Influence of the surface profile on the roughness contribution to the ellipticity coefficient

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The light reflection on a fluid interface is considered for determination of the intrinsic surface profile and roughness. An integral equation derived for the electric displacement vector in the surface layer is iterated to second order in the dielectric permittivity difference $\Delta\epsilon$ of the coexisting phases. The ellipticity coefficient at the Brewster angle of incidence is obtained generally for an arbitrary profile and roughness spectrum assuming their spatial dimensions to be significantly less than the light wavelength. The roughness contribution to the ellipticity coefficient is shown to depend crucially on the surface profile. The ellipticity coefficient value calculated with the Fisk-Widom profile and roughness within the capillary-wave model essentially coincides with that measured in the critical region, contrary to the sharp-boundary result. The dependence of the ellipticity on the capillary-short-wave cutoff changes from linear to logarithmic due to the finiteness of the profile thickness. The term of second order in $\Delta\epsilon$ violates a symmetry with respect to the permutation of coexisting phases.

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I. INTRODUCTION

Light-reflection measurements appear to be a most reliable method of investigation of a fluid surface when thickness parameters of interface are less than the wavelength of the incident radiation. Two physical effects are known to be responsible for deviations from the Fresnel formulas: the intrinsic order-parameter profile and thermal surface oscillations. Since the profile thickness L_S and mean oscillation amplitude $\bar{h}$ both related to wavelength λ are usually of the order of 10^{-3}, rigid requirements on the accuracy of measurements are to be met.

When a system approaches a critical point its correlation length r_c as well as L_S and $\bar{h}$ grow involving a relative increase in surface contributions to the Fresnel formulas. That is why the reflectivity investigations of liquid surfaces have been done mostly in the critical region [1–9]. In a lot of these works the ellipticity coefficient has been measured at the Brewster angle since in this case the Fresnel term vanishes.

A description of experiment is presently based [8–10] on the assumption that the two above-mentioned effects are additive. The permittivity profile is accounted for in the framework of the Drude classical approach considering the light reflection on an ideally smooth boundary of a layered medium. Nowadays much attention is given to the generalization of the Drude method taking into account the problem of a rigorous definition of the local refractive index in the interface and justification of applicability of such a definition [11,12].

The contribution of the thermal oscillations to the reflection coefficients were found by Beaglehole [3] and Zielinska, Bedeaux, and Vlieger [13] who had considered a rough but stepwise boundary between two homogeneous fluid media. The surface oscillations were accounted for within the framework of the capillary-wave theory [14]. The result obtained in Ref. [13] depends heavily on the short-wavelength cutoff q_{max} of the capillary-wave spectrum. An interference of the intrinsic profile and capillary waves was accounted for by Marvin and Toigo [15]. However, the nonadditive term found in Ref. [15] does not transform continuously into the corresponding formula of Ref. [13] when $L_S \to 0$ as one would expect; on the contrary, it brings about unphysical divergence.

Ellipticity coefficient calculations [8,9] based on the additive account for the interface Drude integral accomplished with the Fisk-Widom profile [16] and surface roughness in the framework of the sharp-boundary model have produced a significant overestimate as compared with immediate experimental data measured for three mixtures near the consolute point.

Considering the notion of surface rigidity Meunier [17] eliminated the dependence on the q_{max} cutoff. The author [17] took into account the dependence of the surface tension on curvature as well as terms of higher orders, expanding a surface element in curvature. However, such an approach requires the whole curvature series to be summed up and gives an excessive value of q_{max} as compared with that of the self-consistent consideration [18]. In Ref. [11] the rigidity was used alongside the q_{max} short-wavelength cutoff in an attempt to bring into agreement the calculated and measured results of Refs. [8,9]. The discrepancy was diminished, but insufficiently.

A nonlocality contribution due to a difference of the correlation function of permittivity fluctuations in the surface layer from that in the bulk were also considered in Ref. [11].

In the present paper we derive the expression for the ellipticity coefficient taking into account simultaneously the intrinsic profile as well as the roughness of the surface. We iterate an integral equation considered earlier [19] for the electric displacement vector in terms of permittivity difference $\Delta\epsilon$ of coexisting phases. The formula describing the effect of roughness significantly depends on the form of the profile. The first $\Delta\epsilon$-order result transforms continuously into that of Ref. [13] when $L_S \to 0$. The finiteness of the profile thickness causes the dependence on the cutoff parameter to deteriorate, changing it from linear to logarithmic. The ellipticity coefficient correlation in the second order in $\Delta\epsilon$ violates a symmetry with respect to a permutation of the coexisting phases. Such a violation was found in Refs. [3,4] and discussed theoretically in Ref. [15]. Our asymmetric correction is two orders of magnitude higher than that obtained in Ref. [15] and agrees with experimental estimates. The ellipticity coefficient calculated in the critical region for the Brewster angle using the Fisk-Widom profile coincides closely with experimental data [8,9].

First, starting from the wave equation in the integral form we obtain in Sec. II the reflection coefficients expressed generally through the dielectric permittivity and field in the interface. In Sec. III we derive an integral equation for the displacement vector in the interface. In Sec. IV we obtain expressions for the field and ellipticity coefficient in the main order in $\Delta\epsilon$. The ellipticity coefficient is calculated in Sec. V for the critical region using the Fisk-Widom profile. The results are compared with experimental ones. In Sec. VI we calculate the ellipticity coefficient in the second $\Delta\epsilon$ order. In the last section we summarize and discuss the results.

II. THE REFLECTION COEFFICIENTS

Consider the light reflection on the boundary of two fluid media a and b. Set a plane wave with circular frequency ω incident from the a phase upon the boundary of the b phase. We take into account thermal oscillations of the boundary, considering it planar in a macroscopic sense.

To account for surface effects in the problem of light reflection we consider the wave equation in the integral form. We use the equation for the electric displacement vector since the latter satisfies the transversality condition for any medium, including a heterogeneous one. Considering only the spatial dependence of the field, we write the wave equation in the form [12]

$$\mathbf{D}(\mathbf{r})=\mathbf{D}_a(\mathbf{r})+\int \overleftrightarrow{\mathbf{A}}_a(\mathbf{r}-\mathbf{r}_1)\overleftrightarrow{\mathbf{M}}_a(\mathbf{r}_1,\mathbf{r}_2)\mathbf{D}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \quad (1)$$

where $\mathbf{D}_a(\mathbf{r})=\mathbf{D}_{a0}\exp(i\mathbf{K}_a\cdot\mathbf{r})$ is the electric displacement vector, $\mathbf{K}_a$ is the wave vector and

$$\overleftrightarrow{\mathbf{A}}_a(r)=\epsilon_a(\nabla\nabla-\overleftrightarrow{\mathbf{I}}\Delta)r^{-1}\exp(iK_a r) \quad (2)$$

is the propagator in homogeneous bulk medium a with permittivity ϵ_a. The $\overleftrightarrow{\mathbf{M}}(\mathbf{r}_1,\mathbf{r}_2)$ tensor presents a nonlocal susceptibility and may be expressed as a series in terms of the inverse permittivity fluctuations

$$\overleftrightarrow{\mathbf{M}}_a(\mathbf{r}_1,\mathbf{r}_2)=\overleftrightarrow{\mathbf{I}}\delta(\mathbf{r}_1-\mathbf{r}_2)\psi_a(\mathbf{r}_1) +(4\pi)^{-2}G_a(\mathbf{r}_1,\mathbf{r}_2)\overleftrightarrow{\mathbf{A}}_a(\mathbf{r}_1-\mathbf{r}_2)+\cdots , \quad (3)$$

where

$$\psi_a(\mathbf{r})=(4\pi)^{-1}[\epsilon_a^{-1}-\overline{\epsilon_{\text{fl}}^{-1}(\mathbf{r})}] =(4\pi)^{-1}[\epsilon_a^{-1}-\epsilon^{-1}(\mathbf{r})] , \quad (4)$$

and

$$G_a(\mathbf{r}_1,\mathbf{r}_2)=\overline{[\epsilon_a^{-1}-\epsilon_{\text{fl}}^{-1}(\mathbf{r}_1)][\epsilon_a^{-1}-\epsilon_{\text{fl}}^{-1}(\mathbf{r}_2)]} -(4\pi)^2\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) . \quad (5)$$

Here $\epsilon_{\text{fl}}^{-1}(\mathbf{r})$ is the fluctuating inverse permittivity and an overbar means a statistical average. In particular, one has $\epsilon^{-1}(\mathbf{r})=\overline{\epsilon_{\text{fl}}^{-1}(\mathbf{r})}$. $G_a(\mathbf{r}_1,\mathbf{r}_2)$ is the two-body correlation function. The description in terms of the inverse permittivity fluctuations instead of those of permittivity is due to using the wave equation for the electric displacement vector.

Equations like Eqs. (1)–(5) describing the stochastic character of the permittivity were widely considered previously [11,12,20,21]. They may be applied to heterogeneous two-phase systems (see Ref. [12]).

The essential feature of Eq. (1) is that the nonintegral term describes a plane wave in a homogeneous medium. In the reflection problem considered presently we choose phase a as a reference system. Therefore we consider the deviation of stochastic variable $\epsilon_{\text{fl}}^{-1}(\mathbf{r})$ from the value ϵ_a^{-1}, instead of a local mean value. With the distance from the boundary inward phase b the solution of Eq. (1) takes the form of the plane wave $\mathbf{D}_b(\mathbf{r})=\mathbf{D}_{b0}\exp(i\mathbf{K}_b\cdot\mathbf{r})$, where $\mathbf{K}_b$ is the wave vector of the b bulk phase. The incident wave $\mathbf{D}_a(\mathbf{r})$ therewith eliminates according to the Ewald-Oseen extinction theorem [22,23], and propagator $\overleftrightarrow{\mathbf{A}}_a(\mathbf{r})$ transforms into $\overleftrightarrow{\mathbf{A}}_b(\mathbf{r})$.

Calculating the reflection coefficient one usually neglects the spatial dispersion of the susceptibility tensor $\overleftrightarrow{\mathbf{M}}_a(\mathbf{r}_1,\mathbf{r}_2)$,

$$\int \overleftrightarrow{\mathbf{M}}_a(\mathbf{r}_1,\mathbf{r}_2)\mathbf{D}(\mathbf{r}_2)d\mathbf{r}_2=\psi_a(\mathbf{r}_1)\mathbf{D}(\mathbf{r}_1) . \quad (6)$$

For the sake of simplicity we restrict ourselves to the case of optically isotropic a and b bulk media and surface layer.

In the local approximation (6) Eq. (1) becomes

$$\mathbf{D}(\mathbf{r})=\mathbf{D}_a(\mathbf{r})+\int d\mathbf{r}_1\overleftrightarrow{\mathbf{A}}_a(\mathbf{r}-\mathbf{r}_1)\psi_a(\mathbf{r}_1)\mathbf{D}(\mathbf{r}_1) . \quad (7)$$

Let the Cartesian axis z be directed normally to the boundary, the $z<0$ half space be occupied by phase a, and the $z>0$ half space be occupied by phase b.

We describe the rough boundary with the equation $z=h(\boldsymbol{\rho})$ where $\boldsymbol{\rho}=(x,y)$ are the tangential Cartesian coordinates and $h(\boldsymbol{\rho})$ is the stochastic boundary deviation from the equilibrium plane $z=0$. We assume the optical properties of the system to be averaged already over all the fluctuations except those of $h(\boldsymbol{\rho})$. In specific calculations we suppose that the equilibrium intrinsic profile depends only on the distance from the instant boundary. In particular, it gives for the permittivity and local susceptibility

$$\epsilon(\mathbf{r})=\epsilon(z-h(\boldsymbol{\rho})) , \quad \psi_a(\mathbf{r})=\psi_a(z-h(\boldsymbol{\rho})) . \quad (8)$$

The contribution accounting for the deviation from the spatial dependence of the form (8) was considered in Ref. [11]. The result containing the correlator of such deviations remains theoretically incalculable.

In Ref. [13] a medium was assumed to be homogeneous up to the boundary, that for the susceptibility gives an approximation

$$\psi_a(\mathbf{r})=\Theta(z-h(\rho))\psi_0 , \quad (9)$$

where $\Theta(z)$ is the Heaviside step function and $\psi_0=(4\pi)^{-1}(\epsilon_a^{-1}-\epsilon_b^{-1})$ is the gap of the $\psi_a(z)$ function when one transits from phase a to b.

We present the sought solution of Eq. (7) as a sum of two terms: the plane wave of bulk phase b and the deviation from it,

$$\mathbf{D}(\mathbf{r})=\mathbf{D}_{b0}\exp(i\mathbf{K}_b\cdot\mathbf{r})+\Delta\mathbf{D}(\mathbf{r}) . \quad (10)$$

The advantage of such a representation is that product $\psi_a(\mathbf{r})\Delta\mathbf{D}(\mathbf{r})$ is localized within the surface layer. Indeed variable $\psi_a(\mathbf{r})=(4\pi)^{-1}[\epsilon_a^{-1}-\epsilon^{-1}(\mathbf{r})]$ decreases moving inward phase a and variable $\Delta\mathbf{D}(\mathbf{r})$ vanishes inside phase b. We present $\psi_a(\mathbf{r})$ in the form

$$\psi_a(\mathbf{r})=\psi_a(z)+H(\mathbf{r}) . \quad (11)$$

Assuming the validity of Eq. (8) one may expand $H(\mathbf{r})$ in a series in terms of $h(\rho)$,

$$H(\mathbf{r})=-\psi'(z)h(\rho)+\frac{1}{2!}\psi''(z)h^2(\rho)+\cdots . \quad (12)$$

Subscript a is omitted at derivatives $\psi^{(n)}=\partial^n\psi/\partial z^n$ since they may be expressed through the dielectric profile $\epsilon(z)$. Note that function $H(\mathbf{r})$ specifies the surface roughness. When $h(\rho)\to 0$ $H(\mathbf{r})$ also vanishes. We single out from the profile $\psi_a(z)$ the stepwise term

$$\psi_a(z)=\Theta(z)\psi_0+\Theta(-z)\psi_a(z)+\Theta(z)\psi_b(z)$$
$$\equiv\Theta(z)\psi_0+\delta\psi(z) , \quad (13)$$

where

$$\psi_b(z)=(4\pi)^{-1}[\epsilon_b^{-1}-\epsilon^{-1}(z)] .$$

Note that function $\delta\psi(z)$ is localized in the surface layer.

Using Eqs. (10)–(13) we present the product $\psi_a(\mathbf{r})\mathbf{D}(\mathbf{r})$ as follows:

$$\psi_a(\mathbf{r})\mathbf{D}(\mathbf{r})=\Theta(z)\psi_0\mathbf{D}_b(\mathbf{r})+\Delta\mathbf{P}(\mathbf{r}) , \quad (14)$$

where

$$\Delta\mathbf{P}(\mathbf{r})=[\delta\psi(z)+H(z,\rho)]\mathbf{D}_b(\mathbf{r})+\psi_a(\mathbf{r})\Delta\mathbf{D}(\mathbf{r}) . \quad (15)$$

Here $\Delta\mathbf{P}(\mathbf{r})$ has the meaning of an excess surface polarization vector. The surface corrections to the reflection coefficients may be easily expressed through $\Delta\mathbf{P}(\mathbf{r})$. We have in the first order in L_S/λ

$$K_\parallel=K_\parallel^{(F)}\left[1-\sum_{(\pm)}\frac{(\pm i)(m_b\pm m_a)}{\psi_0\cos(\varphi_a\pm\varphi_b)}D_\parallel^{-1}\int_{-\infty}^{\infty}dz\langle\Delta P_x(z)\cos\varphi_a\pm\Delta P_z(z)\sin\varphi_a\rangle\right] , \quad (16)$$

$$K_\perp=K_\perp^{(F)}\left[1-2im_a\psi_0^{-1}D_\perp^{-1}\int_{-\infty}^{\infty}dz\langle\Delta P_y(z)\rangle\right] , \quad (17)$$

where the angular brackets denote averaging over the roughness oscillations, subscripts $\parallel$ and $\perp$ mean the light polarization parallel and normal to the plane of incidence, respectively, $K_\perp^{(F)}$ and $K_\parallel^{(F)}$ are the Fresnel reflection coefficients, $m_s=K_s\cos\varphi_s$. $s=a$ or b, φ_s is the angle between the normal and wave vector $\mathbf{K}_s$, and $D_\parallel$ and $D_\perp$ are respective components of the electric displacement vector

$$\mathbf{D}_{b0}=(D_\parallel\cos\varphi_b,D_\perp,-D_\parallel\sin\varphi_b) .$$

Formulas like Eqs. (16) and (17) have been derived repeatedly beginning with the Drude classic result [24].

We consider the ellipticity coefficient $\bar\rho=|K_\parallel/K_\perp|$ which at the Brewster angle takes the form

$$\bar\rho_{\rm Br}=2\pi n_a n_b K_0\left|\frac{\epsilon_b+\epsilon_a}{\epsilon_b-\epsilon_a}\right|$$
$$\times\left|\frac{1}{D_\parallel}\int_{-\infty}^{\infty}dz\langle\psi_a(\mathbf{r})[\Delta D_x(\mathbf{r})n_a+\Delta D_z(\mathbf{r})n_b]\rangle\right| , \quad (18)$$

where $K_0=2\pi/\lambda$ is the vacuum wave number and n_a and n_b are the refractive indices in the a and b media.

III. THE ELECTRIC DISPLACEMENT VECTOR IN THE SURFACE LAYER

Substituting Eqs. (10) and (15) into Eq. (7) we solve the latter with respect to $\Delta\mathbf{D}(\mathbf{r})$,

$$\Delta\mathbf{D}(\mathbf{r})=\mathbf{D}_a(\mathbf{r})-D_b(\mathbf{r})+\psi_0\int d\mathbf{r}_1\overleftrightarrow{\mathbf{A}}_a(\mathbf{r}-\mathbf{r}_1)\Theta(z_1)\mathbf{D}_b(\mathbf{r}_1)$$
$$+\int d\mathbf{r}_1\overleftrightarrow{\mathbf{A}}_a(r-r_1)\{[\delta\psi(z_1)+H(z_1,\rho_1)]\mathbf{D}_b(\mathbf{r}_1)$$
$$+\psi_a(\mathbf{r}_1)\Delta\mathbf{D}(\mathbf{r}_1)\} . \quad (19)$$

The first integral in the right-hand side is taken explicitly and produces plane waves: the reflected one for $z<0$ and the plane wave difference $\mathbf{D}_b(\mathbf{r})-\mathbf{D}_a(\mathbf{r})$ for $z>0$. We calculate the rest of the integrals assuming the effective profile thickness as well as characteristic dimensions of the surface oscillations to be small as compared to the light wavelength.

In Eq. (19) the surface localized functions are conveniently expressed by two-dimensional Fourier integrals over the tangential variables. In particular, we have

$$H(\mathbf{r})=\int\frac{d^2\mathbf{q}}{(2\pi)^2}H_{\mathbf{q}}(z)\exp(i\mathbf{q}\cdot\rho) \quad (20)$$

and similarly for the product $\psi_a(\mathbf{r})\Delta\mathbf{D}(\mathbf{r})$. The subscript $\mathbf{q}$ denotes the Fourier transform.

Generally we have to calculate integrals of the form

$$\overleftrightarrow{J}(\mathbf{r})=\int d\mathbf{r}_1\overleftrightarrow{A}_a(\mathbf{r}-\mathbf{r}_1)g_{\mathbf{q}}(z_1)\exp(i\mathbf{q}\cdot\boldsymbol{\rho}_1+i\mathbf{K}_b\mathbf{r}_1)\ , \qquad (21)$$

where $g_{\mathbf{q}}(z)$ denotes some two-dimensional Fourier transform. Since the characteristic wavelength of the roughness oscillations is smaller than that of the light, the wave region $q \gg \lambda^{-1}$ makes the main contribution to integrand (21).

Substituting into Eq. (21) the Fourier transform of the propagator

$$\overleftrightarrow{A}_a(\mathbf{r})=4\pi\epsilon_a(\nabla\nabla-\overleftrightarrow{I}\Delta)\int\frac{d^3\mathbf{K}}{(2\pi)^3}\frac{\exp(i\mathbf{K}\mathbf{r})}{K^2-(K_a+i\eta)^2}\ ,\quad \eta\to 0+ \qquad (22)$$

and taking into account that $q \gg K_a$ and K_b, we easily integrate over tangential variables

$$\overleftrightarrow{J}(\mathbf{r})=2\epsilon_a(\nabla\nabla-\overleftrightarrow{I}\Delta)\exp(i\mathbf{q}\cdot\boldsymbol{\rho})\times\int_{-\infty}^{\infty}g_{\mathbf{q}}(z_1)dz_1\times\int_{-\infty}^{\infty}dK(K^2+q^2)^{-1}\times\exp[iK(z-z_1)+iq_zz_1]\ . \qquad (23)$$

Integrating over K by means of the residue theorem and performing the differentiation while taking into account the identity

$$\frac{d^2}{dz^2}\exp(-q|z-z_1|)=[q^2-2q\delta(z-z_1)]\times\exp[-q|z-z_1|] \qquad (24)$$

we obtain

$$\overleftrightarrow{J}(\mathbf{r})=4\pi\epsilon_a\exp(i\mathbf{q}\cdot\boldsymbol{\rho})\left[g_{\mathbf{q}}(z)\overleftrightarrow{P}_t-\frac{q}{2}\left[\frac{3}{2}\overleftrightarrow{P}_t-\overleftrightarrow{I}\right]\int_{-\infty}^{\infty}dz_1g_{\mathbf{q}}(z_1)\exp(-q|z-z_1|)\right]\ , \qquad (25)$$

where $\overleftrightarrow{P}_t=\overleftrightarrow{I}-\mathbf{e}_z\mathbf{e}_z$ is the projector onto the plane normal to the $\mathbf{e}_z$ unit vector along the z axis.

When $q=0$, substituting Eq. (22) into (21) we get

$$\overleftrightarrow{J}(\mathbf{r})=4\pi\epsilon_a g_{\mathbf{q}}(z)\exp(i\mathbf{K}_b\cdot\mathbf{r})\overleftrightarrow{P}_t\ . \qquad (26)$$

As a result Eq. (19) for $\Delta\mathbf{D}(\mathbf{r})$ may be written in the form

$$[\overleftrightarrow{I}-4\pi\epsilon_a\psi_a(\mathbf{r})\overleftrightarrow{P}_t]\Delta\mathbf{D}(\mathbf{r})=4\pi\epsilon_a[\psi_b(z)+H(\mathbf{r})]\overleftrightarrow{P}_t\mathbf{D}_{b0}-2\pi\epsilon_a\int\frac{d^2\mathbf{q}}{(2\pi)^2}\exp(i\mathbf{q}\cdot\boldsymbol{\rho})q\int_{-\infty}^{\infty}dz_1\exp(-q|z-z_1|)\left[\frac{3}{2}\overleftrightarrow{P}_t-\overleftrightarrow{I}\right]\times\{H_{\mathbf{q}}(z_1)\mathbf{D}_{b0}+[\psi_a(\mathbf{r}_1)\Delta\mathbf{D}(\mathbf{r}_1)]_{\mathbf{q}}\}\ . \qquad (27)$$

Here the plane waves $\mathbf{D}_a(\mathbf{r})$, $\mathbf{D}_{\mathrm{refl}}(\mathbf{r})$, and $\mathbf{D}_b(\mathbf{r})$ are substituted by their amplitudes since the variables in Eq. (27) are localized in the spatial range much smaller than the light wavelength. Note that a rearrangement may be done in Eq. (27),

$$\psi_b(z)+H(z,\boldsymbol{\rho})=\psi_b(\mathbf{r})\ . \qquad (28)$$

We analyze the terms of Eq. (27) with respect to the order of $\Delta\epsilon$. The values of $\psi_a(\mathbf{r})$, $\psi_b(\mathbf{r})$, and $H(\mathbf{r})$ are of the first order in $\Delta\epsilon$. Therefore all the terms in the right-hand side of Eq. (27) not containing the sought function $\Delta\mathbf{D}(\mathbf{r})$ are of the same order, and hence $\Delta\mathbf{D}(\mathbf{r})$ itself is also of the first $\Delta\epsilon$ order. The last term in integrand (27) is of the order of $\psi_a\Delta D\sim\Delta\epsilon^2$. Thus one can solve this integral equation by perturbations.

As is seen, Eq. (27) is separated into two independent equations for tangential and normal components of the $\Delta\mathbf{D}(\mathbf{r})$ vector.

IV. ELLIPTICITY COEFFICIENT IN PRINCIPAL ORDER IN $\Delta\epsilon$

We pass on to solution of Eq. (27) and subsequent calculation of the ellipticity coefficient. We immediately obtain $\Delta\mathbf{D}(\mathbf{r})$ in the principle order in $\Delta\epsilon$, dropping the term containing $\Delta\mathbf{D}(\mathbf{r})$ in the right-hand side of Eq. (27). Substituting this formula for $\Delta\mathbf{D}(\mathbf{r})$ into Eq. (18) we get the ellipticity coefficient in the form

$$\bar{\rho}_{\mathrm{Br}}=\frac{8\pi^2\epsilon_a\epsilon_b\sqrt{\epsilon_a+\epsilon_b}K_0}{|\Delta\epsilon|}\left|\int_{-\infty}^{\infty}dz\langle\psi_a(\mathbf{r})\epsilon(\mathbf{r})\psi_b(\mathbf{r})\rangle-\frac{1}{4}\int_{-\infty}^{\infty}dz\left\langle[\epsilon(\mathbf{r})+2\epsilon_a]\psi_a(\mathbf{r})\int\frac{d^2\mathbf{q}}{(2\pi)^2}\exp(i\mathbf{q}\cdot\boldsymbol{\rho})q\int_{-\infty}^{\infty}dz_1H_{\mathbf{q}}(z_1)\exp(-q|z-z_1|)\right\rangle\right|\ . \qquad (29)$$

We analyze the result obtained. The first integral in Eq. (29) stems from the nonintegral term of Eq. (27). Assuming the dependence on $\mathbf{r}$ in the form $\epsilon(z-h(\rho))=\epsilon(\mathbf{r})$ we get

$$\int_{-\infty}^{\infty} dz \langle \psi_a(\mathbf{r})\epsilon(\mathbf{r})\psi_b(\mathbf{r})\rangle = \int_{-\infty}^{\infty} dz \langle \psi_a(z-h)\epsilon(z-h)\psi_b(z-h)\rangle \equiv -r_D \ . \tag{30}$$

This expression does not depend on the surface oscillations $h(\rho)$ and coincides with the constant factor with the Drude formula for the ellipticity coefficient. The minus is introduced in Eq. (30) to make r_D coincident with the Drude integral. Note that $r_D>0$ since functions $\psi_a(z)$ and $\psi_b(z)$ are opposite in sign.

Consider the second integral term containing the average over the roughness fluctuations. Taking into account Eq. (11) and substituting within the required accuracy $\epsilon(\mathbf{r})+2\epsilon_a=3\epsilon_c$, where $\epsilon_c=(\epsilon_a+\epsilon_b)/2$, we present the average as follows:

$$\langle \psi_a(\mathbf{r})H_{\mathbf{q}}(z_1)\rangle = \psi_a(z)\langle H_{\mathbf{q}}(z_1)\rangle + \langle H(\mathbf{r})H_{\mathbf{q}}(z_1)\rangle \ . \tag{31}$$

The mean value of $H(\mathbf{r})$ is invariant with respect to tangential transpositions due to the spatial homogeneity in the (x,y) plane, and the correlation function depends only on the relative distance between tangential coordinates, i.e.,

$$\begin{aligned} &\langle H(\mathbf{r})\rangle = g^{(1)}(z) \ , \\ &\langle H(\mathbf{r})H(\mathbf{r}_1)\rangle = g^{(2)}(z,z_1,|\rho-\rho_1|) \ . \end{aligned} \tag{32}$$

Thus the first term of Eq. (31) does not contribute to the ellipticity coefficient since

$$q\langle H_{\mathbf{q}}(z)\rangle \sim q\delta(\mathbf{q})=0 \ .$$

Expanding correlation function (32) into the two-dimensional Fourier integral

$$g^{(2)}(z,z_1,|\rho-\rho_1|)=\int \frac{d^2\mathbf{q}}{(2\pi)^2} g_{\mathbf{q}}^{(2)}(z,z_1)\exp[i\mathbf{q}\cdot(\rho-\rho_1)]$$

we present the ellipticity coefficient in the form

$$\bar{\rho}_{\mathrm{Br}} = \frac{8\sqrt{2}\pi^2\epsilon_c^{5/2}K_0}{|\Delta\epsilon|}|r_D+r_R| \ , \tag{33}$$

where

$$r_R = \frac{3}{4}\epsilon_c \int\int_{-\infty}^{\infty} dz\, dz_1 \int \frac{d^2\mathbf{q}}{(2\pi)^2} q g_{\mathbf{q}}^{(2)}(z,z_1) \times \exp(-q|z-z_1|) \ . \tag{34}$$

Equations (30), (33), and (34) give the ellipticity coefficient in the principal order in $\Delta\epsilon$ without any limitation on the relative value of $\langle h^2\rangle^{1/2}/L_S$.

Restricting expansion (12) for $H(\mathbf{r})$ to the first term, the $g_{\mathbf{q}}^{(2)}(z,z_1)$ correlation function can be presented in the form

$$g_{\mathbf{q}}^{(2)}(z,z_1) = \frac{\epsilon'(z)\epsilon'(z_1)}{16\pi^2\epsilon_c^4}\langle |h_{\mathbf{q}}|^2\rangle \ . \tag{35}$$

Substituting this equation into Eq. (34) we get

$$r_R = \frac{3}{64\pi^2\epsilon_c^3}\int\int_{-\infty}^{\infty} dz\, dz_1 \int \frac{d^2\mathbf{q}}{(2\pi)^2} q\langle |h_{\mathbf{q}}|^2\rangle \epsilon'(z)\epsilon'(z_1) \times \exp(-q|z-z_1|) \ . \tag{36}$$

As is seen from Eq. (36) the contributions of the roughness fluctuations and intrinsic profile are not additive.

In the case of the sharp boundary between two media homogeneous up to the plane of separation one has $\epsilon'(z)=\Delta\epsilon\delta(z)$. Substituting Eq. (35) into Eq. (34) one obtains the well-known result of Zielinska, Bedeaux, and Vlieger [13],

$$r_R = r_{\mathrm{SB}} = \frac{3\Delta\epsilon^2}{64\pi^2\epsilon_c^3}\int \frac{d^2\mathbf{q}}{(2\pi)^2} q\langle |h_{\mathbf{q}}|^2\rangle \ . \tag{37}$$

V. COMPARISON WITH EXPERIMENT

Given the permittivity profile and correlation function of roughness the formulas obtained permit an immediate comparison of theory and experiment. We calculate the ellipticity coefficient for the boundary of two fluid media near the critical point. In this case the intrinsic profile is assumed to be described by the Fisk-Widom formula [16]. The correlation function $\langle |h\mathbf{q}|^2\rangle$ for the fluid boundary is given by the capillary-wave theory [14] in the form

$$\langle |h_{\mathbf{q}}|^2\rangle = \frac{k_B T}{g(\rho_b-\rho_a)+\sigma q^2} \ , \tag{38}$$

where g is the acceleration of gravity, ρ_a and ρ_b are the mass densities of the a and b bulk media, and σ is the surface tension.

On the other hand, most reliable experimental data on the ellipticity coefficient are obtained also in the critical region [8,9], since the thickness of the surface layer grows unlimitedly as the critical point is approached and therefore the surface contributions to the reflection become sufficiently large.

Using the Fisk-Widom profile

$$\epsilon(z)=\epsilon_c+\frac{\Delta\epsilon}{2}f(z/(2r_c)) \ ,$$

where the universal function $f(Y)$ has the form

$$f(Y)=\frac{\sqrt{2}\tanh(Y)}{[3-\tanh^2(Y)]^{1/2}} \ , \tag{39}$$

we calculate the ellipticity coefficient terms (36) and (30) due to the roughness and profile, respectively.

Substituting profile (39) into Drude integral (30) we get

$$r_D = \frac{\Delta\epsilon^2 r_c}{32\pi^2\epsilon_c^3}\int_{-\infty}^{\infty}[1-f^2(Y)]dY \ . \tag{40}$$

The value of the universal integral parameter $\eta_D=\int_{-\infty}^{\infty}[1-f^2(Y)]dY$ for the Fisk-Widom profile is well known [8], $\eta_D=2.28$.

Substituting derivative $\epsilon'(z)=[\Delta\epsilon/(4r_c)]f'(Y)$ of Eq. (39) into Eq. (36) and defining the Fourier transform of the localized function $f'(Y)$,

$$f'(Y)=(2\pi)^{-1}\int_{-\infty}^{\infty} d\kappa\, \varphi(\kappa)\exp(i\kappa Y) ,$$

we obtain

$$r_R=\frac{3\Delta\epsilon^2}{256\pi^2\epsilon_c^3 r_c}\int_{-\infty}^{\infty}\frac{d\kappa}{2\pi}\varphi^2(\kappa)\int\frac{d^2\mathbf{q}}{(2\pi)^2}\frac{q^2}{q^2+[\kappa/(2r_c)]^2}\times\langle|h_{\mathbf{q}}|^2\rangle . \quad (41)$$

Substituting Eqs. (40) and (41) into Eq. (33) we rearrange the ellipticity coefficient as follows:

$$\bar{\rho}_{\mathrm{Br}}=\sqrt{2}\pi|n_b-n_a|r_c\lambda^{-1}|\eta_D+\eta_R| ,$$

where

$$\eta_R=\frac{3}{8r_c^2}\int_{-\infty}^{\infty}\frac{d\kappa}{2\pi}\varphi^2(\kappa)\int\frac{d^2\mathbf{q}}{(2\pi)^2}\frac{q^2\langle|h\mathbf{q}|^2\rangle}{q^2+[\kappa/(2r_c)]^2} . \quad (42)$$

Using the capillary-wave theory and Eq. (38), and neglecting the gravity term we obtain

$$\eta_R=\frac{3}{32\pi r_c^2}\frac{k_BT}{\sigma}\int_{-\infty}^{\infty}\frac{d\kappa}{2\pi}\varphi^2(\kappa)\ln[1+(2r_cq_{\max}/\kappa)^2] , \quad (43)$$

where $q_{\max}$ is the short-wavelength cutoff [14].

We emphasize that the finiteness of the surface layer thickness weakens the dependence on the cutoff parameter, namely, changing it from linear to logarithmic.

In the case of a sharp boundary one has

$$f'_{\mathrm{SB}}(Y)=4r_c\delta(z)=2\delta(Y) , \quad \varphi(\kappa)=2$$

and integral (43) is readily calculated,

$$\int_{-\infty}^{\infty}\frac{d\kappa}{2\pi}\varphi^2(\kappa)\ln[1+(2r_cq_{\max}/\kappa)^2]=8r_cq_{\max} .$$

One obtains in this case

$$(\eta_R)_{\mathrm{SB}}=\frac{3}{4\pi r_c}\frac{k_BT}{\sigma}q_{\max} . \quad (44)$$

It is the well-known formula of Zielinska, Bedeaux, and Vlieger [13].

Calculating η_R we use the scaling expressions

$$\sigma=Rk_BTr_c^{-2} , \quad q_{\max}=a_0r_c^{-1}$$

for the surface tension and cutoff, where R and a_0 are universal parameters with known values $R=0.128$ and $a_0=0.748$ [18,25].

The calculated value of dimensionless roughness contribution in case of the Fisk-Widom profile is $\eta_R=0.77$. The total sum of the Drude term and that of roughness gives $\eta_D+\eta_R=3.05$. Figure 1 shows the extent to which the results obtained are consistent with the measurement data of Ref. [8].

For the sharp boundary Eq. (44) gives $\eta_R=1.39$ and $\eta_D+\eta_R=3.67$ in a noticeable discrepancy with the experiment of Ref. [8].

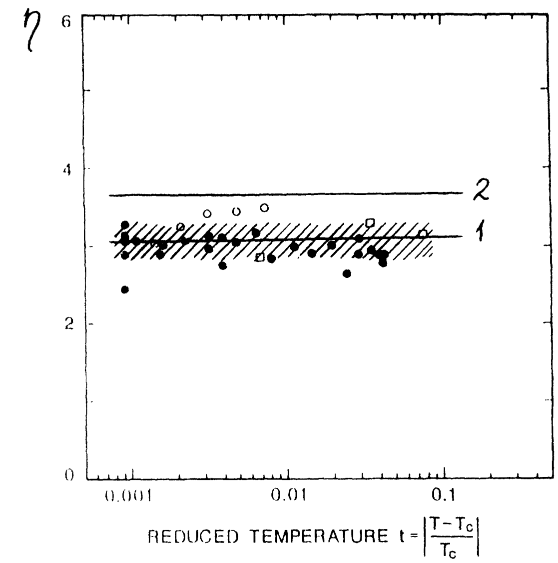

FIG. 1. The universal parameter $\eta=\eta_D+\eta_R$ plotted vs reduced temperature $t=|T-T_c|/T_c$ as measured for three critical mixtures in Ref. [8]. Solid circles, CS_2+CH_3OH; open circles, $C_6H_5NO_2+n\text{-}C_{10}H_{22}$; open squares, $CH_3OH+C_6H_{12}+C_6D_{12}$. The shaded region shows the least-squares error. The lines present the theoretical values of η: 1, $\eta=\eta_D+\eta_R=3.05$, where η_D is Drude's contribution (40) and η_R is the capillary wave term (43); 2, the $\eta=3.67$ value taken from Ref. [8], being the sum of the same Drude term and $(\eta_R)_{\mathrm{SB}}$. The theoretical value $\eta=3.05$ is practically equal to the mean value of experimental data [8].

VI. THE SECOND ORDER IN $\Delta\epsilon$

The result obtained above is valid in principal order in $\Delta\epsilon$ and therefore is applicable to media with a small difference of refractive indices, in particular, to those in the critical point vicinity.

To describe the reflection of light on the boundary with sufficiently larger refractive index difference we solve Eq. (27) in the next order in $\Delta\epsilon$. To this end we iterate this equation. We present the $\Delta\mathbf{D}(\mathbf{r})$ field as a sum of two terms

$$\Delta\mathbf{D}(\mathbf{r})=\Delta\mathbf{D}_0(z)+\Delta\mathbf{D}_H(\mathbf{r}) , \quad (45)$$

where $\Delta\mathbf{D}_0(z)$ is the value of $\Delta\mathbf{D}(\mathbf{r})$ for the ideally smooth surface $H=0$. One easily obtains from Eq. (27)

$$\Delta\mathbf{D}_0(z)=4\pi\epsilon(z)\psi_b(z)\overleftrightarrow{\mathbf{P}}_t\mathbf{D}_{b0} . \quad (46)$$

This formula is the solution of Eq. (27) for the Drude layered surface in main order in L_S/λ.

According to Eq. (18) one has to find the average $\langle\psi_a(\mathbf{r})\Delta\mathbf{D}(\mathbf{r})\rangle$. Multiplying Eq. (27) by $\psi_a(\mathbf{r})$ and averaging afterwards we obtain from the last term of the right-hand side of Eq. (27) the average of the form

$$\langle\psi_a(\mathbf{r})\psi_a(\mathbf{r}_1)\Delta\mathbf{D}(\mathbf{r}_1)\rangle .$$

Taking into account definitions (11) and (45) we rearrange the last average as follows:

$$\langle \psi_a(\mathbf{r})\psi_a(\mathbf{r}_1)\Delta\mathbf{D}(\mathbf{r}_1)\rangle = \langle \psi_a(\mathbf{r})\psi_a(\mathbf{r}_1)\rangle \Delta\mathbf{D}_0(z_1) + \psi_a(z_1)\langle \psi_a(\mathbf{r})\Delta\mathbf{D}_H(\mathbf{r}_1)\rangle + \psi_a(z)\langle H(\mathbf{r}_1)\Delta\mathbf{D}_H(\mathbf{r}_1)\rangle + O(H^3) . \quad (47)$$

Averages of the form $\langle A(\mathbf{r}_1)B(\mathbf{r}_1)\rangle$ do not depend on the x_1, y_1 coordinates due to the translational invariance in the tangential plane. Therefore their two-dimensional Fourier transforms are δ-function-like and do not contribute to the ellipticity coefficient

$$q\langle H(\mathbf{r}_1)\Delta\mathbf{D}_H(r_1)\rangle_{\mathbf{q}} \sim q\delta(\mathbf{q}) = 0 .$$

The same is valid for terms linear in H. As a result we can rearrange the last term of Eq. (27) to the form

$$[\psi_a(\mathbf{r}_1)\Delta\mathbf{D}(\mathbf{r}_1)]_{\mathbf{q}} \Longrightarrow \psi_a(z_1)\Delta\mathbf{D}_{\mathbf{q}}(z_1) + H_{\mathbf{q}}(z_1)\Delta\mathbf{D}_0(z_1) . \quad (48)$$

To obtain the Fourier transform $\Delta\mathbf{D}_{\mathbf{q}}(z)$ we rewrite Eq. (27) in main order in $\Delta\epsilon$ as follows:

$$\Delta\mathbf{D}(\mathbf{r}) = \int \frac{d^2\mathbf{q}}{(2\pi)^2}\exp(i\mathbf{q}\cdot\rho)\left[4\pi\epsilon_c[\psi_b(z)(2\pi)^2\delta(\mathbf{q}) + H_{\mathbf{q}}(z)]\overleftrightarrow{\mathbf{P}}_t + 2\pi\epsilon_c(\overleftrightarrow{\mathbf{P}}_n - \tfrac{1}{2}\overleftrightarrow{\mathbf{P}}_t)q\int_{-\infty}^{\infty} dz_1 \exp(-q|z-z_1|)H_{\mathbf{q}}(z_1)\right]\mathbf{D}_{b0} . \quad (49)$$

As is seen, the expression in the large parentheses just determines the sought Fourier transform $\Delta\mathbf{D}_{\mathbf{q}}(z)$.

Iterating Eq. (27) we obtain, accounting for Eqs. (48) and (49),

$$\overleftrightarrow{\mathbf{P}}_n\Delta\mathbf{D}(\mathbf{r}) = 2\pi\epsilon_a\int\frac{d^2\mathbf{q}}{(2\pi)^2}\exp(i\mathbf{q}\cdot\rho)q\int_{-\infty}^{\infty} dz_1\exp(-q|z-z_1|) \times [H_{\mathbf{q}}(z_1) + 2\pi\epsilon_c q\psi_a(z_1)\int_{-\infty}^{\infty} dz_2 H_{\mathbf{q}}(z_2)\exp(-q|z_1-z_2|)]\overleftrightarrow{\mathbf{P}}_n\mathbf{D}_{b0} , \quad (50)$$

$$\overleftrightarrow{\mathbf{P}}_t\Delta\mathbf{D}(\mathbf{r}) = 4\pi\epsilon(\mathbf{r})\psi_b(\mathbf{r})\overleftrightarrow{\mathbf{P}}_t\mathbf{D}_{b0} - \pi\epsilon(\mathbf{r})\int\frac{d^2\mathbf{q}}{(2\pi)^2}\exp(i\mathbf{q}\cdot\rho)q\int_{-\infty}^{\infty} dz_1\exp(-q|z-z_1|) \times \left[\epsilon_b^{-1}\epsilon(z_1)H_{\mathbf{q}}(z_1) + 4\pi\epsilon_c\psi_a(z_1)\left[H_{\mathbf{q}}(z_1) - \frac{q}{4}\int_{-\infty}^{\infty} dz_2\exp(-q|z_1-z_2|) \times H_{\mathbf{q}}(z_2)\right]\right]\overleftrightarrow{\mathbf{P}}_t D_{b0} . \quad (51)$$

Substituting Eqs. (50) and (51) into the ellipticity coefficient we obtain to the second order in $\Delta\epsilon$

$$\bar{\rho}_{\mathrm{Br}} = \frac{8\pi^2\epsilon_a\epsilon_b\sqrt{\epsilon_a+\epsilon_b}k_0}{\Delta\epsilon}\left[r_D + \frac{\epsilon_c}{4}\int\int_{-\infty}^{\infty} dz\, dz_1\int\frac{d^2\mathbf{q}}{(2\pi)^2}\exp(-q|z-z_1|) \times q\left[\left[3 + 4\frac{\epsilon(z)-\epsilon_c}{\epsilon_c} - \frac{\Delta\epsilon}{2\epsilon_c}\right]g_{\mathbf{q}}^{(2)}(z,z_1) + 3\pi\epsilon_c\psi_a(z_1)q\int_{-\infty}^{\infty} dz_2\exp(-q|z_1-z_2|)g_{\mathbf{q}}^{(2)}(z,z_2)\right]\right] . \quad (52)$$

Equation (52) is valid for the insulator boundary with an arbitrary spectrum of roughness. It may be significantly simplified accounting for roughness in accordance with Eq. (35) in the first $h(\rho)$ order in the sharp-boundary approximation. In this case we have

$$r_R = \frac{3}{4}\epsilon_c\left[\frac{\Delta\epsilon}{4\pi\epsilon_a\epsilon_b}\right]^2\int\frac{d^2\mathbf{q}}{(2\pi)^2}\langle|h_{\mathbf{q}}|^2\rangle q\left[1 - \frac{\Delta\epsilon}{24\epsilon_c}\right] . \quad (53)$$

Equation (52) is improved as compared with Eqs. (33) and (34); it contains corrections of the $\Delta\epsilon/\epsilon_c$ order and thus violates the symmetry with respect to the permutation of coexisting media a and b. Such an asymmetry was first revealed experimentally [3,26,27] and thereafter discussed theoretically [15]. However, an effect predicted in Ref. [15] was two orders of magnitude less than that found experimentally.

The correction term in Eq. (53) agrees in magnitude with the experimental asymmetry value. However, one has to consider Eq. (53) just as an estimate of the ellipticity coefficient asymmetry, since the sharp-boundary model may be applied at most to calculations in the principal order. In particular, the sharp stepwise density

$$\rho(z) = \rho_a + (\rho_b - \rho_a)\Theta(z)$$

of coexisting phases yields the $\epsilon(z)$ profile with the finite thickness in the second order in $\Delta\rho$.

Results which agreed quantitatively have to be computed from Eq. (52) provided that profiles are specified.

VII. CONCLUSION

We have calculated the ellipticity coefficient on a boundary of two insulator media taking into account the permittivity profile as well as surface roughness. The permittivity difference of coexisting phases was chosen as the expansion parameter. The obtained integral equation for the local displacement vector in the surface layer permits us to get a solution by means of the standard iteration procedure. Particular calculations require the profile and roughness correlation function both to be specified.

We have shown that the contribution of roughness depends on the surface profile. The term describing this contribution transforms continuously into the respective formula of the sharp-boundary model when $L_S \to 0$.

Another essential feature of the result obtained is that the dependence of the ellipticity coefficient on the capillary-wave cutoff weakens in the case of a finite thickness profile. Such a weakening is of crucial importance to the theory since the capillary-wave equation has itself been derived assuming the surface curvature to be small and hence is not applicable for short-wavelength oscillations. In our approach as distinct from the sharp-boundary model the relative contribution of long-wavelength oscillations grows and makes more justified the assumption (8) that the profile is conserved with the surface oscillations.

We use the well-known definition for the cutoff as the inverse correlation length. An alternative method of the $q_{\max}$ determination proposed recently [28] using the viscosity and sound velocity of liquid gives in the noncritical region a magnitude of the same order.

The results obtained have eliminated the discrepancy between the theory and ellipticity coefficient measurements [8,9] in the critical region.

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