epsilon^+ + \epsilon^-)}$$

$$\int_0^{k_{\mathrm{m}}} \mathrm{d}k_\parallel \left(\frac{k_\parallel^2}{1 + k_\parallel^2 l^2}\right) \int_0^{2\pi} \mathrm{d}\phi \begin{pmatrix} \cos^2\phi & \cos\phi\sin\phi & 0 \\ \cos\phi\sin\phi & \sin^2\phi & 0 \\ 0 & 0 & -1 \end{pmatrix} \cdot \Pi^{\nu},$$

$$\boldsymbol{\xi}^{\nu}_{\mathrm{m}} = \frac{\nu\epsilon^{\nu}k_{\mathrm{B}}T}{4\pi g\,|\rho^+ - \rho^-|} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \int_0^{k_{\mathrm{m}}} \mathrm{d}k_\parallel \left(\frac{k_\parallel}{1 + k_\parallel^2 l^2}\right). \tag{5.16}$$

In both integrals we have introduced a cut-off k_{m} which is of the order of 2π divided by a molecular length. For such values of $k_\parallel$ the expression for the correlation function, eq. (5.14), which is derived on the basis of macroscopic fluctuation theory, is clearly no longer correct.

Evaluation of the integrals is straightforward and one finds, using $k_m l \gg 1$,

$$\boldsymbol{\xi}^{\nu}_{\mathrm{e}}(\boldsymbol{k}_\parallel = 0, \omega = 0) \equiv \tfrac{1}{2} \begin{pmatrix} \gamma^{\nu} & 0 & 0 \\ 0 & \gamma^{\nu} & 0 \\ 0 & 0 & \beta^{\nu} \end{pmatrix}, \quad \boldsymbol{\xi}^{\nu}_{\mathrm{m}} \equiv \tfrac{1}{2}\tau^{\nu} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{5.17}$$

with

$$\gamma^{\nu} = -\nu\epsilon^{\nu}\left[\frac{(\epsilon^+ - \epsilon^-)k_{\mathrm{B}}T}{2\pi(\epsilon^+ + \epsilon^-)\sigma}\right]k_{\mathrm{m}},$$

$$\beta^{\nu} = -\frac{\nu}{\epsilon^{\nu}}\left[\frac{(\epsilon^+ - \epsilon^-)k_{\mathrm{B}}T}{\pi(\epsilon^+ + \epsilon^-)\sigma}\right]k_{\mathrm{m}},$$

$$\tau^{\nu} = \nu\epsilon^{\nu}\left[\frac{k_{\mathrm{B}}T}{2\pi\sigma}\right]\ln(lk_{\mathrm{m}}). \tag{5.18}$$

In the analysis in section 2 it is sufficient to use the averages

$$\gamma \equiv \tfrac{1}{2}(\gamma^- + \gamma^+) = -\left[\frac{(\epsilon^+ - \epsilon^-)^2 k_{\mathrm{B}}T}{4\pi(\epsilon^+ + \epsilon^-)\sigma}\right]k_{\mathrm{m}},$$

$$\beta \equiv \tfrac{1}{2}(\beta^- + \beta^+) = -2\gamma/\epsilon^-\epsilon^+, \quad \tau \equiv \tfrac{1}{2}(\tau^- + \tau^+) = \left[\frac{(\epsilon^+ - \epsilon^-)k_{\mathrm{B}}T}{4\pi\sigma}\right]\ln(lk_{\mathrm{m}}). \tag{5.19}$$

This is a consequence of the fact that the discontinuity in the $\boldsymbol{N}_{\mathrm{m}}$ and $\boldsymbol{N}_{\mathrm{e}}$ fields is linear in the interfacial constitutive coefficients. One may therefore simplify eq. (5.5) to linear order by

$$\boldsymbol{P}^{\mathrm{s}} = \left[\sum_{\nu} \boldsymbol{\xi}^{\nu}_{\mathrm{e}}\right] \cdot \left[\tfrac{1}{2}\sum_{\nu'} \boldsymbol{N}^{\nu'}_{\mathrm{e}}\right] + \left[\sum_{\nu} \boldsymbol{\xi}^{\nu}_{\mathrm{m}}\right] \cdot \frac{\partial}{\partial t}\left[\tfrac{1}{2}\sum_{\nu'} \boldsymbol{N}^{\nu'}_{\mathrm{m}}\right]$$

$$= \tfrac{1}{2}\begin{pmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \beta \end{pmatrix} \cdot (\boldsymbol{N}^-_{\mathrm{e}} + \boldsymbol{N}^+_{\mathrm{e}}) + \tfrac{1}{2}\tau \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \cdot \frac{\partial}{\partial t}(\boldsymbol{N}^-_{\mathrm{m}} + \boldsymbol{N}^+_{\mathrm{m}}). \tag{5.20}$$

Similarly eq. (5.7) becomes

$$\boldsymbol{M}^{s} = \tfrac{1}{2}\tau \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \cdot \frac{\partial}{\partial t}(\boldsymbol{N}_{e}^{-} + \boldsymbol{N}_{e}^{+}). \tag{5.21}$$

In the introduction the constitutive equations were given in this form.

6. Discussion

Except for a numerical factor our expression for $\rho(\theta_B)$, eq. (2.16) together with eq. (1.2), is identical to eq. (2), together with eq. (17), in Beaglehole's paper[1]). In fact, they become identical* if we identify

$$k_m = \tfrac{4}{3} k_{\max}, \tag{6.1}$$

where $k_{\max}$ is the wavevector cut-off used in ref. 1. Using the formula for $\rho(\theta_B)$, the maximum wavevector $k_{\max}$ was fitted using the experimental data. Using these values we find

$$k_m = \begin{Bmatrix} 1.13\,(\text{Å})^{-1} \\ 1.33\,(\text{Å})^{-1} \end{Bmatrix} \Rightarrow \frac{2\pi}{k_m} = \begin{cases} 5.6\ \text{Å for Carbon tetrachloride at } 18^{\circ}\text{C}, \\ 4.7\ \text{Å for Argon at } 100^{\circ}\text{K}. \end{cases} \tag{6.2}$$

The values of $2\pi/k_m$ are roughly 50% larger than the molecular diameter. The experimental results are thus in essential agreement with the assumptions made in the theoretical analysis. Using $\epsilon^{+} = 2.132$, $\epsilon^{-} = 1.001$, $\sigma = 27\ \text{erg/cm}^2$, $\rho^{+} = 1.58\ \text{g/cm}^3$ and $\rho^{-} \approx 0$, one has the following values of the interfacial constitutive coefficients of carbon tetrachloride at 18°C:

$$\gamma = -5.5 \times 10^{-9}\ \text{cm}, \quad \beta = 5.1 \times 10^{-9}\ \text{cm} \quad \text{and} \quad \tau = 2.2 \times 10^{-15}\ \text{cm}^2.$$

Similarly we have for argon at 100 K, using $\epsilon^{+} = 1.975$, $\epsilon^{-} = 1.006$, $\sigma = 9.42\ \text{erg/cm}^2$, $\rho^{+} = 1.309\ \text{g/cm}^3$, and $\rho^{-} = 0.018\ \text{g/cm}^3$:

$$\gamma = -4.9 \times 10^{-9}\ \text{cm}, \quad \beta = 4.9 \times 10^{-9}\ \text{cm}, \quad \text{and} \quad \tau = 1.8 \times 10^{-15}\ \text{cm}^2.$$

In the experiments on carbon tetrachloride $\rho(\theta_B)$ was measured with the light incident from vapour to liquid ρ_{-+} and from liquid to vapour ρ_{+-}. According to the prediction, eq. (2.16), one has

$$\rho_{-+}(\theta_B) + \rho_{+-}(\theta_B) = 0.$$

In the experiment it was found, however, that

$$\left| \frac{\rho_{-+}(\theta_B) + \rho_{+-}(\theta_B)}{\rho_{-+}(\theta_B) - \rho_{+-}(\theta_B)} \right| = 0.049, \tag{6.3}$$

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*The difference in sign is associated with a different phase convention.

and we shall now discuss a few possibilities to explain this effect. As a first possibility one may take higher than linear terms in γ, β and τ into account. One then finds terms which break the antisymmetry, cf. section 2. The existence of such terms, which depend on $k_{\min}/k_{\max} \sim (lk_{\mathrm{m}})^{-1}$, was suggested in ref. 1. These terms are, however, clearly too small.

A second possibility would be contamination of the surface. Such contamination would, however, change the values of γ and β. As this does not break the antisymmetry it would also not explain this effect. One may furthermore conclude from the values of $2\pi/k_{\mathrm{m}}$, given in eq. (6.2), that the contamination of the surface, if any, must be small. If the bulk fluid would become conductive due to contamination γ, β and τ have small imaginary parts. The imaginary part of τ gives an antisymmetry breaking term but is too small for normal values of this conductivity. Conductivity of the surface area only leads to imaginary contributions to γ and β and consequently does not explain this effect either.

Another possibility is the fact that one measures $\langle r_{\mathrm{p}}/r_{\mathrm{s}}\rangle$ rather than $\langle r_{\mathrm{p}}\rangle/\langle r_{\mathrm{s}}\rangle$ which was evaluated[7]). Correlations between r_{p} and r_{s} could then lead to a breaking of the antisymmetry. To second order in the fluctuations one has

$$\left\langle\frac{r_{\mathrm{p}}}{r_{\mathrm{s}}}\right\rangle = \frac{\langle r_{\mathrm{p}}\rangle}{\langle r_{\mathrm{s}}\rangle} - \frac{\langle(r_{\mathrm{p}} - \langle r_{\mathrm{p}}\rangle)(r_{\mathrm{s}} - \langle r_{\mathrm{s}}\rangle)\rangle}{(r_{\mathrm{s}}^0)^2} + \frac{\langle(r_{\mathrm{s}} - \langle r_{\mathrm{s}}\rangle)^2\rangle r_{\mathrm{p}}^0}{(r_{\mathrm{s}}^0)^3}. \tag{6.4}$$

The difference is therefore related to the correlation matrix for light scattered in the "forward direction". We have calculated the imaginary part of this matrix (see the appendix) and find

$$\mathrm{Im}\langle(r_\alpha - \langle r_\alpha\rangle)(r_{\alpha'} - \langle r_{\alpha'}\rangle)\rangle = \frac{(\omega/c)^2}{32\epsilon^-}\left(\frac{k_{\mathrm{B}}T}{\sigma}\right)\left(\frac{\epsilon^+ - \epsilon^-}{\cos\theta}\right)^2 a_\alpha a_{\alpha'}, \tag{6.5}$$

where

$$a_{\mathrm{s}} = (t_{\mathrm{s}}^{(0)})^2 \quad \text{and} \quad a_{\mathrm{p}} = (t_{\mathrm{p}}^{(0)})^2(\cos^2\theta_{\mathrm{t}} - \sin^2\theta). \tag{6.6}$$

If $\theta = \theta_{\mathrm{B}}$ the constant $a_{\mathrm{p}} = 0$ and $r_{\mathrm{p}}^0 = 0$; consequently

$$\mathrm{Im}\left\langle\frac{r_{\mathrm{p}}}{r_{\mathrm{s}}}\right\rangle\bigg|_{\theta=\theta_{\mathrm{B}}} = \mathrm{Im}\frac{\langle r_{\mathrm{p}}\rangle}{\langle r_{\mathrm{s}}\rangle}\bigg|_{\theta=\theta_{\mathrm{B}}}. \tag{6.7}$$

We conclude that correlations between r_{p} and r_{s} do not lead to a breaking of the antisymmetry. Even if $\theta \neq \theta_{\mathrm{B}}$ the correlation contribution is only a few promille.

Appendix

Using eq. (3.20) we have

$$\boldsymbol{n}_e - \langle \boldsymbol{n}_e \rangle = -\boldsymbol{K}_0 \cdot (\boldsymbol{p}^s - \langle \boldsymbol{p}^s \rangle)\delta(z) + \boldsymbol{L}_0 \cdot (\boldsymbol{m}^s - \langle \boldsymbol{m}^s \rangle)\delta(z). \tag{A.1}$$

In order to calculate the correlation matrix for the scattered light only terms linear in f must be retained on the right-hand side of this expression. We then obtain, cf. also eqs. (4.6) and (4.7),

$$\boldsymbol{n}_e - \langle \boldsymbol{n}_e \rangle = -\boldsymbol{K}_0 \cdot (\boldsymbol{\xi}_b^{(1)-} \cdot \boldsymbol{N}_e^{(0)-} + \boldsymbol{\xi}_b^{(1)+} \cdot \boldsymbol{N}_e^{(0)+})\delta(z). \tag{A.2}$$

In view of the fact that $\boldsymbol{N}_e^{(0)}$ is continuous in $z = 0$ and using eq. (4.7) we then find

$$\boldsymbol{n}_e - \langle \boldsymbol{n}_e \rangle = (\epsilon^+ - \epsilon^-)\boldsymbol{K}_0 \cdot f \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (\epsilon^-\epsilon^+)^{-1} \end{pmatrix} \cdot \boldsymbol{N}_e^{(0)+}\delta(z). \tag{A.3}$$

Using eq. (2.4) for the zeroth order transmitted field gives, $z < 0$,

$$r_s - \langle r_s \rangle = (\epsilon^+ - \epsilon^-) t_s^{(0)} \mathrm{e}^{-\mathrm{i}n^-\omega r} \int_{O_s} \mathrm{d}\boldsymbol{r}_\parallel' [\boldsymbol{K}_0(\boldsymbol{r}_\parallel - \boldsymbol{r}_\parallel', z, \omega \,|\, z' = 0)]_{yy}$$
$$f(\boldsymbol{r}_\parallel')\mathrm{e}^{\mathrm{i}n^-\omega x' \sin\theta}, \tag{A.4}$$

where O_s is the illuminated surface area. We note that the propagator $\boldsymbol{K}_0$ is continuous in $z' = 0$. Similarly one finds

$$r_p - \langle r_p \rangle = -(\epsilon^+ - \epsilon^-) t_p^{(0)} \mathrm{e}^{-\mathrm{i}n^-\omega r} \left(\cos\theta, 0, \frac{\sin\theta}{\epsilon^-}\right)$$
$$\cdot \left[\int_{O_s} \mathrm{d}\boldsymbol{r}_\parallel' \boldsymbol{K}_0(\boldsymbol{r}_\parallel - \boldsymbol{r}_\parallel', z, \omega \,|\, z' = 0) f(\boldsymbol{r}_\parallel')\, \mathrm{e}^{\mathrm{i}n^-\omega x' \sin\theta} \right] \cdot \left(\cos\theta_t, 0, -\frac{\sin\theta_t}{\epsilon^-}\right). \tag{A.5}$$

In view of the fact that the observer is far away from O_s we may use the asymptotic propagator given by[6]

$$\boldsymbol{K}_{0,\,\mathrm{asymp}}(\boldsymbol{r}_\parallel, z, \omega \,|\, z' = 0) = -\frac{\omega^2}{4\pi r}\mathrm{e}^{\mathrm{i}n^-\omega r}$$
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \epsilon^- \end{pmatrix} \cdot (1 - \hat{r}\hat{r}) \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \epsilon^- \end{pmatrix} \cdot$$
$$\cdot \boldsymbol{A}^{--}(\boldsymbol{k}_{\parallel,s} = \omega n^- \boldsymbol{r}_\parallel / r, \omega) \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & (\epsilon^-)^{-1} \end{pmatrix} \cdot \tag{A.6}$$

The matrix $\mathbf{A}^{--}$ is given in terms of the reflection coefficients of the equilibrium surface and is equal to6), choosing $\mathbf{r}_\parallel$ in the x-direction,

$$\mathbf{A}^{--} = \begin{pmatrix} 1-r_{\mathrm{p}}^{(0)} & 0 & 0 \\ 0 & t_{\mathrm{s}}^{(0)} & 0 \\ 0 & 0 & n^{-}n^{+}t_{\mathrm{p}}^{(0)} \end{pmatrix}. \tag{A.7}$$

Upon substitution in eq. (A.6) one finds

$$\begin{aligned} &\mathbf{K}_{0,\,\mathrm{asymp}}(\mathbf{r}_\parallel, z, \omega \,|\, z' = 0) \\ &= -\frac{\omega^2}{4\pi r} \mathrm{e}^{\mathrm{i}n^{-}\omega r} \begin{pmatrix} (1-r_{\mathrm{p}}^{(0)})\cos^2\theta & 0 & n^{-}n^{+}t_{\mathrm{p}}^{(0)}\sin\theta\cos\theta \\ 0 & t_{\mathrm{s}}^{(0)} & 0 \\ \epsilon^{-}(1-r_{\mathrm{p}}^{(0)})\sin\theta\cos\theta & 0 & \epsilon^{-}n^{-}n^{+}t_{\mathrm{p}}^{(0)}\sin^2\theta \end{pmatrix}. \end{aligned} \tag{A.8}$$

In this equation $\mathbf{r}_\parallel$ must be replaced by $\mathbf{r}_\parallel - \mathbf{r}'_\parallel$ and the result substituted into eqs. (A.4) and (A.5). Using the fact that the diameter of O_{s} is much smaller than the distance to the observer, one obtains

$$r_\alpha - \langle r_\alpha \rangle = -\frac{\omega^2}{4\pi r}(\epsilon^{+} - \epsilon^{-}) a_\alpha \int_{O_{\mathrm{s}}} \mathrm{d}\mathbf{r}'_\parallel \exp\left[\frac{\mathrm{i}n^{-}\omega}{2r}\left(r_\parallel'^2 - (\hat{\mathbf{r}}\cdot\mathbf{r}'_\parallel)^2\right)\right] f(\mathbf{r}'_\parallel)$$

$$, \text{ for } \alpha = \mathrm{s,p}, \tag{A.9}$$

where

$$a_{\mathrm{s}} = (t_{\mathrm{s}}^{(0)})^2 \quad \text{and} \quad a_{\mathrm{p}} = (t_{\mathrm{p}}^{(0)})^2(\cos^2\theta_{\mathrm{t}} - \sin^2\theta). \tag{A.10}$$

We note that in the forward direction the first non-vanishing term in the exponential is quadratic in $\mathbf{r}'_\parallel$.

The correlation matrix thus becomes

$$\langle (r_\alpha - \langle r_\alpha \rangle)(r_{\alpha'} - \langle r_{\alpha'} \rangle) \rangle = \frac{\omega^4}{16\pi^2 r^2}(\epsilon^{+} - \epsilon^{-})^2 a_\alpha a_{\alpha'} I, \tag{A.11}$$

where the integral is given by

$$\begin{aligned} I &= \int_{O_{\mathrm{s}}} \mathrm{d}\mathbf{r}'_\parallel \int_{O_{\mathrm{s}}} \mathrm{d}\mathbf{r}''_\parallel S(\mathbf{r}'_\parallel - \mathbf{r}''_\parallel) \exp\left\{\frac{\mathrm{i}n^{-}\omega}{2r}\left[(\mathbf{r}'_\parallel)^2 - (\hat{\mathbf{r}}\cdot\mathbf{r}'_\parallel)^2 + (\mathbf{r}''_\parallel)^2 - (\hat{\mathbf{r}}\cdot\mathbf{r}''_\parallel)^2\right]\right\} \\ &= (2\pi)^{-2} \int \mathrm{d}\mathbf{k}_\parallel\, S(\mathbf{k}_\parallel) J^2(\mathbf{k}_\parallel) \end{aligned} \tag{A.12}$$

Here J is defined by

$$J(\mathbf{k}_\parallel) \equiv \int_{O_{\mathrm{s}}} \mathrm{d}\mathbf{r}'_\parallel \exp\left\{-\mathrm{i}\mathbf{k}_\parallel\cdot\mathbf{r}'_\parallel + \frac{\mathrm{i}n^{-}\omega}{2r}\left[(\mathbf{r}'_\parallel)^2 - (\hat{\mathbf{r}}\cdot\mathbf{r}'_\parallel)^2\right]\right\}. \tag{A.13}$$

We shall now take O_s to be a square. One then has

$$J(\boldsymbol{k}_\parallel) = \int_{-d}^{d} \mathrm{d}x \exp\left\{-\mathrm{i}\left[k_x x - \frac{1}{2}\frac{n^- \omega}{r} x^2 \cos^2\theta\right]\right\}$$

$$\times \int_{-d}^{d} \mathrm{d}y \exp\left\{-\mathrm{i}\left[k_y y - \frac{1}{2}\frac{n^- \omega}{r} y^2\right]\right\}$$

$$= \exp\left\{-\frac{\mathrm{i}r}{2n^- \omega}\left[\frac{k_x^2}{\cos^2\theta} + k_y^2\right]\right\} \int_{-d}^{d} \mathrm{d}x \exp\left\{\frac{\mathrm{i}n^- \omega \cos^2\theta}{2r}\left(x - \frac{rk_x}{n^- \omega \cos^2\theta}\right)^2\right\}$$

$$\times \int_{-d}^{d} \mathrm{d}y \exp\left\{\frac{\mathrm{i}n^- \omega}{2r}\left(y - \frac{rk_y}{n^- \omega}\right)^2\right\}.$$

Substitution of

$$s \equiv \left(\frac{n^- \omega \cos^2 \omega}{2r}\right)^{1/2}\left(x - \frac{rk_x}{n^- \omega \cos^2\theta}\right) \quad \text{and} \quad v \equiv \left(\frac{n^- \omega}{2r}\right)^{1/2}\left(y - \frac{rk_y}{n^- \omega}\right)$$

reduces J to

$$J(\boldsymbol{k}_\parallel) = \frac{2r}{n^- \omega \cos\theta} \exp\left\{-\frac{\mathrm{i}r}{2n^- \omega}\left[\frac{k_x^2}{\cos^2\theta} + k_y^2\right]\right\} \int_{s_-}^{s_+} \mathrm{d}s\, \mathrm{e}^{\mathrm{i}s^2} \int_{v_-}^{v_+} \mathrm{d}v\, \mathrm{e}^{\mathrm{i}v^2}, \qquad \text{(A.14)}$$

where

$$s_\pm \equiv \pm d\left(\frac{n^- \omega \cos^2\theta}{2r}\right)^{1/2} - k_x\left(\frac{r}{2n^- \omega \cos^2\theta}\right)^{1/2}$$

$$v_\pm = \pm d\left(\frac{n^- \omega}{2r}\right)^{1/2} - k_x\left(\frac{r}{2n^- \omega}\right)^{1/2}.$$

Using the experimental values of the various quantities[1]) we have $|s_\pm|$ and $|v_\pm|$ larger than 5. For such values one may extend the limits of the integration to infinity making only a small error. One then obtains

$$J(\boldsymbol{k}_\parallel) = \frac{2\pi \mathrm{i}r}{n^- \omega \cos\theta} \exp\left\{-\frac{\mathrm{i}r}{2n^- \omega}\left[\frac{k_x^2}{\cos^2\theta} + k_y^2\right]\right\}. \qquad \text{(A.15)}$$

Substitution in eq. (A.12) gives

$$I = -\left(\frac{r}{n^- \omega \cos\theta}\right)^2 \int \mathrm{d}\boldsymbol{k}_\parallel S(\boldsymbol{k}_\parallel) \exp\left\{-\frac{\mathrm{i}r}{n^- \omega}\left[\frac{k_x^2}{\cos^2\theta} + k_y^2\right]\right\}. \qquad \text{(A.16)}$$

Using S as given in eq. (5.14) the imaginary part of I becomes

$$\mathrm{Im}\, I = \frac{k_\mathrm{B}T}{2\sigma}\left(\frac{r}{n^{-}\omega \cos\theta}\right)^2 \int_0^{2\pi} \mathrm{d}\phi \int_0^{\infty} \mathrm{d}k_\parallel^2 (k_\parallel^2 + l^{-2})^{-1}$$

$$\times \sin\Big\{\frac{rk_\parallel^2}{n^{-}\omega}\Big[\frac{\sin^2\phi}{\cos^2\theta} + \cos^2\phi\Big]\Big]\Big\}. \qquad \text{(A.17)}$$

For the experimental values of the various quantities¹) l^{-2} is sufficiently small compared to $(n^{-}\omega/r)$ to replace l^{-2} in good approximation by zero. The resulting integrals are simple and one obtains

$$\mathrm{Im}\, I = \tfrac{1}{2}\pi^2(k_\mathrm{B}T/\sigma)(r/n^{-}\omega\cos\theta)^2. \qquad \text{(A.18)}$$

This equation together with eq. (A.11) gives eq. (6.5). Note that $c = 1$ was used in the appendix.

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ELECTRIC AND MAGNETIC SUSCEPTIBILITIES FOR A FLUID–FLUID INTERFACE

II. CRITICAL BEHAVIOUR

1. Introduction

In a previous paper[1]), called hereafter I, we studied the electromagnetic properties of a fluid–fluid interface using interfacial constitutive coefficients. Expressions for these coefficients were given in terms of the height–height correlation function. In the subsequent calculation of these coefficients we used for this correlation function the one given by the capillary wave-model[2,3]). In paper I we restricted ourselves to systems far from the critical point and considered the ellipsometric coefficient in particular.

When one approaches the critical point there are two phenomena of interest in this case. In the first place the interface becomes more diffuse and in the second place the bulk correlation length increases. As a consequence the transmission and reflection amplitudes become rather different from the Fresnel values for a sharp interface. In the usual analysis of this problem[4,5,6]) one uses the average profile but neglects modifications due to correlations. In our analysis these correlations are taken into account.

The method using interfacial constitutive coefficients does assume that the wavelength of the incident light is larger than the thickness of the average density profile. Very close to the critical point this is no longer correct (see in this context section 3).

In the rest of this section we present the formulae for the constitutive coefficients derived partly in paper I and in section 2 of this paper. The resulting reflection and transmission amplitudes are also given. In section 3 we compare our results with expressions obtained using the average dielectric constant profile. In the last section the various contributions are analysed in detail for cyclohexane–aniline and a comparison is made with experimental results by Beaglehole[7]).

The equilibrium position of the dividing surface is assumed to be flat and the x–y plane is chosen along this surface. The electromagnetic properties of the fluctuating interface can be described in terms of equilibrium averages of the interfacial excess polarisation and magnetisation, $\boldsymbol{P}^s(x, y, t)$ and $\boldsymbol{M}^s(x, y, t)$ respectively. In paper I we have shown that $\boldsymbol{P}^s$ and $\boldsymbol{M}^s$ can be expressed in terms of half the sum of the limits of the bulk fields (indicated by a subindex +) at the equilibrium dividing surface

$$\boldsymbol{P}^s = \boldsymbol{\xi} \cdot (E_x, E_y, D_z)_+ - \tau \frac{1}{c} \hat{\boldsymbol{z}} \wedge \frac{\partial}{\partial t} \boldsymbol{H}_+, \tag{1.1}$$

$$\boldsymbol{M}^s = -\tau \frac{1}{c} \hat{\boldsymbol{z}} \wedge \frac{\partial}{\partial t} \boldsymbol{E}_+, \tag{1.2}$$

where $\hat{\boldsymbol{z}} = (0, 0, 1)$ is the normal on the equilibrium interface and c is the velocity of light. The coefficient τ couples $\boldsymbol{P}^s$ to the time derivative of the bulk magnetic field $\boldsymbol{H}$ and $\boldsymbol{M}^s$ to the time derivative of the bulk electric field $\boldsymbol{E}$. The dielectric susceptibility tensor of the interface $\boldsymbol{\xi}$ couples the interfacial excess polarisation to the parallel components of the bulk electric field and the normal component of the bulk displacement field $\boldsymbol{D}$. In general τ and $\boldsymbol{\xi}$ are functions of frequency and wavevector $\boldsymbol{k}_{//} = (k_x, k_y, 0)$ parallel to the x–y plane. Because of rotational symmetry around the z-axis and translational symmetry, $\boldsymbol{\xi}$ is an isotropic tensor with the general form

$$\begin{aligned}\boldsymbol{\xi}(\boldsymbol{k}_{//}, \omega) = {} & \gamma_{\text{l}}(k_{//}, \omega)\hat{\boldsymbol{k}}_{//}\hat{\boldsymbol{k}}_{//} + \gamma_{\text{tr}}(k_{//}, \omega)(1 - \hat{\boldsymbol{k}}_{//}\hat{\boldsymbol{k}}_{//} - \hat{\boldsymbol{z}}\hat{\boldsymbol{z}}) \\ & + \beta(k_{//}, \omega)\hat{\boldsymbol{z}}\hat{\boldsymbol{z}} + \mathrm{i}\, \delta(k_{//}, \omega)(\hat{\boldsymbol{z}}\boldsymbol{k}_{//} - \boldsymbol{k}_{//}\hat{\boldsymbol{z}}),\end{aligned} \tag{1.3}$$

where

$$k_{//} \equiv |\boldsymbol{k}_{//}| \quad \text{and} \quad \hat{\boldsymbol{k}}_{//} \equiv \boldsymbol{k}_{//}/k_{//}$$

In the next section we will show, using general expressions for $\boldsymbol{\xi}$ and τ derived in paper I, that the coefficients γ_{l}, γ_{tr}, β and δ can be expressed in terms of the position autocorrelation function of the interface $S(k_{//})$ in the following way:

$$\begin{aligned}\gamma_{\text{l}}(k_{//}, \omega) = \hat{\boldsymbol{k}}_{//} \cdot \boldsymbol{\xi} \cdot \hat{\boldsymbol{k}}_{//} = {} & \frac{\mathrm{i}}{(2\pi)^2} (\epsilon^+ - \epsilon^-)^2 \int \mathrm{d}\boldsymbol{k}'_{//}\, S(|\boldsymbol{k}_{//} - \boldsymbol{k}'_{//}|) \\ & \times \left\{\cos^2 \phi \, \frac{q_\perp^+ q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+} + \sin^2 \phi \, \frac{(\omega/c)^2}{q_\perp^+ + q_\perp^-}\right\},\end{aligned}$$

$$\gamma_{\mathrm{tr}}(k_{//}, \omega) = \hat{k}_{\mathrm{tr}} \cdot \xi \cdot \hat{k}_{\mathrm{tr}} = \frac{\mathrm{i}}{(2\pi)^2} (\epsilon^+ - \epsilon^-)^2 \int \mathrm{d}\boldsymbol{k}'_{//}\, S(|\boldsymbol{k}_{//} - \boldsymbol{k}'_{//}|)$$

$$\times \left\{ \sin^2\phi \, \frac{q_\perp^+ q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+} + \cos^2\phi \, \frac{(\omega/c)^2}{q_\perp^+ + q_\perp^-} \right\},$$

$$\beta(k_{//}, \omega) = \hat{z} \cdot \xi \cdot \hat{z} = \frac{\mathrm{i}}{(2\pi)^2} \frac{(\epsilon^+ - \epsilon^-)^2}{\epsilon^+ \epsilon^-} \int \mathrm{d}\boldsymbol{k}'_{//}\, S(|\boldsymbol{k}_{//} - \boldsymbol{k}'_{//}|) \frac{k'^2_{//}}{\epsilon^+ q_\perp^- + \epsilon^- k_\perp^+}, \tag{1.4}$$

$$\delta(k_{//}, \omega) = \hat{z} \cdot \xi \cdot \hat{k}_{//} (\mathrm{i}k_{//})^{-1} = \frac{\epsilon^+ - \epsilon^-}{(2\pi)^2 k_{//}} \int \mathrm{d}\boldsymbol{k}'_{//}\, S(|\boldsymbol{k}_{//} - \boldsymbol{k}'_{//}|) k'_{//} \cos\phi \, \frac{q_\perp^+ + q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+},$$

$$\tau(k_{//}, \omega) = \tfrac{1}{2}(\epsilon^+ - \epsilon^-) \frac{1}{(2\pi)^2} \int \mathrm{d}\boldsymbol{k}'_{//}\, S(|\boldsymbol{k}_{//} - \boldsymbol{k}'_{//}|),$$

where $\hat{k}_{\mathrm{tr}} \equiv (\hat{k}_y, -\hat{k}_x, 0)$ is a unit vector in the x–y plane orthogonal to $\hat{k}_{//}$ and $q_\perp^\pm \equiv (\epsilon^\pm(\omega/c)^2 - k'^2_{//})^{1/2}$. ϵ^+ and ϵ^- are the dielectric constants of the two fluid phases and ϕ is the angle between $\boldsymbol{k}_{//}$ and $\boldsymbol{k}'_{//}$ ($\hat{k}_{//} \cdot \hat{k}'_{//} \equiv \cos\phi$).

We will use the usual equilibrium position autocorrelation function^{3})

$$S(k_{//}) = \frac{k_{\mathrm{B}}T}{\sigma k_{//}^2 + g|\rho^+ - \rho^-|} = \frac{k_{\mathrm{B}}T/g|\rho^+ - \rho^-|}{1 + k_{//}^2 l^2}, \tag{1.5}$$

where k_{B} is the Boltzmann's constant, T is the temperature, σ is the surface tension, g is the gravitational acceleration, ρ^+ and ρ^- are the densities of the fluid phases and $l \equiv (\sigma/g|\rho^+ - \rho^-|)^{1/2}$ is the capillary length.

In paper I we analysed ellipsometry in more detail. For that case it is sufficient to calculate the real parts of γ_{l}, γ_{tr} and β for zero wavevector and frequency. They are found to be given by

$$\mathrm{Re}\,\gamma_{\mathrm{l}} = \mathrm{Re}\,\gamma_{\mathrm{tr}} = -\tfrac{1}{2}\epsilon^+\epsilon^-\,\mathrm{Re}\,\beta = -\frac{k_{\mathrm{B}}T}{4\pi\sigma} \frac{(\epsilon^+ - \epsilon^-)^2}{\epsilon^+ + \epsilon^-} k_{\mathrm{m}}, \tag{1.6}$$

$$\tau = \frac{k_{\mathrm{B}}T}{4\pi\sigma} (\epsilon^+ - \epsilon^-) \ln(l k_{\mathrm{m}}). \tag{1.7}$$

Here k_m is the upper limit of the integration over the wavevector and may be interpreted as 2π divided by the intrinsic thickness of the interface, cf. section 3 in this context.

Later in this section we will see that reflectivity, transmittivity and the loss of energy due to scattering contain imaginary parts of γ_{l}, γ_{tr} and β and the real parts of δ and τ. In some recent measurements by Beaglehole^{7}) of the reflectivity near the critical point the angular dependence seems to suggest that the modification of the reflectivity due to scattering is important. These experiments motivated us to calculate these modifications in the present paper. In the next section we derive the following approximate expressions for $\mathrm{Im}\,\gamma_l$, $\mathrm{Im}\,\gamma_{tr}$, $\mathrm{Im}\,\beta$ and $\mathrm{Re}\,\delta$ for optical values of $k_{/\!/}$ and ω:

$$\begin{aligned}
\mathrm{Im}\,\gamma_l &\approx \frac{k_B T}{2\pi\sigma}(\epsilon^+ - \epsilon^-)^2 \frac{k_\perp^+ k_\perp^-}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+} \ln(l k_\perp^-), \\
\mathrm{Im}\,\gamma_{tr} &\approx \frac{k_B T}{2\pi\sigma}(\epsilon^+ - \epsilon^-)^2 \frac{(\omega/c)^2}{k_\perp^+ + k_\perp^-} \ln(l k_\perp^-), \\
\mathrm{Im}\,\beta &\approx \frac{k_B T}{2\pi\sigma} \frac{(\epsilon^+ - \epsilon^-)^2}{\epsilon^+ \epsilon^-} \frac{k_{/\!/}^2}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+} \ln(l k_\perp^-), \\
\delta \approx \mathrm{Re}\,\delta &\approx \frac{k_B T}{2\pi\sigma}(\epsilon^+ - \epsilon^-)\left[\frac{k_\perp^+ + k_\perp^-}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+} \ln(l k_\perp^-) + \frac{2}{\epsilon^+ + \epsilon^-} \ln\left(\frac{c k_m}{\omega}\right)\right],
\end{aligned} \tag{1.8}$$

where $k_\perp^\pm = (\epsilon^\pm(\omega/c)^2 - k_{/\!/}^2)^{1/2}$. The approximations were made assuming that $\epsilon^- < \epsilon^+$ and that the light was incident from the (−) phase into the (+) phase. If $\epsilon^- > \epsilon^+$ one must replace $\ln(l k_\perp^-)$ by $\ln(l k_\perp^+)$ as this logarithm should contain the normal component of the wavevector corresponding to the medium with the lowest optical density. For the detailed derivation of eq. (1.8) and comparison with the values obtained by numerical integration we refer to chapters 2 and 3. The approximation is usually good within a few percent except for $\mathrm{Im}\,\beta$ for small angles of incidence. For such angles β is not very important anyway. In the case of normal incidence, where one needs the susceptibilities for $k_{/\!/} = 0$, the integrals in eq. (1.4) simplify considerably and one obtains

$$\begin{aligned}
\mathrm{Im}\,\gamma_l(k_{/\!/} = 0) &= \mathrm{Im}\,\gamma_{tr}(k_{/\!/} = 0) \\
&= \frac{k_B T}{4\pi\sigma} \frac{\epsilon^+ - \epsilon^-}{\epsilon^+ + \epsilon^-} \frac{\omega}{c} \Big\{ -(\epsilon^+ + \epsilon^-)(n^+ - n^-) - \epsilon^+ n^+ + \epsilon^- n^- \\
&\quad + 2(\epsilon^+ + \epsilon^-)\left[n^+ \ln\left(2n^+ \frac{\omega}{c} l\right) - n^- \ln\left(2n^- \frac{\omega}{c} l\right)\right] \\
&\quad + \tfrac{1}{2} \frac{\epsilon^+ \epsilon^-}{\sqrt{\epsilon^+ + \epsilon^-}} \left[\ln \frac{\sqrt{\epsilon^+ + \epsilon^-} - n^+}{\sqrt{\epsilon^+ + \epsilon^-} + n^+} - \ln \frac{\sqrt{\epsilon^+ + \epsilon^-} - n^-}{\sqrt{\epsilon^+ + \epsilon^-} + n^-}\right]\Big\}.
\end{aligned} \tag{1.9}$$

There is no need to calculate $\mathrm{Im}\,\beta$ and $\mathrm{Re}\,\delta$ for normal incidence because of the fact that they do not contribute in that case.

Using eq. (1.1) and (1.2) and the boundary conditions at the dividing surface, *cf.* eq. (I.2.1), we can calculate the reflected and transmitted amplitudes of the electric field analogous to the analysis in paper I. If the polarisation of the incident beam is normal to the plane of incidence one finds for the reflected and transmitted amplitudes to the first order in the constitutive coefficients

$$\begin{aligned}
r_s &= r_s^0 + (\omega/c)^2 \tau (1 - (r_s^0)^2) + \tfrac{1}{2}\mathrm{i}\, \gamma_{tr}(\omega/c n^- \cos\theta)(t_s^0)^2, \\
t_s &= t_s^0 - (\omega/c)^2 \tau r_s^0 t_s^0 + \tfrac{1}{2}\mathrm{i}\, \gamma_{tr}(\omega/c n^- \cos\theta)(t_s^0)^2.
\end{aligned} \tag{1.10}$$

Here r_s^0 and t_s^0 are the Fresnel amplitudes.

$$\begin{aligned} r_s^0 &= (n^- \cos\theta - n^+ \cos\theta_t)/(n^- \cos\theta + n^+ \cos\theta_t), \\ t_s^0 &= 2n^- \cos\theta/(n^- \cos\theta + n^+ \cos\theta_t) = 1 + r_s^0. \end{aligned} \tag{1.11}$$

θ and θ_t are the angles of incidence and transmission and $n^\pm \equiv \sqrt{\epsilon^\pm}$ are refractive indices of the fluid phases. The resulting expressions for the reflectivities and transmittivities to the first order in the constitutive coefficients are

$$\begin{aligned} R_s \equiv |r_s|^2 = R_s^0 \Big[& 1 - 8\left(\frac{\omega}{c}\right)^2 \tau n^+ n^- \cos\theta \cos\theta_t/(\epsilon^+ - \epsilon^-) \\ & + 4\frac{\omega}{c} \operatorname{Im} \gamma_{tr} n^- \cos\theta/(\epsilon^+ - \epsilon^-)\Big], \end{aligned} \tag{1.12}$$

$$T_s \equiv \frac{n^+ \cos\theta_t}{n^- \cos\theta} |t_s|^2 = T_s^0 \Big[1 - 2\left(\frac{\omega}{c}\right)^2 \tau r_s^0 - \frac{\omega}{c} (\operatorname{Im} \gamma_{tr}/n^- \cos\theta) t_s^0\Big].$$

The loss of energy due to scattering is the difference between the incident energy (put equal to unity in our analysis) and the reflected and transmitted energy. Consequently, using eq. (1.11) one finds

$$Q_s \equiv 1 - R_s - T_s = \frac{\omega}{c} \operatorname{Im} \gamma_{tr} (t_s^0)^2/n^- \cos\theta. \tag{1.13}$$

A similar analysis for the case that the polarisation is parallel to the plane of incidence yields

$$\begin{aligned} r_p = r_p^0 - & \left(\frac{\omega}{c}\right)^2 (\tau - \epsilon^- \delta \sin^2\theta)(1 - (r_p^0)^2) - \tfrac{1}{2}\mathrm{i}(\omega/cn^- \cos\theta) \\ & \times (\gamma_l \cos^2\theta_t - \beta\epsilon^+\epsilon^- \sin^2\theta)(t_p^0)^2, \\ t_p = t_p^0 + & \left(\frac{\omega}{c}\right)^2 (\tau - \epsilon^- \delta \sin^2\theta) r_p^0 t_p^0 + \tfrac{1}{2}\mathrm{i}(\omega/cn^- \cos\theta)(\gamma_l \cos\theta \cos\theta_t \\ & + \beta\epsilon^+\epsilon^- \sin\theta \sin\theta_t)(t_p^0)^2, \end{aligned} \tag{1.14}$$

where r_p^0 and t_p^0 are Fresnel amplitudes,

$$\begin{aligned} r_p^0 &= (n^+ \cos\theta - n^- \cos\theta_t)/(n^+ \cos\theta + n^- \cos\theta_t), \\ t_p^0 &= 2n^- \cos\theta/(n^+ \cos\theta + n^- \cos\theta_t) = (n^-/n^+)(r_p^0 + 1). \end{aligned} \tag{1.15}$$

From eq. (1.14) one finds for the reflectivity and transmittivity

$$\begin{aligned} R_p \equiv |r_p|^2 = R_p^0 \Big[& 1 - 2\left(\frac{\omega}{c}\right)^2 (\tau - \epsilon^- \delta \sin^2\theta)((t_p^0)^2/r_p^0) \frac{n^+ \cos\theta_t}{n^- \cos\theta} \\ & + (\omega/cn^- \cos\theta)(\operatorname{Im} \gamma_l \cos^2\theta_t - \operatorname{Im} \beta\, \epsilon^+\epsilon^- \sin^2\theta)((t_p^0)^2/r_p^0)\Big], \end{aligned} \tag{1.16}$$

$$T_p \equiv \frac{n^+ \cos\theta_t}{n^- \cos\theta} |t_p|^2 = T_p^0 \Big[1 + 2\Big(\frac{\omega}{c}\Big)^2 r_p^0 (\tau - \epsilon^- \delta \sin^2\theta)$$

$$- \frac{\omega}{c} t_p^0 (\mathrm{Im}\, \gamma_l \cos\theta \cos\theta_t + \mathrm{Im}\, \beta \epsilon^+ \epsilon^- \sin\theta \sin\theta_t)/n^- \cos\theta \Big].$$

Consequently the loss of energy due to scattering is

$$Q_p \equiv 1 - R_p - T_p = \frac{\omega}{c} ((t_p^0)^2/n^- \cos\theta)(\mathrm{Im}\, \gamma_1 \cos^2\theta_t + \mathrm{Im}\, \beta \epsilon^+ \epsilon^- \sin^2\theta). \tag{1.17}$$

We note that eqs. (1.10)–(1.17) were derived in the case of light incident from the (−) phase into the (+) phase.

2. The interfacial constitutive coefficients in the case of frequency and spacial dispersion

We have shown in paper I that the susceptibility tensor can be expressed in terms of the position autocorrelation function of the interface as*), *cf.* eq. (I.5.13),

$$\boldsymbol{\xi}(\boldsymbol{k}_{/\!/}, \omega) = - \sum_{\nu,\nu'=\pm} \nu\nu' \boldsymbol{\Pi}^{\nu} \cdot (2\pi)^{-2} \int \mathrm{d}\boldsymbol{k}'_{/\!/}\, S(|\boldsymbol{k}_{/\!/} - \boldsymbol{k}'_{/\!/}|)$$

$$\times \boldsymbol{K}_0(\boldsymbol{k}'_{/\!/}, z = \nu 0, \omega | z' = 0) \cdot \boldsymbol{\Pi}^{\nu'}, \tag{2.1}$$

where

$$\boldsymbol{\Pi}^{\nu} \equiv \begin{pmatrix} \epsilon^{\nu} & 0 & 0 \\ 0 & \epsilon^{\nu} & 0 \\ 0 & 0 & -1/\epsilon^{\nu} \end{pmatrix}.$$

$\boldsymbol{K}_0$ is the propagator giving the (E_x, E_y, D_z) fields in the bulk media due to a polarisation density and contains all effects due to reflection and transmission by the interface in its equilibrium position. The general expression for $\boldsymbol{K}_0$ is given in ref. 8. In the present case we only need $\boldsymbol{K}_0(\boldsymbol{k}_{/\!/}, z = \nu 0, \omega | z' = 0)$ which gives the limits of the fields at the equilibrium dividing surface (lim $z \downarrow 0$ for $\nu = +$ and lim $z \uparrow 0$ for $\nu = -$) due to sources located on the dividing surface. In this limit the propagator describes the electromagnetic interaction along the

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* We note that the general expression for $\boldsymbol{K}_0$ contains a term proportional to sign($z - z'$). While this term did not contribute to the terms calculated in paper I, it leads in the present paper to δ. This is the reason to write $z = \nu 0$ which is meant to imply sign $(z - z') = \nu$ in eq. (2.1) while we wrote $z = 0$ in eq. (I.5.13). Furthermore $\boldsymbol{K}_0$ contains Fresnel reflectivities. One may use a more general form with reflectivities containing the interfacial constitutive coefficients ξ and τ. As we always linearise in these coefficients this may be neglected.

interface and is given by

$$\boldsymbol{K}_0(\boldsymbol{k}_{/\!/}, z = \nu 0, \omega | z' = 0) = -\mathrm{i}\frac{k_\perp^+ k_\perp^-}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+}\hat{\boldsymbol{k}}_{/\!/}\hat{\boldsymbol{k}}_{/\!/} - \frac{\mathrm{i}(\omega/c)^2}{k_\perp^+ + k_\perp^-}(1 - \hat{\boldsymbol{k}}_{/\!/}\hat{\boldsymbol{k}}_{/\!/} - \hat{\boldsymbol{z}}\hat{\boldsymbol{z}})$$
$$- \mathrm{i}\frac{\epsilon^+\epsilon^- k_{/\!/}^2}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+}\hat{\boldsymbol{z}}\hat{\boldsymbol{z}} + \frac{\mathrm{i}\nu}{\epsilon^+ k_\perp^- + \epsilon^- k_\perp^+}(\epsilon^{-\nu} k_\perp^{\nu} \boldsymbol{k}_{/\!/}\hat{\boldsymbol{z}} + \epsilon^{\nu} k_\perp^{-\nu}\hat{\boldsymbol{z}}\boldsymbol{k}_{/\!/}). \tag{2.2}$$

This summation over ν and ν' in eq. (2.1) can now be carried out and one obtains

$$\boldsymbol{\xi}(\boldsymbol{k}_{/\!/}, \omega) = \mathrm{i}(2\pi)^{-2}\int \mathrm{d}\boldsymbol{k}'_{/\!/}\, S(|\boldsymbol{k}_{/\!/} - \boldsymbol{k}'_{/\!/}|)\Big\{\Big[\frac{q_\perp^+ q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+}\hat{\boldsymbol{k}}'_{/\!/}\hat{\boldsymbol{k}}'_{/\!/}$$
$$+ \frac{(\omega/c)^2}{q_\perp^+ + q_\perp^-}(1 - \hat{\boldsymbol{k}}'_{/\!/}\hat{\boldsymbol{k}}'_{/\!/} - \hat{\boldsymbol{z}}\hat{\boldsymbol{z}})\Big](\epsilon^+ - \epsilon^-)^2$$
$$+ \frac{k'^2_{/\!/}}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+}\hat{\boldsymbol{z}}\hat{\boldsymbol{z}}\frac{(\epsilon^+ - \epsilon^-)^2}{\epsilon^+\epsilon^-} + \frac{q_\perp^+ + q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+}$$
$$\times (\hat{\boldsymbol{z}}\boldsymbol{k}'_{/\!/} - \boldsymbol{k}'_{/\!/}\hat{\boldsymbol{z}})(\epsilon^+ - \epsilon^-)\Big\}. \tag{2.3}$$

Formulae (1.4) follow immediately from this expression.

We shall now proceed to derive the approximations given in eq. (1.8). Substituting the explicit expression (1.5) for the correlation function into eq. (1.4), one may perform the integration over the angle variable. This gives

$$\gamma_l(k_{/\!/}, \omega) = \frac{\mathrm{i}k_\mathrm{B}T}{2\pi\sigma}(\epsilon^+ - \epsilon^-)^2 \int_0^{k_m} \frac{\mathrm{d}k'_{/\!/}k'_{/\!/}}{k'^2_{/\!/} + k^2_{/\!/} + l^{-2}}\frac{1}{b^2}$$
$$\times \Big\{\Big(\frac{1}{\sqrt{1 - b^2}} - 1\Big)\frac{q_\perp^+ q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+} + (1 - \sqrt{1 - b^2})\frac{(\omega/c)^2}{q_\perp^+ + q_\perp^-}\Big\},$$

$$\gamma_{tr}(k_{/\!/}, \omega) = \frac{\mathrm{i}k_\mathrm{B}T}{2\pi\sigma}(\epsilon^+ - \epsilon^-)^2 \int_0^{k_m} \frac{\mathrm{d}k'_{/\!/}k'_{/\!/}}{k'^2_{/\!/} + k^2_{/\!/} + l^{-2}}\frac{1}{b^2}$$
$$\times \Big\{(1 - \sqrt{1 - b^2})\frac{q_\perp^+ q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+} + \Big(\frac{1}{\sqrt{1 - b^2}} - 1\Big)\frac{(\omega/c)^2}{q_\perp^+ + q_\perp^-}\Big\},$$

$$\beta(k_{/\!/}, \omega) = \frac{\mathrm{i}k_\mathrm{B}T}{2\pi\sigma}\frac{(\epsilon^+ - \epsilon^-)^2}{\epsilon^+\epsilon^-}\int_0^{k_m} \frac{\mathrm{d}k'_{/\!/}k'^3_{/\!/}}{k'^2_{/\!/} + k^2_{/\!/} + l^{-2}}\frac{1}{\sqrt{1 - b^2}}\frac{1}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+}, \tag{2.4}$$

$$\delta(k_{/\!/}, \omega) = \frac{k_\mathrm{B}T}{2\pi\sigma k_{/\!/}}(\epsilon^+ - \epsilon^-)\int_0^{k_m} \frac{\mathrm{d}k'_{/\!/}k'^2_{/\!/}}{k'^2_{/\!/} + k^2_{/\!/} + l^{-2}}\frac{1}{b}\Big(\frac{1}{\sqrt{1 - b^2}} - 1\Big)\frac{q_\perp^+ + q_\perp^-}{\epsilon^+ q_\perp^- + \epsilon^- q_\perp^+},$$

where

$$b = \frac{2k_{/\!/}k'_{/\!/}}{k'^{2}_{/\!/} + k^2_{/\!/} + l^{-2}}.$$

These expressions may be evaluated by numerical integration for arbitrary $k_{/\!/}$ and ω. Using the fact that ω and $k_{/\!/}$ are in the optical range one may, however, derive approximate expressions.

The approximation is based on the fact that $l^{-1} \ll \omega/c \ll k_m$. Note that $k_{/\!/}$ is of the same order of magnitude as ω/c. Very close to the critical point this inequality is no longer valid. In that case many aspects of our analysis should be improved on anyway. We now introduce the following dimensionless parameters

$$\begin{aligned} &s \equiv c^2 k'^{2}_{/\!/}/\epsilon^- \omega^2, \quad s_0 \equiv c^2 k^2_{/\!/}/\epsilon^- \omega^2, \quad s_m \equiv c^2 k^2_m/\epsilon^- \omega^2, \\ &s_l \equiv c^2/l^2 \epsilon^- \omega^2, \quad \Delta \equiv \epsilon^+/\epsilon^-. \end{aligned} \tag{2.5}$$

The expression for γ_l in terms of these parameters becomes

$$\begin{aligned} \gamma_l(k_{/\!/}, \omega) = \mathrm{i}\frac{k_B T}{16\pi\sigma}(\epsilon^+ - \epsilon^-)^2 \frac{n^-\omega^3}{k^2_{/\!/} c^3} \int_0^{s_m} \frac{\mathrm{d}s}{s}\left(s + s_0 + s_l - \sqrt{(s + s_0 + s_l)^2 - 4ss_0}\right) \\ \times \left[\frac{s + s_0 + s_l}{\sqrt{(s + s_0 + s_l)^2 - 4ss_0}}\left(\frac{\sqrt{(1-s)(\Delta - s)}}{\Delta\sqrt{1-s} + \sqrt{\Delta - s}}\right) \right. \\ \left. + \frac{1}{\sqrt{1-s} + \sqrt{\Delta - s}}\right]. \end{aligned} \tag{2.6}$$

The expressions for γ_{lr}, β and δ are analogous but we will only discuss the approximation procedure for γ_l as the others may be done in the same way. The integral in eq. (2.6) is real for $s < 1$, complex for $1 < s < \Delta$ and imaginary for $\Delta < s$. The fact that $s_l \ll 1$ implies that the integrand in eq. (2.6) has a sharp maximum at $s \approx s_0 < 1$ since

$$\sqrt{(s + s_0 + s_l)^2 - 4ss_0}\Big|_{s=s_0} = \sqrt{s_l(4s_0 + s_l)} \approx \sqrt{4s_0 s_l}. \tag{2.7}$$

As $s_0 < 1$ this gives the dominant contribution to Im γ_l. Taking only the contribution due to this maximum one has

$$\begin{aligned} \operatorname{Im} \gamma_l(k_{/\!/}, \omega) \approx \frac{k_B T\omega}{4\pi\sigma n^- c}(\epsilon^+ - \epsilon^-)^2 \left(\frac{\sqrt{1-s_0}\sqrt{\Delta - s_0}}{\Delta\sqrt{1-s_0} + \sqrt{\Delta - s_0}}\right) \\ \times \int_0^1 \mathrm{d}s[(s + s_0 + s_l)^2 - 4ss_0]^{-1/2}. \end{aligned} \tag{2.8}$$

This integral can readily be performed and yields the expression given in eq.

(1.8). Numerical integration of the remaining contributions to Im γ_l for the case of liquid argon and cyclohexane-aniline binary mixture shows, that this approximation deviates from the exact expression at most a few percent for all temperatures under consideration as long as the angle of incidence ($\sin\theta = ck_{/\!/}/n^-\omega$) is not too close to 90°. For a more detailed discussion of how the approximated values for Im γ_l, Im γ_{tr}, Im β and Re δ compare with the values obtained numerically, in the case of cyclohexane-aniline, we refer to the next section.

The major contribution to the real part of γ_l is obtained for $s > \Delta$. For these values of s one may put s_l equal to zero in eq. (2.6) and the remaining integral can be evaluated exactly. This exact result is in very good approximation given by formula (1.6) obtained for zero wavevector and frequency, which was already obtained in paper I.

3. Comparison with expressions obtained from the average dielectric constant profile

In our analysis we accounted for correlations between the fluctuations of the dielectric constant and the resulting fluctuations of the electromagnetic fields. In the more usual calculation of the reflected and transmitted amplitudes one uses the average dielectric constant profile. In the context of the capillary wave model this profile is given by[3,4])

$$\langle\epsilon(z)\rangle = \langle\epsilon^-\theta(f(x,y)-z)+\epsilon^+\theta(z-f(x,y))\rangle = \epsilon^- + (\epsilon^+-\epsilon^-)\langle\theta(z-f(x,y))\rangle$$
$$= \tfrac{1}{2}(\epsilon^+ + \epsilon^-) + \tfrac{1}{2}(\epsilon^+ - \epsilon^-)\,\mathrm{erf}(z/L\sqrt{2}), \tag{3.1}$$

where $f(x, y)$ is the location of the fluctuating surface and, cf. eq. (1.5),

$$L^2 = \langle f^2(x,y)\rangle = \frac{1}{2\pi}\int_0^{k_m} \mathrm{d}k_{/\!/}\, k_{/\!/} S(k_{/\!/})$$
$$= \frac{k_B T}{4\pi\sigma}\ln(1+k_m^2 l^2) \approx \frac{k_B T}{2\pi\sigma}\ln(k_m l). \tag{3.2}$$

k_m is the cut off wavevector and may be interpreted as 2π divided by the intrinsic interface width[3,9]). This interpretation will be motivated later in this section. The error function is defined as $\mathrm{erf}\,x \equiv (2/\sqrt{\pi})\int_0^x e^{-s^2}\,\mathrm{d}s$. The average density or concentration profiles are given by similar expressions[3,4]).

One may now calculate r_p and r_s using $\langle\epsilon(z)\rangle$. The relevant expressions are given by Lekner[10]) until second order in L/λ. Comparing his expressions with our formulae, eq. (1.10) and (1.14), in terms of interfacial constitutive coefficients one may identify

$$\gamma = \int_{-\infty}^{\infty} (\langle\epsilon(z)\rangle - \epsilon_0(z))\,dz,$$

$$\beta = -\int_{-\infty}^{\infty} (\langle\epsilon(z)\rangle^{-1} - \epsilon_0^{-1}(z))\,dz = \frac{1}{\epsilon^{-}\epsilon^{+}}\int_{-\infty}^{\infty} dz\,\frac{(\epsilon^{-} - \langle\epsilon(z)\rangle)(\langle\epsilon(z)\rangle - \epsilon^{+})}{\langle\epsilon(z)\rangle},$$

$$\tau = -\int_{-\infty}^{\infty} z(\langle\epsilon(z)\rangle - \epsilon_0(z))\,dz, \tag{3.3}$$

$$\delta = \int_{-\infty}^{\infty} (\langle\epsilon(z)\rangle - \epsilon_0(z))\left[\frac{z}{\langle\epsilon(z)\rangle} + \int_{0}^{z}\frac{dz'}{\langle\epsilon(z')\rangle}\right]dz.$$

Here $\epsilon_0(z) \equiv \epsilon^{-}\theta(-z) + \epsilon^{+}\theta(z)$ is the profile which gives the Fresnel amplitudes. Clearly all these coefficients are real and therefore do not account for losses due to scattering. If one evaluates the coefficients using eq. (3.1) for $\langle\epsilon(z)\rangle$ one finds for τ exactly the same expression, eq. (1.7), as found in our analysis. All the other coefficients are different. If one considers our expression for τ, eq. (1.4), it is clear that τ is proportional to the average square displacement $\langle f^2\rangle$ of the surface. τ does not contain any electromagnetic interactions between fluctuations located at different points on the surface as the expressions, eq. (1.4), for γ, β and δ do. Because of this difference it is indeed to be expected that replacing the fluctuating profile by the average profile will not change τ to second order in L/λ but does effect γ, β and δ in that order.

Considering the reflectivity R_s for perpendicularly polarised light, we see that the result using the average profile only differs because it does not contain the term proportional to Im γ_{tr}, which accounts for losses due to scattering. As in most practical cases (see also section 4) these losses are comparatively small, one may usually neglect this term and only retain the term proportional to τ in R_s. For the reflectivity of s-polarised light the two approaches are therefore equivalent. The resulting expression is useful for the interpretation of experimental results if one is not too close to the critical point. If L/λ exceeds 2π close to the critical point, however, it is no longer correct to neglect contributions to the reflectivity of higher than second order in this parameter. In that case neither Lekner's nor our approach can be used. It is possible to give an expression for R for normally incident light using the average profile which is also correct for values of L/λ larger than 2π[4,5,6]). Using this expression one may conclude that the erf profile gives the best fit with the experimental data[6]).

The expressions for the reflectivity R_p in the two approaches are different. Again Im γ_I and Im β which appear in our expression, eq. (1.16), may usually be neglected. The term proportional to δ, however, is important in both cases, but the expression for δ is different. It should be emphasised that δ as given in eq. (1.3) depends on the frequency and the angle of incidence. If one would use the general expression of $\delta(k_{//}, \omega)$ in terms of the correlation function, eq. (1.4), (not the approximate one given in eq. (1.8)) and one takes the limit $k_{//} \rightarrow 0$ and $\omega \rightarrow 0$ one may show that

$$\lim_{k_{//}\rightarrow 0} \lim_{\omega \rightarrow 0} \delta(k_{//}, \omega) \simeq \frac{4}{\epsilon^+ + \epsilon^-} \tau = 2\left(\frac{\epsilon^+ - \epsilon^-}{\epsilon^+ + \epsilon^-}\right) L^2. \tag{3.4}$$

If one calculates δ using eq. (3.3) one also obtains an expression for δ proportional to L^2. As one may easily verify (using e.g. the value of the various coefficients for cyclohexane–aniline given in the next section) a much better approximation for δ for optical frequencies is the expression given in eq. (1.8). The resulting values are considerably smaller than the value given in eq. (3.4). In general the value of δ is not sufficiently large compared to τ to make δ very important for angles of incidence smaller than the Brewster angle θ_B. For angles of incidence larger than the Brewster angle δ becomes rather important.

Finally we consider the ellipsometric coefficient which is given by, cf. eq. (I.2.16),

$$\rho(\theta_B) = \tfrac{1}{2}\left(\frac{\omega}{c}\right) \frac{(\epsilon^+ + \epsilon^-)^{1/2}}{(\epsilon^+ - \epsilon^-)} (\mathrm{Re}\ \gamma_I - \epsilon^+\epsilon^-\ \mathrm{Re}\ \beta). \tag{3.5}$$

Substituting eq. (1.6) we obtain

$$\rho(\theta_B) = -\tfrac{3}{4}\left(\frac{\omega}{c}\right) \frac{(\epsilon^+ - \epsilon^-)}{(\epsilon^+ + \epsilon^-)^{1/2}} \left(\frac{k_B T}{\sigma}\right)\left(\frac{k_m}{2\pi}\right). \tag{3.6}$$

Comparing this expression with experimental results for argon and CCl_4[11]) one finds values for $(2\pi/k_m)$ which are approximately $1\frac{1}{2}$ times the diameter of the particles. These results are consistent with the interpretation of $(2\pi/k_m)$ as the intrinsic thickness of the interface. It should be noted in this context that in both cases $\sqrt{k_B T/\sigma}$ is in the order of 20% smaller than $(2\pi/k_m)$. In Weeks' analysis[9]) the minimum column width is written as $K\sqrt{k_B T/\sigma}$ where K is a constant larger than unity. This minimum column width may be interpreted as intrinsic thickness l_I[12]) and one then has

$$l_I \equiv \frac{2\pi}{k_m} = K\sqrt{k_B T/\sigma}. \tag{3.7}$$

This relation implies that the intrinsic thickness diverges near the critical point in agreement with the more general form first proposed by Widom[17,18]).

If we substitute β as found using the average profile one finds

$$\rho(\theta_B) = -\tfrac{1}{2}\left(\frac{\omega}{c}\right)\frac{(\epsilon^+ + \epsilon^-)^{1/2}}{(\epsilon^+ - \epsilon^-)}\int_{-\infty}^{\infty} dz\, \frac{(\epsilon^- - \langle\epsilon(z)\rangle)(\langle\epsilon(z)\rangle - \epsilon^+)}{\langle\epsilon(z)\rangle}. \tag{3.8}$$

This is the well-known Drude formula[13]) for the ellipsometric coefficient. If one uses eq. (3.1) for the average profile one obtains

$$\rho(\theta_B) \approx \left(\frac{\omega}{c}\right)L = \frac{\omega}{c}\sqrt{\frac{k_B T}{2\pi\sigma}\ln k_m l}. \tag{3.9}$$

It is clear that our approach leads to an expression proportional to the intrinsic thickness of the profile while the other approach leads to an expression proportional to the thickness of the average profile. In our analysis all effects due to correlations have been taken into account (to second order). This is not the case if one uses the average profile. The ellipsometric coefficient brings out the difference between the two approaches most clearly and we conclude that the result obtained using the average profile is not correct for $\rho(\theta_B)$.

4. The cyclohexane–aniline binary mixture

In this section we shall evaluate the constitutive coefficients for the special case of the cyclohexane–aniline binary mixture. The results are compared with experimental results of Beaglehole[7]) obtained near the critical mixing point. In this experiment the light is incident on the surface from below.

We first consider the ellipsometric coefficient which is given by, cf. eqs. (3.6) and (3.7),

$$\rho(\theta_B) = -\tfrac{3}{4}\left(\frac{\omega}{c}\right)\frac{(\epsilon^+ - \epsilon^-)}{(\epsilon^+ + \epsilon^+)^{1/2}}\left(\frac{k_B T}{\sigma l_1}\right). \tag{4.1}$$

The dielectric constants are given near the critical point by Clausius–Mossotti in good approximation[14]) and one has in this case

$$\epsilon_c = n_c^2 = \tfrac{1}{2}(\epsilon^+ + \epsilon^-) = 2.2 \quad \text{and} \quad \epsilon^- - \epsilon^+ = 0.89\, t^{\beta}, \tag{4.2}$$

where the exponent equals $\beta = 0.34$. The behaviour of the surface tension close to the critical point is given by[15])

$$\sigma = \sigma_0 t^{\mu}, \tag{4.3}$$

where $t = (T_c - T)/T_c$. The value of the exponent is[15]) $\mu = 1.28$ while

$\sigma_0 = 66.8$ erg cm^{-2} (ref. 16) and $T_c = 28.45°$ C (ref. 7). The critical behaviour of the intrinsic interfacial thickness[17,18]) is

$$l_I = \frac{2\pi}{k_m} = l_{I,0} t^{-\nu}, \tag{4.4}$$

where $\nu = 0.64$ is the exponent for the bulk correlation length. The two exponents are related by[17,18]) $\mu = 2\nu$. Close to the critical point the ellipsometric coefficient may now be written as

$$\rho(\theta_B) = -0.32 \left(\frac{\omega}{c}\right) \frac{k_B T_c}{\sigma_0 l_{I,0}} t^{\beta - \mu + \nu}, \tag{4.5}$$

where the dielectric constant for cyclohexane–aniline has been substituted. The experimental results[7]) for $\rho(\theta_B)$ can be given in the following form:

$$\sigma l_I = \sigma_0 l_{I,0} t^{\mu+\nu} = 2.74 \times 10^{-6}\, t^{0.715} \text{ erg/cm}. \tag{4.6}$$

It is clear that the value for the exponent $\mu - \nu = \nu$ is somewhat too large. Using the value of σ_0 given in ref. 16 we obtain $l_{I,0} = 4.10$ Å. This value is rather small compared to the diameter of the molecules. For argon one has $l_{I,0} = 2.35$ Å and for carbon tetrachloride $l_{I,0} = 3.52$ Å[11,1]). Both values are slightly smaller than the molecular diameter. This would suggest that the value of $l_{I,0}$ for cyclohexane–aniline should be somewhat larger than 4.10 Å and consequently the value of σ_0 smaller (not more than approximately 50%).

The Brewster angle is defined by $\mathrm{Re}(r_p/r_s) = 0$. The Fresnel amplitude, eq. (1.15), gives the usual value

$$\theta_B^0 = \arccos[n^-/(\epsilon^- + \epsilon^+)^{1/2}]. \tag{4.7}$$

Up to linear order in the constitutive coefficients we now find from eq. (1.14)

$$\theta_B = \theta_B^0 - \left(\frac{\omega}{c}\right) \frac{\epsilon^+ n^+ n^-}{(\epsilon^+)^2 - (\epsilon^-)^2} \left[2\left(\frac{\omega}{c}\right)\left(\tau - \delta \frac{\epsilon^+ \epsilon^-}{\epsilon^+ + \epsilon^-}\right) - \frac{1}{\sqrt{\epsilon^+ + \epsilon^-}} (\mathrm{Im}\, \gamma_I - \epsilon^+ \epsilon^- \,\mathrm{Im}\, \beta) \right]. \tag{4.8}$$

Substituting eqs. (1.7) and (1.8) and using eq. (3.7) one obtains

$$\theta_B - \theta_B^0 = \frac{k_B T}{2\pi\sigma} \left(\frac{\omega}{c}\right)^2 \frac{\epsilon^+ n^+ n^-}{\epsilon^+ + \epsilon^-} \left[\ln\left(\frac{\omega \epsilon^-}{2\pi c \sqrt{\epsilon^+ + \epsilon^-}} l_I\right) - \frac{4\epsilon^+ \epsilon^-}{(\epsilon^+ + \epsilon^-)^2} \ln\left(\frac{\omega}{2\pi c} l_I\right) \right]. \tag{4.9}$$

There are two remarkable features when one substitutes τ, δ, Im γ_I and Im β. The first is that the contributions due to Im γ_I and Im β cancel each other. In other words the Brewster angle is not modified to this order by the scattering losses. The second feature is that the τ and the δ term combine in a way such that the dependence on the capillary length drops out. The change in the Brewster angle is thus independent of the constant of gravity. Close to the critical point the expression becomes

$$\theta_B - \theta_B^0 = \frac{k_B T_c}{8\pi\sigma_0}\left(\frac{\omega}{c}\right)^2 \epsilon_c t^{-\mu} \ln(\tfrac{1}{2}\epsilon_c). \tag{4.10}$$

For optical frequencies at $\Delta T = 0.5\,°\mathrm{C}$ the resulting shift of the Brewster angle is $\approx 0.02°$. We may therefore conclude that the change in the Brewster angle will be unobservable.

Next we consider the reflectivity R_s. Using eqs. (1.12), (1.7) and (1.8) one has (note that $k_{/\!/} = (n^- \omega/c) \sin\theta = (n^+ \omega/c) \sin\theta_t$ and consequently $k_\perp^- = (n^- \omega/c) \cos\theta$ and $k_\perp^+ = (n^+ \omega/c) \cos\theta_t$)

$$\begin{aligned}\frac{R_s^0 - R_s}{R_s^0} &= 8\left(\frac{\omega}{c}\right)^2 \left(\frac{n^- n^+}{\epsilon^+ - \epsilon^-}\right)\tau \cos\theta \cos\theta_t - 4\left(\frac{\omega}{c}\right)\left(\frac{n^-}{\epsilon^+ - \epsilon^-}\right) \operatorname{Im} \gamma_{tr} \cos\theta \\ &= 2\frac{k_B T}{\pi\sigma}\left(\frac{\omega}{c}\right)^2 n^- \cos\theta\left[n^+ \cos\theta_t \ln l k_m + \left(\frac{\epsilon^- - \epsilon^+}{n^- \cos\theta + n^+ \cos\theta_t}\right)\right. \\ &\qquad \left.\times \ln\left(\frac{n^+ \omega l}{c} \cos\theta_t\right)\right]. \end{aligned} \tag{4.11}$$

The values of $\operatorname{Im} \gamma_{tr}$ obtained from eq. (1.4) by numerical integration never differ more than 3% from the approximate value obtained from eq. (1.8). Close to the critical point the expression becomes, using the fact that $\theta_t = \theta$ in the critical point,

$$\begin{aligned}\frac{R_s^0 - R_s}{R_s^0} &= 2\frac{k_B T_c}{\pi\sigma_0}\left(\frac{\omega}{c}\right)^2 t^{-\mu}\left[\epsilon_c \cos^2\theta \ln\left(\frac{2\pi l_0}{l_{1,0}} t^{\mu-\beta/2}\right)\right. \\ &\qquad \left. + 0.45\, t^\beta \ln\left(\frac{n_c \omega l_0}{c} t^{\nu-\beta/2} \cos\theta\right)\right]. \end{aligned} \tag{4.12}$$

The capillary length in this expression was written as

$$l = \sqrt{\frac{\sigma}{g(\rho^- - \rho^+)}} = l_0 t^{(\mu-\beta)/2} = l_0 t^{\nu-\beta/2}, \tag{4.13}$$

where for cyclohexane–aniline one has $l_0 = 0.36\,\mathrm{cm}$. In eq. (4.12) only the leading terms corresponding to τ and $\operatorname{Im} \gamma_{tr}$ have been accounted for. Clearly the dominant contribution to the decrease of R_s below the Fresnel value comes from τ and is therefore due to the average profile. The contribution proportional to $\operatorname{Im} \gamma_{tr}$, which is due to scattering losses, decreases compared to the τ term as t^β if one approaches T_c. The comparison with the experiment may therefore be done using

$$\frac{R_s^0 - R_s}{R_s^0} = 2\frac{k_B T}{\pi\sigma_0}\left(\frac{\omega}{c}\right)^2 \epsilon_c \cos^2\theta\, t^{-\mu} \ln\left(\frac{2\pi l_0}{l_{1,0}} t^{\mu-\beta/2}\right). \tag{4.14}$$

It should be emphasized that the relative order of magnitude of the τ and the Im γ_{tr} contribution depends rather strongly on the angle of incidence. For cyclohexane–analine at $\Delta T = 0.5°\,\mathrm{C}$ e.g. the Im γ_{tr} term contributes only 1.5% for normal incidence. If the angle of incidence is 70°, however, it contributes 15%. The values obtained using this expression agree extremely well with measured values for normal incidence in a number of systems[4,5,6]), this in particular if one is not too close to the critical point. If one approaches the critical point too closely, R_s becomes practically zero. In evaluating $\Delta R_s/R_s$ we only retained terms linear in τ and γ_{tr}. This is clearly no longer justified if $|\Delta R_s/R_s|$ is close to unity. With respect to the τ term this implies that sufficiently close to T_c the precise shape of the average profile will become increasingly important, a fact which is also indicated by experimental results[4,5,6]). One may account for the precise shape of the average profile[4,5,6]). In the analysis in this paper we have been interested in particular in the contributions due to correlations to R_s, R_p and ρ which one does not obtain if one uses the average profile. The logical next step very close to the critical point would be then to calculate the contributions to the z-dependent dielectric constant for the average fields expanding in fluctuations $\Delta\epsilon$ around the average profile

$$\Delta\epsilon(\boldsymbol{r}) = \tfrac{1}{2}(\epsilon^+ - \epsilon^-)[\theta(z - f(x, y)) - \theta(f(x, y) - z) - \mathrm{erf}(z/L\sqrt{2})].$$

Note the fact that $\langle\Delta\epsilon(\boldsymbol{r})\rangle = 0$. This is not the case if one would use[19])

$$\Delta\epsilon(\boldsymbol{r}) = \tfrac{1}{2}(\epsilon^+ - \epsilon^-)[\mathrm{erf}((z - f(x, y))/L\sqrt{2}) - \mathrm{erf}(z/L\sqrt{2})],$$

which therefore easily leads to a situation in which certain contributions to the average thickness are counted twice. While neglecting correlations seems to be reasonable for R_s, even close to the critical point, this is not the case for R_p and ρ for which our more general approach is clearly more appropriate.

Using eq. (4.14) to calculate $\Delta R_s/R_s^0$ for cyclohexane–aniline with $\sigma_0 = 66.8\,\mathrm{erg\,cm^{-2}}$ (ref. 16) and $\mu = 2\nu = 1.28$ leads to values considerably smaller (a factor 3 for $\theta = 44.5°$ and a factor 8 for $\theta = 69.6°$) than the experimental values[7]). One may fit the data using μ and σ_0 as adjustable parameters. This leads however to values of μ which are rather large (1.64 ± 0.06) and values of σ_0 which are significantly smaller. The value of the fitted σ_0 changes by as much as a factor of three from the smallest to the largest angle of incidence. It seems clear that neither the size nor the angular dependence of the measured values of $\Delta R_s/R_s^0$ agree with eq. (4.14). The angular dependence, in particular, does not improve significantly if one takes the contribution due to Im γ_{tr} into account as suggested by Beaglehole[7]). The use of the precise profile does not improve this situation either.

Finally we consider the reflectivity R_p. Using eqs. (1.16), (1.7) and (1.8) one has in this case

$$
\begin{aligned}
\frac{R_p^0 - R_p}{R_p^0} &= \Big[2\Big(\frac{\omega}{c}\Big)^2 (\tau - \epsilon^- \delta \sin^2 \theta) n^+ \cos \theta_t \\
&\qquad - \frac{\omega}{c} (\mathrm{Im}\, \gamma_1 \cos^2 \theta_t - \epsilon^+ \epsilon^- \,\mathrm{Im}\, \beta \sin^2 \theta)\Big] \frac{4 n^- \cos \theta}{\epsilon^+ \cos^2 \theta - \epsilon^- \cos^2 \theta_t} \\
&= 2 \frac{k_B T}{\pi \sigma} \Big(\frac{\omega^2}{c^2}\Big) \frac{n^- \cos \theta (\epsilon^+ - \epsilon^-)}{\epsilon^+ \cos^2 \theta - \epsilon^- \cos^2 \theta_t} \\
&\qquad \times \Big\{ n^+ \cos \theta_t \Big[\ln(l k_m) - \frac{4 \epsilon^-}{\epsilon^+ + \epsilon^-} \sin^2 \theta \ln\Big(\frac{c k_m}{\omega}\Big)\Big] \\
&\qquad - \frac{\ln\Big(\frac{n^+ \omega l}{c} \cos \theta_t\Big)}{n^+ \cos \theta + n^- \cos \theta_t} [2 n^- (n^+ \cos \theta_t + n^- \cos \theta) \cos \theta_t \sin^2 \theta \\
&\qquad + (\epsilon^+ - \epsilon^-)(\cos \theta \cos^3 \theta_t - \sin \theta_t \sin^3 \theta)] \Big\}.
\end{aligned}
\tag{4.15}
$$

It should be noted that to zeroth order in the constitutive coefficients the Brewster angle is given by $n^+ \cos \theta_B = n^- \cos \theta_{t,B}$. The denominator in eq. (4.15) in fact approaches zero at the Brewster angle proportionally to the Fresnel reflectivity R_p^0. Close to the Brewster angle, where both R_p^0 and R_p are very small, it is better to use eq. (1.16) for R_p directly rather than eq. (4.15). In order to see how the approximate values, given in eq. (1.8), of δ, $\mathrm{Im}\, \gamma_l$ and $\mathrm{Im}\, \beta$ differ from the values obtained by numerical integration from eq. (1.4) together with eq. (1.5) we have tabulated both values 1° C below T_c for cyclohexane–aniline.

The behaviour for other temperatures is very similar. We did similar calculations for argon where the relative error was again practically the same. The errors in $\mathrm{Im}\, \gamma_l$ and $\mathrm{Im}\, \beta$ are rather large for large, respectively small,

TABLE I

The values of δ (in cm^{-1}), $\mathrm{Im}\, \gamma_l$ (in cm) and $\mathrm{Im}\, \beta$ (in cm) for cyclohexane–aniline 1° C below T_c for various angles of incidence θ. The numerical values are indicated by a subindex n and the approximate values by a subindex a

θ	$\delta_n \times 10^{14}$	$\delta_a \times 10^{14}$	$\mathrm{Im}\, \gamma_{l,n} \times 10^{11}$	$\mathrm{Im}\, \gamma_{l,a} \times 10^{11}$	$\mathrm{Im}\, \beta_n \times 10^{11}$	$\mathrm{Im}\, \beta_a \times 10^{11}$
10°	11.36	11.38	74.63	72.65	2.32	0.45
20°	11.36	11.33	71.20	69.02	3.65	1.83
30°	11.35	11.25	65.74	63.15	5.92	4.19
40°	11.35	11.14	58.45	55.28	8.77	7.18
50°	11.33	10.97	49.72	45.79	13.98	12.59
60°	11.29	10.73	40.09	35.13	20.65	19.61
70°	11.21	10.38	30.25	23.91	30.75	30.41
80°	10.91	9.75	21.12	12.66	47.81	48.83

angles of incidence. Because of the fact that they appear in eq. (4.15) in the combination $(\mathrm{Im}\,\gamma_l \cos^2\theta_t - \epsilon^+\epsilon^- \,\mathrm{Im}\,\beta \sin^2\theta)$ the error in the resulting $\Delta R_p/R_p^0$ is much smaller.

Close to the critical point the dominant contributions due to the various constitutive coefficients are

$$\frac{R_p^0 - R_p}{R_p^0} = 2\epsilon_c \frac{k_B T_c}{\pi\sigma_0}(1-\mathrm{tg}^2\,\theta)^{-1}\left(\frac{\omega}{c}\right)^2 t^{-\mu}\Big[\ln\left(2\pi\frac{l_0}{l_{1,0}}t^{\mu-\beta/2}\right)$$
$$-2\sin^2\theta\ln\left(2\pi n_c\cos\theta\frac{l_0}{l_{1,0}}t^{\mu-\beta/2}\right)$$
$$+0.20t^{\beta}(\cos^2\theta - \sin^2\theta\,\mathrm{tg}^2\,\theta)\ln\left(n_c\left(\frac{\omega}{c}\right)l_0\cos\theta t^{\nu-\beta/2}\right)\Big], \qquad (4.16)$$

where we used the fact that close to the critical point the denominator $\epsilon^+\cos^2\theta - \epsilon^-\cos^2\theta_t$ approaches $(\epsilon^+ - \epsilon^-)(\cos^2\theta - \sin^2\theta)$. At the critical point $\theta = \theta_t$. The difference $\theta_t - \theta$ yields the $\sin^2\theta$ term. Clearly, the resulting denominator $(1-\mathrm{tg}^2\,\theta)$ seems to lead to a divergence if the angle of incidence is 45°. In fact 45° is the value of the Brewster angle in the critical point, cf. eq. (4.7), and the corresponding divergence is simply the divergence we also discussed after eq. (4.15). Not only the factor $(1-\mathrm{tg}^2\,\theta)$ changes sign at the critical Brewster angle $\theta_B = 45°$, also the term between square brackets changes sign at this angle if one neglects a term $2\sin^2\theta_B\ln(n_c\cos\theta_B) = \frac{1}{2}\ln(\frac{1}{2}\epsilon_c)$. This term is clearly related to the difference between θ_B and θ_B^0, cf. eq. (4.10), and on the basis of this we expect $(R_p^0 - R_p)/R_p^0$ to be finite and positive for all angles of incidence. It should be emphasized in this context that eq. (4.16) should not be used in the immediate neighbourhood of the Brewster angle. The importance of the contributions to R_p proportional to δ and $\mathrm{Im}\,\beta$ are evident in view of the above result. Otherwise the above cancellations would not occur.

The last term between square brackets is the leading term due to scattering losses. Clearly this term becomes unimportant, when one approaches the critical point, relative to the contribution due to τ and δ. In the present case it contributes less than 1% if $\Delta T \leqslant 0.5°\,\mathrm{C}$ for all angles of incidence. This is therefore noticeably different for $\Delta R_s/R_s^0$ where the contribution due to scattering losses is 15% for $\Delta T = 0.5°\,\mathrm{C}$ at large angles of incidence. We may neglect this term in the present case and one obtains

$$\frac{R_p^0 - R_p}{R_p^0} = 2\epsilon_c \frac{k_B T_c}{\pi\sigma_0}(1-\mathrm{tg}^2\,\theta)^{-1}\left(\frac{\omega}{c}\right)^2 t^{-\mu}$$
$$\times\left[\ln\left(2\pi\frac{l_0}{l_{1,0}}t^{\mu-\beta/2}\right) - 2\sin^2\theta\ln\left(2\pi n_c\cos\theta\frac{l_0}{l_{1,0}}t^{\mu-\beta/2}\right)\right] \qquad (4.17)$$

close to the critical point.

Using eq. (4.17) to calculate $\Delta R_p/R_p^0$ for cyclohexane–aniline again leads to values considerably smaller (a factor 6 for $\theta = 44.5°$ and a factor 10 for $\theta = 69.6°$) then the experimental values$^{7)}$. If one fits the data using μ and σ_0 as adjustable parameters one obtains a value of μ which is rather large and values of σ_0 which are significantly smaller and dependent on the angle of incidence. Clearly neither the size nor the angular dependence of $\Delta R_p/R_p^0$ found experimentally$^{7)}$ agree with values obtained using eq. (4.17). The same discrepency was found for $\Delta R_s/R_s^0$.

The fact that both the intrinsic thickness l_I as measured by ellipsometry and the average thickness L are small compared to the wavelength in the temperature range under consideration implies that the use of interfacial constitutive coefficients is justified. The origin of the disagreement between the experimental and the theoretical results for cyclohexane–aniline is unclear.

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SAMENVATTING

In dit proefschrift worden de eigenschappen van een gas-vloeistof oppervlak bestudeerd. In de grenslaag tussen gas en vloeistof variëren de dichtheden (zoals bv. de massa- of energiedichtheid) van de gas- naar de vloeistofwaarde. Dit kan op verschillende manieren gebeuren. De massadichtheid bv. varieert geleidelijk van gas naar vloeistof, terwijl de vrije energiedichtheid een scherp maximum in de grenslaag vertoont. In dit geval manifesteert zich zo'n maximum als de oppervlaktespanning. Voldoende ver van het kritisch punt is de grenslaag tussen gas en vloeistof van de orde van de moleculaire diameter. In een thermo-hydrodynamische beschrijving kan men in dat geval de grenslaag vervangen door een scherp scheidingsvlak. Op dit scheidingsvlak worden de exces dichtheden gedefinieerd zoals bv. de energie-, entropie- en massadichtheid. De precieze keus van de positie van het scheidingsvlak binnen de grenslaag is enigszins arbitrair. De meest gebruikelijke keus, die van Gibbs, wordt gedaan door de exces massadichtheid nul te kiezen. Ook de stromen (zoals de impuls- of energiestroom) variëren in de grenslaag en hebben als gevolg daarvan oppervlakte componenten op het scheidingsvlak. Op deze manier ontstaat er een model van het gas-vloeistof systeem dat behalve de gebruikelijke dichtheden en stromen in de bulk fasen ook de dichtheden op en stromen langs het scheidingsvlak bevat.

Op een dergelijk systeem wordt in de laatste jaren thermodynamica van irreversibele processen toegepast. In het tweede deel van hoofdstuk 1 wordt een toepassing van de irreversibele thermodynamica op een systeem met oppervlaktedichtheden en stromen in een uitwendig gravitatiepotentiaal besproken. Eerst worden de behoudswetten voor de oppervlaktedichtheden geformuleerd en vervolgens wordt met behulp van een Gibbs-Duhem relatie voor het oppervlak de entropieproductie afgeleid. Uit de entropieproductie volgt de identificatie van de thermodynamische stromen en krachten en vervolgens kunnen de lineaire wetten gegeven worden. De wetten voor de stromen langs het oppervlak zijn van dezelfde vorm als de overeenkomstige wetten in een bulk vloeistof. Dit betekent dat de oppervlakte thermodynamische stromen door middel van dissipatieve coëfficiënten gerelateerd worden aan de thermodynamische krachten. Andere lineaire wetten daarentegen hebben de vorm van randvoorwaarden op het oppervlak. Dit betekent dat de sprongen van de normale componenten van de bulk stromen worden uitgedrukt in oppervlakte en bulk thermodynamische krachten. De uit de lineaire wetten volgende Onsager symmetrierelaties voor de dissipatieve coëfficiënten worden gegeven. Verder wordt in dit deel aangetoond dat voor het gas-vloeistof oppervlak de normale componenten van de snelheid aan beide kanten van het oppervlak vrijwel hetzelfde zijn tengevolge van de grote waarde van de latente warmte die bij condensatie in de grenslaag vrijkomt.

In het derde deel van hoofdstuk I worden de evenwichtsfluctuaties besproken. De fluctuaties van de totale entropie van het systeem van twee vloeistoffen met een scheidingsvlak zijn het gevolg van de fluctuaties in de entropie in de bulk fasen en op het oppervlak en van de fluctuaties in de positie van het oppervlak. De entropie wordt vervolgens tot de tweede orde in deze fluctuerende grootheden ontwikkeld. Omdat het fluctuerende oppervlak gekromd is, bleek het nuttig om curvilineaire coördinaten te gebruiken. De uit de entropieontwikkeling volgende evenwichtscorrelatiefuncties van de temperatuur-, dichtheid- en snelheidsvelden in de bulk en op het oppervlak worden afgeleid. Er zijn in evenwicht geen correlaties tussen de velden van de bulk fasen en die van het oppervlak. De termen in de entropieontwikkeling die afhangen van de afstand d van het oppervlak tot zijn evenwichtspositie zijn ingewikkelder. De eerste van die termen is evenredig met het kwadraat van d en is een gevolg van gravitatie. De tweede bevat het kwadraat van de gradiënt van d en heeft de oppervlaktespanning als evenredigheidsconstante. Deze term correspondeert met het feit dat de kromming van het oppervlak een toename van de grootte van het oppervlak veroorzaakt. De totale oppervlakteenergie groeit dan evenredig met deze grootte. De daaruit volgende correlatiefunctie van d heeft de gebruikelijke vorm, zoals gevonden in de context van het capillaire golven model. De daarmee samenhangende correlatielengte (de zgn. capillaire lengte) divergeert in de limiet van geen gravitatie. Als gevolg hiervan vertoont de wortel van het gemiddelde van het kwadraat van d een logarithmische divergentie in dezelfde limiet. Deze divergentie hangt samen met het feit dat de positie van het oppervlak een symmetriebrekende collectieve variabele is.

De stochastische bewegingsvergelijkingen (de zgn. Landau-Lifshitz vergelijkingen) worden verkregen door toevoeging van random stromen aan de lineaire wetten. Door het fluctuatie-dissipatie theorema worden de correlatiefuncties van deze stromen gerelateerd aan de dissipatieve coëfficiënten. De tijdsafhangelijke correlatiefuncties van de fluctuerende vloeistofvelden zijn dan uit de stochastische eigenschappen van de random krachten af te leiden. In het vierde deel van hoofdstuk 1 wordt het fluctuatie-dissipatie theorema voor het oppervlak tussen twee vloeistoffen geformuleerd. Deze vergelijkingen maken het in principe mogelijk om de eigenschappen van de tijdsafhankelijke correlatiefunctie van o.a. de positie van het oppervlak te bestuderen.

De eigenschappen van een scheidingsvlak tussen twee fluïda kunnen met behulp van licht bestudeerd worden. Als in een dergelijk systeem van twee fluïda de dielectrische constante een stap-functie op het evenwichtsoppervlak is, zijn de gereflecteerde en getransmitteerde amplitudes van het electromagnetisch veld de Fresnel amplitudes. Tengevolge van de fluctuaties in de positie van het oppervlak wijken de werkelijke amplitudes af van de Fresnel waarde. Dit wordt enerzijds veroorzaakt doordat het gemiddelde profiel geen stapfunctie meer is, en anderzijds door de correlaties tussen het locale veld en de fluctuaties in de positie van het oppervlak. Deze afwijkingen kunnen in een optisch experiment gemeten worden. In hoofdstuk 2 en 3 worden twee grootheden besproken die in een dergelijk experiment gemeten kunnen worden: de ellipsometrische coëfficiënt (het quotiënt van de amplitude van het gereflecteerde, parallel in het invalsvlak (p) gepolariseerde licht en de amplitude van het gereflecteerde, loodrecht op het invalsvlak (s) gepolariseerde licht) en de reflectiviteit (het kwadraat van de amplitude van het gereflecteerde, (p) of (s) gepolariseerde licht).

In het vierde deel van hoofdstuk 2 wordt de methode van equivalente polarisatiedichtheid op het evenwichtsoppervlak besproken. Deze methode vervangt de randvoorwaarden van het electromagnetisch veld op het gekromde fluctuerende oppervlak door randvoorwaarden van dit veld op het platte evenwichtsoppervlak. Door deze procedure verkrijgen sommige componenten van dit veld fluctuerende exces bijdragen. Deze bijdragen worden vervolgens ontwikkeld tot op tweede orde in een kleine parameter (de dikte van het gemiddelde profiel gedeeld door de golflengte van het licht). Bij de middeling van de fluctuerende polarisatie en magnetisatie (hoofdstuk 2 §5) wordt gebruik gemaakt van de in hoofdstuk 1 afgeleide evenwichtscorrelatiefunctie van de positie van het oppervlak. Uit de randvoorwaarden voor de gemiddelde velden worden in het tweede deel van hoofdstuk 2 de amplitudes van het (p) en (s) gepolariseerde licht verkregen en wordt vervolgens de ellipsometrische coëfficiënt afgeleid. De ellipsometrische coëfficiënt is lineair in de afkapgolfvector, die wordt geïnterpreteerd als omgekeerd evenredig met de intrinsieke dikte van het oppervlak. Ver van het kritisch punt is deze dikte van de orde van de moleculaire diameter. Vergelijking met experiment bevestigt deze interpretatie (hoofdstuk 2 §6). Het toont aan dat voor vloeistoffen ver van het kritisch punt de intrinsieke dikte ongeveer 50% groter is dan de moleculaire diameter. Verder wordt de conclusie getrokken dat de waarde van de ellipsometrische coëfficiënt practisch onafhankelijk is van het feit of het licht van de kant van de vloeistof of van het gas invalt.

Gebruik makend van de amplitudes van het gereflecteerde en getransmitteerde em veld berekend in hoofdstuk 2, worden in hoofdstuk 3 §1 de reflectiviteit en de transmittiviteit afgeleid. Vergeleken met oudere theoriën bevatten deze formules een aantal nieuwe termen die het gevolg zijn van de correlaties langs het oppervlak. Deze termen bevatten bv. het totale verlies van energie ten gevolge van verstrooiïng. De nieuwe termen hangen op een gecompliceerde wijze van de frequentie en de golfvector af. In het tweede deel van hoofdstuk 3 worden voor die termen eenvoudige benaderende relaties afgeleid en vervolgens vergeleken met de waarden verkregen met computerberekeningen van de exacte uitdrukkingen. Evenals de ellipsometrische coëfficiënt hangt de reflectiviteit en de transmittiviteit af van de intrinsieke dikte. In dit geval echter is de afhankelijkheid logarithmisch, terwijl het bij de ellipsometrische coëfficiënt lineair was.

Als men de reflectiviteit op basis van het gemiddelde dielectrische profiel berekent, zoals gebruikelijk is, dan verschilt het resultaat van datgene verkregen in hoofdstuk 3 §2. In §3 wordt de vergelijking tussen de twee benaderingen gemaakt en daarbij wordt geconcludeerd dat de gemiddelde profiel methode minder toereikend is omdat hij geen rekening houdt met de correlaties langs het oppervlak. Ook voor de ellipsometrische coëfficiënt worden verschillende resultaten gevonden. In de gemiddelde dielectrische profiel methode is de ellipsometrische coëfficiënt evenredig met de dikte van het gemiddelde profiel. Zoals eerder opgemerkt leidt de in dit proefschrift gebruikte methode tot een evenredigheid van deze coëfficiënt met de intrinsieke dikte. In deze methode zijn alle effecten ten gevolge van correlaties in rekening gebracht zodat men de conclusie kan trekken dat het resultaat van de gemiddelde profiel methode niet correct is.

Er zijn twee belangrijke verschijnselen die optreden wanneer het systeem van twee fluïda het kritisch punt nadert. Ten eerste wordt het oppervlak diffuser en ten tweede wordt de correlatielengte in de vloeistof groter. Zeer dicht bij het kritisch punt wordt de dikte van het gemiddelde profiel groter dan de golflengte van het licht. In dit geval is de methode die gebruik maakt van de equivalente oppervlakte polarisatie en magnetisatie niet meer correct. Hoewel in dit proefschrift een gas-vloeistof systeem wordt beschreven, zijn de meeste resultaten ook op het oppervlak tussen twee fluïda van toepassing. In het vierde deel van hoofdstuk 3 wordt de vergelijking met een experiment aan een binair vloeistofmengsel dicht bij het kritische mengpunt gemaakt. De verschillende bijdragen tot de ellipsometrische coëfficiënt en tot de (s) en (p) reflectiviteit worden in detail daarin besproken.

CURRICULUM VITAE

van

Barbara Józefa Anna ZIELIŃSKA

geboren te

Jarocin (Polen)

op

19 april 1951

Ingevolge de wens van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

Na het behalen van het einddiploma van het Lyceum te Poznań (Polen) in 1968, ben ik, na het afleggen van entree examens, natuurkunde gaan studeren aan de Universiteit in Poznań. In het vijfde en tevens laatste jaar van mijn studie werkte ik in de vakgroep moleculaire fysica. Mijn doctoraalscriptie over niet-lineaire optische activiteit kwam tot stand onder begeleiding van Prof. Dr. S. Kielich. Na het behalen van het doctoraaldiploma in 1973 werkte ik de twee volgende jaren in dezelfde vakgroep.

In 1976 emigreerde ik naar Nederland. Een commissie van het Ministerie van Onderwijs en Wetenschappen heeft mijn Poolse doctoraaldiploma niet hoger gewaardeerd dan het Nederlandse kandidaatsdiploma en mij toestemming verleend om de doctoraal-cursus natuurkunde aan de Rijksuniversiteit te Leiden te volgen. Dat gebeurde in de jaren 1977-1979 en werd afgesloten met het behalen van het doctoraaldiploma natuurkunde met bijvak wiskunde. De doctoraalscriptie over het 2-dimensionale XY-model kwam tot stand onder begeleiding van Prof. Dr. P. Kasteleyn. Tijdens mijn experimentele stage werkte ik in de groep van Prof. Dr. N. Poulis. Op 1 september 1979 trad ik in dienst van de Stichting FOM om in de groep van Prof. Dr. P. Mazur van het Instituut-Lorentz voor Theoretische Natuurkunde onderzoek te gaan doen op het gebied van fluctuerende vloeistofoppervlakken. Dit onderzoek verrichtte ik onder begeleiding van Dr. D. Bedeaux en Dr. J. Vlieger.

Aan onderwijs droeg ik bij door in het academisch jaar 1980/1981 Dr. D. Bedeaux te assisteren bij de organisatie van een studentenseminarium over hydrodynamica en door tentamens af te nemen.

In 1980 nam ik deel aan de NUFFIC Zomerschool "Fundamental Problems in Statistical Mechanics V" in Enschede en in 1981 aan een van de cursussen van het "Ettore Majorana Centre for Scientific Culture" getiteld: "Interfacial Aspects of Phase Transformation", in Erice (Sicilië). In juli 1982 bezocht ik de "2nd Trieste International Symposium on Statistical Mechanics of Adsorption".

Leiden, maart 1983

Voor hulp bij de typografische voorbereiding van dit proefschrift wil ik mijn erkentelijkheid betuigen aan Mevr. M. de C. Bridgen, die het typewerk verzorgde.

STELLINGEN

1. De beschrijving van een vloeistof-gas oppervlak met oppervlaktemassadichtheid, zoals gegeven in het eerste hoofdstuk van dit proefschrift, kan uitgebreid worden tot de beschrijving van een vloeistof-gas grensvlak met een 'elastische' filmlaag van een andere stof. De dispersierelatie voor een propagerende compressiegolf langs de filmlaag kan daaruit afgeleid worden.

2. In een ellipsometrisch experiment wordt de intrinsieke (en niet de totale) dikte van het vloeistofoppervlak gemeten.

   Dit proefschrift, hoofdstuk 3

3. De viriaalontwikkeling voor de hoge-temperatuur susceptibiliteit van RKKY spinglazen, zoals door J.C. Owen is toegepast, kan het experimentele gedrag voor hoge temperaturen van CuMn (0.2 at%Mn tot 6 at%Mn) niet verklaren.

   J.C. Owen J. Phys. <u>C16</u> (1983) 1129
   A.F.J. Morgownik, J.A. Mydosh Phys. Rev. <u>B24</u> (1981) 5277

4. Het gebruik van uitgebreide precisie bij computerberekeningen van tweephoton processen kan vermeden worden door toepassing van stroombehoud; de door sommige auteurs gedane beweringen dat de noodzakelijke numerieke stabiliteit alleen bereikt kan worden door het gebruik van invarianten, zijn ongegrond.

   R. Bhattacharya, J. Smith, G. Gremmer Jr, Phys. Rev. <u>D15</u> (1977) 3267

5. In het twee-dimensionale gaussische kolommodel voor een gas-vloeistof oppervlak, met variërende dracht van de kolomwisselwerking, kan de dichtheidscorrelatie gediagonaliseerd worden m.b.v. de eigenfuncties van de harmonische oscillator.

   D. Bedeaux, J.D. Weeks, B.J.A. Zielinska, in voorbereiding

6. In tegenstelling tot het resultaat van de moleculaire veld theorie vertonen alle eigenwaarden bij de ontwikkeling van dichtheidscorrelatiefunctie naar een volledig stel eigenfuncties, in de context van het capillaire golven model in twee dimensies, een infrarood divergentie in de limiet waarin

de uitwendige potentiaal naar nul gaat.

D. Bedeaux, J.D. Weeks, B.J.A. Zielinska, in voorbereiding

7. Ten onrechte suggereren Wong en Rando dat 'all trans' retinal een reactie geeft met opsine.

C.G. Wong, R.R. Rando, J. Am. Chem. Soc. 104 (1982) 7374
H. Matsumoto et al, J. Am. Chem. Soc. 102 (1980) 4259

8. Men kan de ellipsometrische experimenten van Beaglehole aan verschillende vloeistofoppervlakken niet verklaren, indien men voor de Fourier-getransformeerde van de correlatiefunctie van de fluctuaties in de positie van een vloeistofoppervlak een gaussische vorm zou aannemen, zoals dat vaak bij vaste, ruwe oppervlakken wordt gedaan, of een algebraïsche vorm die sneller naar nul gaat dan $1/k^2$ voor grote waarden van k. Dit is een experimentele aanwijzing voor de aanwezigheid van lange-dracht correlaties langs een vloeistofoppervlak.

D. Beaglehole, Physica 100B (1980) 163
D. Beaglehole, Physica 112B (1982) 320

9. Voor een systeem dat zich niet te dicht bij het kritisch punt bevindt, is het mogelijk om met een simpel macroscopisch model de orde van de 'wetting' overgang te bepalen, een uitdrukking voor de contact-hoek te geven en de condities voor de 'wetting'- en kritische 'wetting'-temperatuur te formuleren.

10. De tweede orde fase overgangen zijn een goed voorbeeld van dialectische processen, zoals door F. Engels bedoeld.

Friedrich Engels 'Dialektik der Natur' (Dietz Verlag Berlin 1961)p.53-60

Barbara Zielinska
Leiden, 1 juni 1983