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Ellipsometry of the Liquid–Vapor Interface Close to the Critical Point: A Theoretical Analysis[1]

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It is shown that the ellipsometric coefficient for a liquid–vapor interface may be written as the sum of three contributions. The first is given by Drude's formula. The second contribution is due to capillary wave fluctuations. Finally, the third contribution is due to fluctuations of the density profile around the Fisk–Widom profile with a wavelength up to roughly the bulk correlation length and thus short compared to the capillary length. Close to the critical point the first two contributions scale as $(T-T_c)^{\beta-\nu}$. The expression for the third contribution contains an integral over the excess density correlation function over wave vectors large compared to the inverse bulk correlation length. The scaling behavior of the third contribution is probably such that this term becomes unimportant close to the critical point. The formulae given in this paper only for the liquid–vapor interface may be used for a binary fluid if one makes the usual substitutions. An experimental analysis of the ellipsometric coefficient for binary fluids close to the critical point by Schmidt [1] indicates that the sum of the first two terms predicts a value which is somewhat to large but which has the correct scaling behavior. A discussion of this difference in amplitude is given.

KEY WORDS: critical point; ellipsometric coefficient; liquid–vapor interface.

1. INTRODUCTION

In two previous papers [2, 3], called hereafter I and II, Zielinska et al. studied the electromagnetic properties of a liquid–vapor interface using interfacial constitutive coefficients. These coefficients express the excess

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polarisation and magnetization in terms of the extrapolated bulk fields. Using a dielectric coefficient which changes from a nonfluctuating value ε_l in the liquid to a nonfluctuating value ε_g in the gas at the fluctuating location of the dividing surface, we were able to derive explicit expressions for these constitutive coefficients in terms of the height autocorrelation function [2]. We then analyzed the resulting behavior of the ellipsometric coefficient when one approaches the critical point [3]. The agreement with existing experimental data [4] was not very satisfactory. The more usual approach is to calculate the dielectric constant profile by substitution of the Fisk–Widom [5] density profile into Clausius–Mossotti. The ellipsometric coefficient is then given by Drude's formula [6]. In this second approach capillary waves are not properly taken into account. It is clear that agreement of either one of the two approaches with the experimental results should not be expected. Marvin and Toigo [7] have proposed to simply add the results of the above two methods. As both contributions have the same scaling properties close to the critical point this results in adding the amplitudes. While the resulting exponent agrees with the experimental results for binary liquids the predicted amplitude is somewhat too large [1].

It is the aim of this contribution to derive an expression for the ellipsometric coefficient in which not only capillary waves and the Fisk–Widom profile are taken into account but also the effects of density fluctuations around this profile with a wavelength of the order of the bulk correlation length and thus short compared to the capillary length [8].

The equilibrium position of the dividing surface is assumed to be flat and the $x-y$ plane is chosen along this surface. The optical properties of the surface of discontinuity can be described in terms of the average excess polarization, $\vec{P}^s$, and magnetization, $\vec{M}^s$, densities. These, as we discussed in I and II, are expressed in terms of the value of the extrapolated bulk fields at the dividing surface in the following way:

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

$$\vec{M}^s(x, y, t) = -\tau\hat{z} \wedge \frac{\partial}{c\,\partial t}\vec{E}_+ \tag{2}$$

where $\hat{z} = (0, 0, 1)$ is the normal on the equilibrium dividing surface, $\wedge$ indicates a vectorproduct, c is the velocity of light, $\vec{E}(\vec{r}, t)$ the electric field, $\vec{H}(\vec{r}, t)$ the magnetic field, and $\vec{D}(\vec{r}, t)$ the displacement field. Furthermore, the subscript $+$ indicates half the sum of the extrapolated (i.e., $z=0$) values on both sides of the surface. The tensor $\vec{\vec{\xi}}$, as well as τ, depend in principle on the projection of the wavevector $\vec{k}_{||} \equiv (k_x, k_y, 0)$ along the

dividing surface and the frequency ω. Because of rotational symmetry around the z-axis and translational symmetry along the surface, $\vec{\vec{\xi}}$ is an isotropic tensor with the general form

$$\vec{\vec{\xi}} = \gamma(1 - \hat{z}\hat{z}) + \beta\hat{z}\hat{z} + i\eta\hat{z}\vec{k}_{||} - i\delta\vec{k}_{||}\hat{z} \tag{3}$$

As the dependence of γ, β, δ, η, and τ on $k_{||} \equiv |\vec{k}_{||}|$ and ω is unimportant for the problem on hand, we neglect such a dependence.

To obtain the optical properties of the surface of discontinuity one needs the boundary conditions [9]:

$$(E_x, E_y, D_z)_- = \frac{\partial}{c\,\partial t}(-M_y^s, M_x^s, 0) - (\hat{z}\nabla_{||} - \nabla_{||}\hat{z}).\vec{P}^s \tag{4}$$

$$(H_x, H_y, B_z)_- = \frac{\partial}{c\,\partial t}(P_y^s, -P_x^s, 0) - (\hat{z}\nabla_{||} - \nabla_{||}\hat{z}).\vec{M}^s \tag{5}$$

where $\nabla_{||} \equiv (\partial/\partial x, \partial/\partial y, 0)$ and where, in view of the nonmagnetic nature of the system, we use $\vec{B} = \vec{H}$. Using these boundary conditions one finds for the ellipsometric coefficient [2, 10]

$$r = \tfrac{1}{2}(\omega/c)(\gamma - \varepsilon_l\varepsilon_g\beta)(\varepsilon_l + \varepsilon_g)^{1/2}/(\varepsilon_l - \varepsilon_g) \tag{6}$$

In the following sections we derive explicit expressions for γ and β. In view of the fact that τ, η, and δ do not contribute to the ellipsometric coefficient, we simplify the analysis in such a way that τ, η, and δ will end up being zero. In a subsequent paper a more complete analysis will be given in which all these coefficients are calculated consistently to the second order in the thickness of the surface of discontinuity.

2. THEORY

In order to derive formulae for the interfacial constitutive coefficients one must calculate the excess polarization and magnetization densities. As contributions due to correlations are important, one must first calculate the fluctuating excess polarization and magnetization densities, $\vec{p}^s$ and $\vec{m}^s$, respectively, and then average these in order to obtain $\vec{P}^s$ and $\vec{M}^s$. One may generally show that the fluctuating excess polarization density is given by [11]

$$\vec{p}^s(x, y, t) = \int_{-\infty}^{\infty} dz\,[d_{ex,x}(\vec{r}, t), d_{ex,y}(\vec{r}, t), -e_{ex,z}(\vec{r}, t)] \tag{7}$$

where the fluctuating fields are indicated by lowercase letters. Furthermore, the subscript ex indicates the real field minus the bulk field extrapolated into the surface of discontinuity. For the excess magnetization density one may write down a similar expression. It is crucial to notice the fact that d_x, d_y, and e_z are fields which change considerably as a function of z through the surface of discontinuity, whereas e_x, e_y, and d_z do not change more than in the bulk regions over a comparable distance. As a consequence e_x, e_y, and d_z have no excess. Such an excess would in fact be incompatible with the Maxwell equations [9, 11]. Similar observations may be made about the magnetic fields. In the analysis of the optical properties of surfaces it is convenient to introduce so-called nonsingular fields

$$\vec{n}_e(\vec{r}, t) \equiv (e_x, e_y, d_z)(\vec{r}, t) \qquad \text{and} \qquad \vec{n}_m(\vec{r}, t) \equiv (h_x, h_y, b_z)(\vec{r}, t) \tag{8}$$

In terms of these fields the constitutive relations become

$$\vec{d}_{||}(\vec{r}, t) = \varepsilon(\vec{r}, t)\, \vec{n}_{e,||}(\vec{r}, t) \qquad \text{and} \qquad e_z(\vec{r}, t) = \varepsilon^{-1}(\vec{r}, t)\, n_{e,z}(\vec{r}, t) \tag{9}$$

Similar relations are valid for the magnetic fields with the magnetic permeability equal to unity. The dielectric constant ε depends on the position through the local value of the density

$$\varepsilon(\vec{r}, t) = \varepsilon[\vec{\rho}(r, t)] \tag{10}$$

The relationship between ε and ρ close to the critical point has been discussed in an earlier review [12].

In order to give explicit expressions for the extrapolated $\vec{d}_{||}^{\pm}$ and $e_z^{\pm}$ fields we express them in the extrapolated nonsingular fields using the extrapolated dielectric constants

$$\vec{d}_{||}^{\pm}(\vec{r}, t) = \varepsilon^{\pm}(\vec{r}, t)\, \vec{n}_{||}^{\pm}(\vec{r}, t) \qquad \text{and} \qquad e_z^{\pm}(\vec{r}, t) = [\varepsilon^{\pm}(\vec{r}, t)]^{-1}\, n_z^{\pm}(\vec{r}, t) \tag{11}$$

The extrapolated dielectric constants are equal to the constant bulk values $\varepsilon^- = \varepsilon_g$ and $\varepsilon^+ = \varepsilon_l$ plus a fluctuating contribution due to density fluctuations in the bulk.

$$\varepsilon^{\pm}(\vec{r}, t) = \varepsilon^{\pm} + \delta\varepsilon^{\pm}(\vec{r}, t) \tag{12}$$

Subtracting Eq. (11) from Eq. (9) one obtains for the excess fields

$$\begin{aligned} \vec{d}_{||,\mathrm{ex}}(\vec{r}, t) &= \varepsilon(\vec{r}, t)\, \vec{n}_{e,||}(\vec{r}, t) - \varepsilon^-(\vec{r}, t)\, \vec{n}_{e,||}^-(\vec{r}, t)\, \theta(-z) - \varepsilon^+(\vec{r}, t)\, \vec{n}_{e,||}^+(\vec{r}, t)\, \theta(z) \\ e_{z,\mathrm{ex}}(\vec{r}, t) &= [\varepsilon(\vec{r}, t)]^{-1}\, n_{e,z}(\vec{r}, t) - [\varepsilon^-(\vec{r}, t)]^{-1}\, n_{e,z}^-(\vec{r}, t)\, \theta(-z) \\ &\quad - [\varepsilon^+(\vec{r}, t)]^{-1}\, n_{e,z}^+(\vec{r}, t)\, \theta(z) \end{aligned} \tag{13}$$

We now use the crucial fact that the nonsingular $\vec{n}_e$ field differs only very little from the extrapolated nonsingular field. They are both also almost constant inside the surface of discontinuity. In Eq. (13) we therefore make the following replacement

$$\vec{n}_e(\vec{r}, t) = \vec{n}_e^{\pm}(\vec{r}, t) = \vec{n}_e^{\pm}(x, y, 0, t) \qquad \text{for} \quad \pm z > 0 \tag{14}$$

The difference gives contributions to τ, η, and δ of second order in the thickness of the surface of discontinuity and of even higher order to all coefficients; they are therefore not important for our present analysis. Equation (13) then becomes

$$\begin{aligned} \vec{d}_{||,\mathrm{ex}}(\vec{r}, t) &= [(\varepsilon(\vec{r}, t) - \varepsilon^-(\vec{r}, t)]\, \vec{n}^-_{e,||}(\vec{r}_{||}, 0, t)\, \theta(-z) \\ &\quad + [(\varepsilon(\vec{r}, t) - \varepsilon^+(\vec{r}, t)]\, \vec{n}^+_{e,||}(\vec{r}_{||}, 0, t)\, \theta(z) \\ e_{z,\mathrm{ex}}(\vec{r}, t) &= \{\varepsilon^{-1}(\vec{r}, t) - [\varepsilon^-(\vec{r}, t)]^{-1}\}\, n^-_{e,z}(\vec{r}_{||}, 0, t)\, \theta(-z) \\ &\quad + \{\varepsilon^{-1}(\vec{r}, t) - [\varepsilon^+(\vec{r}, t)]^{-1}\}\, n^+_{e,z}(\vec{r}_{||}, 0, t)\, \theta(z) \end{aligned} \tag{15}$$

Substitution of this equation into Eq. (7) gives for the fluctuating excess polarization densities,

$$\vec{p}^{\,s}(\vec{r}_{||}, t) = \sum_{\nu = \pm} \vec{\vec{\xi}}^{\,\nu}_b \cdot \vec{n}^{\nu}_e(\vec{r}_{||}, t) \tag{16}$$

with

$$\vec{\vec{\xi}}^{\,\nu}_b = \gamma_b(1 - \hat{z}\hat{z}) + \beta_b \hat{z}\hat{z} \tag{17}$$

and

$$\begin{aligned} \gamma^{\nu}_b(\vec{r}_{||}, t) &= \int_{-\infty}^{\infty} dz\, [\varepsilon(\vec{r}, t) - \varepsilon^{\nu}(\vec{r}, t)]\, \theta(\nu z) \\ \beta^{\nu}_b(\vec{r}_{||}, t) &= \int_{-\infty}^{\infty} dz\, \{[\varepsilon^{\nu}(\vec{r}, t)]^{-1} - [\varepsilon(\vec{r}, t)]^{-1}\}\, \theta(\nu z) \end{aligned} \tag{18}$$

Notice that γ^{ν}_b and β^{ν}_b are both of the order of the thickness of the surface of discontinuity.

In order to obtain the constitutive equations for the average polarization density, we must average Eq. (16):

$$\vec{P}^{\,s}(\vec{r}_{||}, t) = \langle \vec{p}^{\,s}(\vec{r}_{||}, t) \rangle = \sum_{\nu = \pm} \langle \vec{\vec{\xi}}^{\,\nu}_b(\vec{r}_{||}, t) \cdot \vec{n}^{\nu}_e(\vec{r}_{||}, 0, t) \rangle \tag{19}$$

It is crucial to realize that the fluctuations of $\vec{\vec{\xi}}^{\,\nu}_b$ and $\vec{n}^{\nu}_e$ are correlated and that as a consequence the average in Eq. (19) may not be broken up. In

order to evaluate the contribution of these correlations to second order in the thickness of the surface of discontinuity, we write the extrapolated nonsingular field as a sum of the incident nonsingular field $\vec{N}_e^0$ plus the contribution due to $\vec{p}^s$:

$$\vec{n}_e^{\pm}(\vec{r}, t) = \vec{N}_e^0(\vec{r}, t) - \int d\vec{r}'_{||}\, dt'\, \vec{\vec{K}}_0(\vec{r}_{||} - \vec{r}'_{||}, z, t - t' \mid z' = 0) \cdot \vec{p}^s(\vec{r}'_{||}, t') \tag{20}$$

For the definition of the propagator $\vec{\vec{K}}_0$ we refer to I. Substitution of this equation into Eq. (19) gives to second order in the thickness

$$\vec{P}^s = \left[\sum_{\nu = \pm} \langle \vec{\vec{\xi}}_b^{\nu} \rangle - \sum_{\nu, \mu = \pm} \langle \vec{\vec{\xi}}_b^{\nu} \cdot \vec{\vec{K}}_0 \cdot \vec{\vec{\xi}}_b^{\mu} \rangle \right] \cdot \vec{N}_e^0 \tag{21}$$

where for the sake of simplicity a somewhat more formal notation has been used. Up to the order we are interested in we may for the calculation of the ellipsometric coefficient replace $\vec{N}_e^0$ by $\vec{N}_{e,+}$. Comparing the result with Eq. (1) we thus find

$$\vec{\vec{\xi}} = \langle \vec{\vec{\xi}}_b \rangle - \langle \vec{\vec{\xi}}_b \cdot \vec{\vec{K}}_0 \cdot \vec{\vec{\xi}}_b \rangle \tag{22}$$

where

$$\vec{\vec{\xi}}_b = \gamma_b(1 - \hat{z}\hat{z}) + \beta_b \hat{z}\hat{z} \equiv \sum_{\nu = \pm} \vec{\vec{\xi}}_b^{\nu} \tag{23}$$

Using Eqs. (17) and (18) one has

$$\gamma_b(\vec{r}_{||}, t) = \int_{-\infty}^{\infty} dz\, [\varepsilon(\vec{r}, t) - \varepsilon^-(\vec{r}, t)\, \theta(-z) - \varepsilon^+(\vec{r}, t)\, \theta(z)] \tag{24a}$$

$$\beta_b(\vec{r}_{||}, t) = \int_{-\infty}^{\infty} dz\, \{[\varepsilon^-(\vec{r}, t)]^{-1}\, \theta(-z) + [\varepsilon^+(\vec{r}, t)]^{-1}\, \theta(z) - [\varepsilon(\vec{r}, t)]^{-1}\} \tag{24b}$$

for the fluctuating interfacial constitutive coefficients.

3. THE MODEL

Until now we have made no assumptions about the dielectric constant and, in particular, not about its behavior in the surface of discontinuity. Using the average density profile found by Fisk and Widom [5] and Clausius–Mossotti, one finds a dielectric constant profile which we $\varepsilon_{FW}(z)$. As a general choice for the fluctuating dielectric constant we take

$$\varepsilon(\vec{r}, t) = \varepsilon_{FW}[z - h(\vec{r}_{||}, t)] + \delta\varepsilon(\vec{r}, t) \tag{25}$$

where $h(\vec{r}_{||}, t)$ is the fluctuating height of the dividing surface and where $\delta\varepsilon(\vec{r}, t)$ is a fluctuation of ε around ε_{FW} due to density fluctuations with a wavelength of the order of the bulk correlation length or shorter [8]. As the fluctuations of the height correspond to density fluctuations with a much longer wavelength, we assume that h and $\delta\varepsilon$ are uncorrelated. For the extrapolated dielectric constants we write

$$\varepsilon^{v}(\vec{r}, t) = \varepsilon_0^{v} + \delta\varepsilon^{v}(\vec{r}, t) \qquad \text{with} \qquad \varepsilon_0^{-} = \varepsilon_g \qquad \text{and} \qquad \varepsilon_0^{+} = \varepsilon_l \tag{26}$$

where ε_g and ε_l are the nonfluctuating dielectric constants of the vapor and the liquid away from the surface. Furthermore, $\delta\varepsilon^{v}$ are the fluctuations of the dielectric constant away from the surface around ε_g and ε_l due to density fluctuations in the bulk regions. We take ε_g and ε_l independent of z neglecting a small density gradient due to gravity. This would matter only near the surface and in that region is not large enough to have any effect on the value of the interfacial constitutive coefficients.

Substituting Eq. (25) for ε into Eq. (24a) for γ_b one finds

$$\begin{aligned}
\gamma_b(\vec{r}_{||}, t) = & \int dz\, \{\varepsilon_{FW}[z - h(\vec{r}_{||}, t)] - \varepsilon_g \theta[h(\vec{r}_{||}, t) - z] - \varepsilon_l \theta[z - h(\vec{r}_{||}, t)]\} \\
& + \int dz\, (\varepsilon_g \{\theta[h(\vec{r}_{||}, t) - z] - \theta(-z)\} + \varepsilon_l \{\theta[z - h(\vec{r}_{||}, t)] - \theta(z)\}) \\
& + \int dz\, [\delta\varepsilon(\vec{r}, t) - \delta\varepsilon^{-}(\vec{r}, t)\, \theta(-z) - \delta\varepsilon^{+}(\vec{r}, t)\, \theta(z)] \\
= & \int dz\, [\varepsilon_{FW}(z) - \varepsilon_g \theta(-z) - \varepsilon_l \theta(z)] - (\varepsilon_l - \varepsilon_g)\, h(\vec{r}_{||}, t) \\
& + \int dz\, [\delta\varepsilon(\vec{r}, t) - \delta\varepsilon^{-}(\vec{r}, t)\, \theta(-z) - \delta\varepsilon^{+}(\vec{r}, t)\, \theta(z)]
\end{aligned} \tag{27}$$

in a similar way we find

$$\begin{aligned}
\beta_b(\vec{r}_{||}, t) = & \int dz\, [\varepsilon_g^{-1} \theta(-z) + \varepsilon_l^{-1} \theta(z) - \varepsilon_{FW}^{-1}(z)] + (\varepsilon_l^{-1} - \varepsilon_g^{-1})\, h(\vec{r}_{||}, t) \\
& + \int dz\, (\delta\{[\varepsilon^{-}(\vec{r}, t)]^{-1}\}\, \theta(-z) \\
& + \delta\{[\varepsilon^{+}(\vec{r}, t)]^{-1}\, \theta(z) - \delta[\varepsilon^{-1}(\vec{r}, t)]\})
\end{aligned} \tag{28}$$

Equations (27) and (28) show that γ_b and β_b can be written as the sum of three terms. As we see below the first nonfluctuating term gives the Drude

formula for the ellipsometric coefficient in the absence of fluctuations. The second term is the one considered in I and II and gives a contribution to the ellipsometric coefficient due to capillary waves. Finally, the third term gives a contribution due to density fluctuations with a shorter wavelength which has not been considered before.

Averaging Eqs. (27) and (28) one obtains

$$\begin{aligned}\langle \gamma_b(\vec{r}_{||}, t)\rangle &= \int dz\, [\varepsilon_{FW}(z) - \varepsilon_g\theta(-z) - \varepsilon_l\theta(z)] \equiv \gamma_{FW} \\ \langle \beta_b(\vec{r}_{||}, t)\rangle &= \int dz\, [\varepsilon_g^{-1}\theta(-z) + \varepsilon_l^{-1}\theta(z) - \varepsilon_{FW}^{-1}(z)] \equiv \beta_{FW}\end{aligned} \tag{29}$$

If one substitutes these averages into Eq. (6) for the ellipsometric coefficient, one obtains

$$r_{FW} = -\frac{\omega(\varepsilon_l + \varepsilon_g)^{1/2}}{2c(\varepsilon_l - \varepsilon_g)} \int_{-\infty}^{\infty} dz \left[\frac{[\varepsilon_g - \varepsilon_{FW}(z)][\varepsilon_{FW}(z) - \varepsilon_l]}{\varepsilon_{FW}(z)}\right] \tag{30}$$

which is the expression given by Drude [6].

The second contribution in $\vec{\vec{\xi}}$ given in Eq. (22) gives, in view of the fact that $\langle h\rangle$, $\langle \delta\varepsilon\rangle$, and $\langle \delta\varepsilon^{\nu}\rangle$ are all zero, three contributions in principle. The first is due to the nonfluctuating first contribution to $\vec{\vec{\xi}}_b$ and may be shown, upon substitution of the explicit expression for the propagator, to be zero. The second contribution due to capillary waves was given in Eq. (5.19) in paper I and is given by

$$\gamma_{cap} = -\frac{1}{2}\varepsilon_l\varepsilon_g\beta_{cap} = -\left[\frac{(\varepsilon_l - \varepsilon_g)^2 k_B T}{4\pi(\varepsilon_l + \varepsilon_g)\sigma}\right] k_\xi \tag{31}$$

where k_B is Boltzmann's constant, T the temperature, σ the surface tension, and k_ξ a cutoff wavevector of the order of the inverse bulk correlation length ξ. For the third contribution we find along essentially the same lines as those used in I to derive Eq. (31),

$$\gamma_{\rho\rho} = -\frac{1}{2}\varepsilon_l\varepsilon_g\beta_{\rho\rho} = \frac{1}{8\pi\varepsilon_c}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_c^2 \int_{k_\xi}^{k_m} dk_{||}\, k_{||}^2 S_{ex}^{\rho\rho}(k_{||}, k_z = 0 | k_z' = 0) \tag{32}$$

where the subscript c indicates that the value at the critical density should be used and where k_m is a cutoff wavevector of the order of 2π divided by the diameter of the particles. $S_{ex}^{\rho\rho}$ is the excess of the short-wavelength equilibrium density–density correlation function and is defined by

$$S_{ex}^{\rho\rho}(\vec{r}\,|\,\vec{r}') = S_{ex}^{\rho\rho}(\vec{r}_{||} - \vec{r}'_{||}, z\,|\,z') \equiv \langle \delta\rho(\vec{r})\,\delta\rho(\vec{r}')\rangle - \langle \delta\rho^{-}(\vec{r})\,\delta\rho^{-}(\vec{r}')\rangle\,\theta(-z)\,\theta(-z') - \langle \delta\rho^{+}(\vec{r})\,\delta\rho^{+}(\vec{r}')\rangle\,\theta(z)\,\theta(z') \tag{33}$$

Due to translational invariance along the surface this correlation function depends only on the difference $\vec{r}_{||} - \vec{r}'_{||}$. The Fourier transform of this expression yields the excess correlation function as a function of $\vec{k}_{||}$, k_z, and k'_z, which function should be used in Eq. (32). It is clear that the problem is to find a proper expression for $S_{ex}^{\rho\rho}$. We return to this point in the Discussion.

4. DISCUSSION

The above analysis leads to an expression for the ellipsometric coefficient which is a sum of three terms

$$r = r_{FW} + r_{cap} + r_{\rho\rho} \tag{34}$$

r_{FW} is given by Eq. (30) and has the usual form given by Drude. The second contribution is due to capillary waves and is given by [2]

$$r_{cap} = -\left[\frac{3\omega(\varepsilon_l - \varepsilon_g)\,k_B T}{8c(\varepsilon_l + \varepsilon_g)^{1/2}\,\sigma}\right] k_\xi \tag{35}$$

Finally, the third contribution is given by

$$r_{\rho\rho} = -\frac{3\omega(2/\varepsilon_c)^{1/2}}{16\pi c(\varepsilon_l - \varepsilon_g)}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_c^2 \int_{k_\xi}^{k_m} dk_{||}\,k_{||}^2\,S_{ex}^{\rho\rho}(k_{||}, k_z = 0\,|\,k'_z = 0) \tag{36}$$

The above formulae may be used not only for the liquid–vapor interface but also for an interface in a binary liquid. One merely replaces ρ by the appropriate order parameter in Eq. (36). As in a binary liquid one should in principle account for the dependence of ε on the density of both components, an additional term similar to the one given in Eq. (36) will occur. We expect that such an additional contribution will not be important close to the critical point. An important property of the first two terms is the fact that they scale in the same way close to the critical point [1]. Furthermore, the predicted exponent is confirmed by the experimental data [1]. As the experimental amplitude is somewhat lower than the theoretical prediction of this amplitude using only the first two terms, the hope is that the third term $r_{\rho\rho}$ has the same scaling properties and corrects the theoretical amplitude to the experimental value. The problem is therefore to use

the properties of $S_{ex}^{\rho\rho}$ for $k_\xi < k_{||} < k_m$ to study $r_{\rho\rho}$. As these properties are not really known it is illuminating to use an alternative expression for r_{cap}. Using the explicit expression for the contribution to the excess of the density autocorrelation function due to capillary waves given in Ref. 13, one may verify the following identity

$$r_{cap} = -\frac{3\omega(2/\varepsilon_c)^{1/2}}{16\pi c(\varepsilon_l - \varepsilon_g)}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_c^2 \int_0^{k_\xi} dk_{||}\, k_{||}^2 S_{cap}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) \quad (37)$$

In fact one may argue that $S_{ex}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) = S_{cap}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0)$ for $k_{||} < k_\xi$; see in this context, in particular, Ref. 13. As a consequence one may combine Eqs. (36) and (37) and write

$$r_{cap} + r_{\rho\rho} = -\frac{3\omega(2/\varepsilon_c)^{1/2}}{16\pi c(\rho_l - \rho_g)}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_c \int_0^{k_m} dk_{||}\, k_{||}^2 S_{ex}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) \quad (38)$$

where we used the fact that close to the critical point $\varepsilon_l - \varepsilon_g = (\partial\varepsilon/\partial\rho)_c\,(\rho_l - \rho_g)$. This shows that the total contribution due to correlations between the fluctuating susceptibilities and the fluctuating fields can be written in terms of the total excess of the density autocorrelation function. In order to find the scaling behavior of the above integral, one must use the properties of the correlation function. For small values of $k_{||}$ one may expand $S_{ex}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0)$ in powers of $k_{||}$ and it follows from the Wertheim [14] and the Triezenburg–Zwanzig [15] identities that, to second order,

$$S_{ex}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) = (\rho_l - \rho_g)\frac{k_B T}{g}(1 - k_{||}^2 L_c^2) \quad (39)$$

The validity of this expression is based on general identities and thus not restricted to a particular model. In the capillary wave model one finds that

$$S_{ex}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) = (\rho_l - \rho_g)\frac{k_B T}{g}(1 + k_{||}^2 L_c^2)^{-1} \quad (40)$$

For $k_{||} L_c \ll 1$ this expression found from the capillary wave model is in agreement with the expression found on the basis of microscopic identities. Using a rather different approach Sikkenk et al. [16] also calculate the small-$k_{||}$ behavior of the density autocorrelation function in a gravitational field to second power and one may verify that their analysis reproduces Eq. (39). One may argue that for $k_{||} \ll k_\xi$ the excess of the correlation function is given by the expression found from the capillary wave theory [13]. In view of the fact that $k_\xi L_c \gg 1$, the integration up to k_ξ then contributes

a term to the ellipsometric coefficient which scales as $(T-T_c)^{\beta-\nu}$. This contribution is in fact the capillary wave contribution given in Eq. (37). In evaluating this contribution one writes $k_\xi = a/\xi$, where a is a constant. The choice of this constant is a problem to which no unique answer as yet exists. Sengers and van Leeuwen [17] analyze the contribution due to capillary waves to the surface tension and find on the basis of this analysis $a = 0.748$, which is the value used by Schmidt [1] in his evaluation of r_{cap}. It is clear, however, that a more fundamental understanding of the precise role of the cutoff would be benificial for the quantitative aspects of the analysis.

There remains the contribution $r_{\rho\rho}$ given in Eq. (36). As no explicit expression for $S_{\text{ex}}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0)$ is known for $k_\xi < k_{||} < k_m$, it is difficult to give a specific prediction. In fact it is easier to turn the problem around by asking the question how the scaling behavior of the excess of the correlation function must be in order to find a contribution which scales in the same way as the other two contributions. If we postulate the following scaling behavior for the contribution to the excess of the density autocorrelation function due to fluctuations with a wavelength shorter than or roughly equal to the bulk correlation length

$$S_{\text{ex}}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) = (\rho_l - \rho_g)^2 \, \xi^4 f_{\text{ex}}^{\rho\rho}(k_{||}\xi) \tag{41}$$

and assume that $f_{\text{ex}}^{\rho\rho}(k_{||}\xi)$ approaches zero fast enough for large values of $k_{||}\xi$ to make the upper cutoff k_m unimportant, we find that $r_{\rho\rho}$ indeed scales in the same way as the other two contributions. If, however, the large-$k_{||}\xi$ behavior of $f_{\text{ex}}^{\rho\rho}(k_{||}\xi)$ approaches zero proportional to $(k_{||}\xi)^{-2}$, the appropriate expression would be

$$S_{\text{ex}}^{\rho\rho}(k_{||}, k_z = 0 \,|\, k_z' = 0) = (\rho_l - \rho_g)^2 \, \xi^3 f_{\text{ex}}^{\rho\rho}(k_{||}\xi) \tag{42}$$

While the occurrence of the factor $(\rho_l - \rho_g)^2$ is not unexpected, the power of ξ and the behavior of the scaling function for a large argument are rather more hypothetical.

As an overall conclusion it seems likely that $r_{\rho\rho}$ does not have the right scaling behavior and is probably not important. The most likely reason for the remaining quantitative disagreement between theory and experiment is the precise choice of the parameter a in the relation $k_\xi = a/\xi$. At present this choice is made by analyzing the contribution of capillary waves to the surface tension [17]. While this is clearly appropriate for quantities which depend on the surface tension, the integral over the correlation function in Eq. (38) seems to need a more fundamental understanding of the behavior of the correlation function for $k_{||}\xi$ in the neighborhood of unity.

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