

## VARIATION OF THE LOCAL FIELD THROUGH THE LIQUID–VAPOUR INTERFACE

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We derive an integral equation for the self-consistent local field  $E^{\text{loc}}(z)$  within an inhomogeneous non-polar fluid, with particular application to the liquid–vapour interface. Approximate solutions are given for the cases of induced atomic dipoles oriented perpendicular and parallel to the interface. For the perpendicular case we relate the average field to the local field and thus obtain an equation for the static dielectric constant  $\epsilon(z)$  in terms of the density profile  $n(z)$ . The departures of the local field from Lorentz form  $E^{\text{ext}}/(1+(8/3)\pi an(z))$  and of the dielectric constant from the Clausius–Mossotti form  $(1+(8/3)\pi an(z))/(1-(4/3)\pi an(z))$  are shown to be small. For the parallel case we discuss fringing of the external field and show that the dipoles align themselves with the average field, not the external field. The departure of the local field from  $E^{\text{ave}}/(1-(4/3)\pi an(z))$  is shown to be small.

Ellipsometric measurements of the surface structure of liquids require for their interpretation a theory relating the dielectric functions  $\epsilon_{\perp}(z)$  and  $\epsilon_{\parallel}(z)$  to the density profile  $n(z)$ . We approach this problem by deriving equations for the local field  $E^{\text{loc}}(z)$ . In our preceding paper<sup>1</sup>) we considered the local field near the surface of a crystalline solid. Discussion of topics covered there will correspondingly be abbreviated.

### 1. Dipoles oriented perpendicular to the surface: general formalism

The system under consideration is a non-polar fluid of finite but macroscopic depth, with the liquid–vapour interface (of very large extent) lying in the  $x$ – $y$  plane. Two oppositely charged plates, lying parallel to the interface, provide the external field  $E^{\text{ext}}$  polarizing the atoms in the liquid. The self-consistent local field  $E^{\text{loc}}(z)$  satisfies the equation

$$E^{\text{loc}} = E^{\text{ext}} + E^{\text{dip}}, \quad (1)$$

where  $E^{\text{dip}}$  is the contribution to the field at an atom due to dipoles induced on all the other atoms in the fluid. Consider the local field polarizing an atom at  $r_1$ . The conditional probability that another atom is within  $dr_2$  about  $r_2$ , given that an atom is within  $dr_1$  about  $r_1$ , is  $n_2(r_1, r_2)dr_1 dr_2/n(r_1)dr_1$ , where  $n_2$  is the

pair density (see for example ref. 2). As in ref. 2, we introduce a generalised pair correlation function  $g$ :

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2). \quad (2)$$

For the geometry under consideration, the density is a function of  $z$  only, and  $g$  is a function of  $r = \sqrt{x_{12}^2 + y_{12}^2 + z_{12}^2}$  and of  $z_1$  and  $z_2$ . The conditional probability is thus  $n(z_2)g(r, z_1, z_2)dr_2$ . The  $z$ -component at  $\mathbf{r}_1$  of the field due to an atomic dipole of magnitude  $p_2$  at  $\mathbf{r}_2$  is  $p_2r^{-5}(3z_{12}^2 - r^2)$ ; by definition of  $E^{\text{loc}}$ ,  $p_2$  has the value  $\alpha E^{\text{loc}}(z_2)$ , where  $\alpha$  is the atomic polarizability. (We have replaced the polarized atoms by point dipoles (this approximation is discussed in ref. 1), and assumed that the dipoles are oriented in the  $z$ -direction with magnitude dependent on the  $z$ -coordinate only. The effect of dipole fluctuations on the dielectric constant of a homogeneous fluid is discussed by Kirkwood<sup>3</sup>).

The self-consistency equation (2) thus reads (c.f. section 3 of ref. 4)

$$E^{\text{loc}}(z_1) = E^{\text{ext}} + \alpha \int_{z_b}^{z_t} dz_2 n(z_2) E^{\text{loc}}(z_2) \int \int_{-\infty}^{\infty} dx_2 dy_2 r^{-5} (3z_{12}^2 - r^2) g(r, z_1, z_2), \quad (3)$$

where  $z_b$  and  $z_t$  give the positions of the bottom and top capacitor plates. By changing to cylindrical coordinates (see p. 339 of ref. 2) we can perform one integration:

$$E^{\text{loc}}(z_1) = E^{\text{ext}} + 2\pi\alpha \int_{z_b}^{z_t} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{|z_{12}|}^{\infty} dr r^{-4} (3z_{12}^2 - r^2) g(r, z_1, z_2). \quad (4)$$

In appendix A we show that

$$\int_{|z|}^{\infty} dr r^{-4} (3z^2 - r^2) = -\frac{4}{3}\delta(z). \quad (5)$$

Thus in the limit of a structureless fluid ( $g \equiv 1$ ) we regain the Lorentz local field at the local density (see figs. 1 and 2):

$$E_L^{\text{loc}}(z) = \frac{E^{\text{ext}}}{1 + (8/3)\pi\alpha n(z)}. \quad (6)$$

In section 3 we show that the dielectric function  $\epsilon = E^{\text{ext}}/E^{\text{ave}}$  is given by

$$\epsilon(z) = [1 - 4\pi\alpha n(z)E^{\text{loc}}(z)/E^{\text{ext}}]^{-1},$$

so that (6) leads to the structureless fluid dielectric function, which has the Clausius-Mossotti form at the local density:

$$\epsilon_{\text{CM}}(z) = \frac{1 + (8/3)\pi\alpha n(z)}{1 - (4/3)\pi\alpha n(z)}.$$

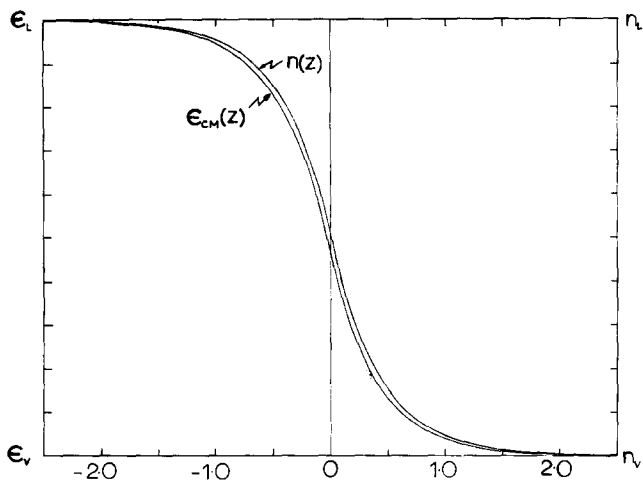


Fig. 1. Density  $n(z)$  (upper curve) and structureless fluid dielectric function  $\epsilon_{CM}(z) = (1 + (8/3)\pi\alpha n(z))/(1 - (4/3)\pi\alpha n(z))$  (lower curve), with  $n(z) = \frac{1}{2}n_l[1 - \text{sgn } z(1 - e^{-|z|/\lambda})]$ ,  $\lambda = 0.415 d$ ,  $\alpha n_l = 0.03444$ . This profile and  $\alpha n_l$  value are used in calculating the results of figs. 2-4. Note that the dielectric function has a profile of nearly the same shape as the density profile, shifted to the liquid side. (For the Fermi (or tanh) profile  $\epsilon_{CM}(z)$  is exactly a shifted Fermi function. The shift is a fixed fraction (approximately  $(4/3)\pi\alpha(n_l - n_v)$ ) of the interface thickness).

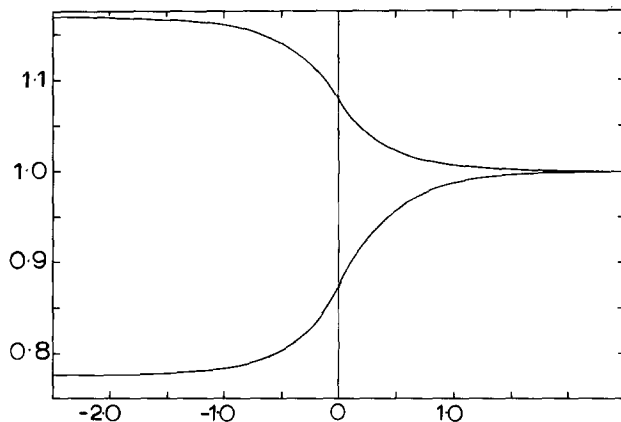


Fig. 2. Local field for a structureless fluid. Upper curve is  $E_{sf}^{loc}(z)/E^{ave} = (1 - (4/3)\pi\alpha n(z))^{-1}$ , applicable to the case of atomic dipoles aligned parallel to the surface (the limiting value in the liquid = 1.169). Lower curve is  $E_L^{loc}(z)/E^{ext} = (1 + (8/3)\pi\alpha n(z))^{-1}$ , applicable to the case of atomic dipoles aligned perpendicular to the surface (limiting value in the liquid = 0.776).

In the general case, we write  $g = 1 + (g - 1)$  to obtain

$$E^{\text{loc}}(z_1) = E^{\text{ext}} - \frac{8}{3}\pi\alpha n(z_1)E^{\text{loc}}(z_1) + 2\pi\alpha \int_{z_b}^{z_1} dz_2 n(z_2)E^{\text{loc}}(z_2) \int_{|z_{12}|}^{\infty} dr r^{-4}(3z_{12}^2 - r^2)[g(r, z_1, z_2) - 1]. \quad (7)$$

At first sight, the final term in (7) appears to be singular at  $r = 0$  when  $z_2 = z_1$ ; we shall show that it is not. First we replace the limits  $z_b$  and  $z_1$  by  $-\infty$  and  $+\infty$  respectively (we take the interface to be near zero  $z$ , and do not consider  $z_1$  values near the capacitor plates). This step is valid because  $g(r, z_1, z_2)$  can differ from unity only when  $|z_{12}|$  is smaller than the correlation length, which is microscopic except at the critical point. The final term in (7) can therefore be written as

$$2\pi\alpha \int_0^{\infty} dr r^{-4} \int_{-r}^r dz (3z^2 - r^2) n(z_1 + z) E^{\text{loc}}(z_1 + z) [g(r, z_1, z_1 + z) - 1]. \quad (8)$$

Expanding  $n(z_1 + z)E^{\text{loc}}(z_1 + z)[g(r, z_1, z_1 + z) - 1]$  in a Taylor series about  $z_1$  and using

$$\int_{-r}^r dz (3z^2 - r^2) z^n = \begin{cases} 0 & \text{if } n = 0 \text{ or } n \text{ odd} \\ 4nr^{n+3}/(n+1)(n+3) & \text{otherwise} \end{cases} \quad (9)$$

gives:

$$E^{\text{loc}}(z_1) = E^{\text{ext}} - \frac{8}{3}\pi\alpha n(z_1)E^{\text{loc}}(z_1) + \frac{16}{15}\pi\alpha \int_0^{\infty} dr r \frac{\partial^2}{\partial z^2} [n(z)E^{\text{loc}}(z)(g(r, z_1, z) - 1)]_{z=z_1} + \dots, \quad (10)$$

which is manifestly non-singular.

Within each bulk phase  $n$ ,  $E^{\text{loc}}$  and  $g$  each become independent of  $z$ . The deviation of the local field from the Lorentz value is then zero (in the point-dipole approximation, and neglecting fluctuations in magnitude and orientation of the atomic dipoles). Thus we have shown in passing that

$$E_{l,v}^{\text{loc}} = \frac{E^{\text{ext}}}{1 + (8/3)\pi\alpha n_{l,v}}, \quad (11)$$

so that (11) leads to the Clausius–Mossotti dielectric constant

$$\epsilon_{l,v} = \frac{1 + (8/3)\pi\alpha n_{l,v}}{1 - (4/3)\pi\alpha n_{l,v}}. \quad (12)$$

Using (8) we may rewrite (7) as

$$\left[1 + \frac{8}{3}\pi\alpha n(z_1)\right]E^{\text{loc}}(z_1) = E^{\text{ext}} + 2\pi\alpha \int_0^\infty dr r^{-4} \int_{-r}^r dz (3z^2 - r^2)n(z_1 + z)E^{\text{loc}}(z_1 + z)[g(r, z_1, z_1 + z) - 1], \quad (13)$$

which determines the local field in terms of the density profile  $n$  and the generalised pair correlation function  $g$  via a linear integral equation.

## 2. Dipoles oriented perpendicular to the surface: an approximate solution

The last term in (13) (which we have demonstrated to be an interface or inhomogeneity term) is small, because  $g - 1$  has a negative part (the correlation hole) at small  $r$ , and is mainly positive at intermediate  $r$ . Thus a large amount of cancellation occurs in the integral; this will be confirmed by numerical calculation. We shall therefore make simplifying approximations in the evaluation of this correction to the Lorentz value (6) of the local field. First we note that while  $n(z)$  varies by a factor of several hundred or more in passing from vapour to liquid near the triple point,  $E^{\text{loc}}$  varies by 20 to 30% ( $\pi\alpha n_1$  is small, of order  $10^{-1}$ , for most liquids). Thus, in the interface term of (13), we can approximate  $E^{\text{loc}}(z_1 + z)$  by  $E^{\text{loc}}(z_1)$  and obtain a linear *algebraic* equation for the local field, giving

$$E^{\text{loc}}(z_1) = E^{\text{ext}} \left/ \left\{ 1 + \frac{8}{3}\pi\alpha n(z_1) - 2\pi\alpha \int_0^\infty dr r^{-4} \int_{-r}^r dz (3z^2 - r^2)n(z_1 + z)[g(r, z_1, z_1 + z) - 1] \right\} \right. \quad (14)$$

Correction terms to the analogous approximation in ref. 1 were shown to be insignificant.

Second, we are forced to approximate  $g(r, z_1, z_2)$ , since this function has not been determined either theoretically or experimentally. We know that  $g$  tends to  $g_l(r)$  in the liquid and to  $g_v(r)$  in the vapour, and that  $g_l$  and  $g_v$  are qualitatively similar. The simplest approximation is to take  $g$  equal to  $g_l$  or  $g_v$  or some combination of these. Taking it to be purely a function of  $r$  will enable us to perform the  $z$  integration analytically for a simple profile. For an arbitrary density profile we can write

$$n(z) = \frac{1}{2}(n_1 + n_v) - \frac{1}{2}(n_1 - n_v)\theta(z), \quad (15)$$

where  $\theta$  ranges from  $-1$  at  $z = -\infty$  to  $+1$  at  $z = +\infty$ . In terms of  $\theta$  (and with

$E^{\text{loc}}(z_1 + z) \approx E^{\text{loc}}(z_1)$ ,  $g \approx g(r)$  in the interface term), (14) can be written as

$$\frac{E^{\text{ext}}}{E^{\text{loc}}(z_1)} \approx 1 + \frac{8}{3}\pi\alpha n(z_1) + \pi\alpha(n_1 - n_v) \int_0^\infty dr r^{-4} [g(r) - 1] \int_{-r}^r dz (3z^2 - r^2) \theta(z_1 + z). \quad (16)$$

In our numerical estimate of the interface term, we shall use the exponential profile

$$\theta(z) = \text{sgn } z (1 - e^{-|z|/\lambda}). \quad (17)$$

That this functional form is correct for large  $|z|$  (at least near the critical point) has been shown by Fisk and Widom<sup>5</sup>) from a generalised van der Waals theory. For  $\theta$  given by (17), the  $z$  integration is carried out in appendix B. Our numerical calculations (shown in fig. 3) are for this profile, with  $\lambda = 0.415d$ , where  $d$  is the atomic diameter defined in (19). This value of  $\lambda$  is the average of  $0.40d$  and  $0.43d$  obtained by comparing theory with experimental data on the surface tension and energy of Ar, Kr and Xe near their triple points<sup>6</sup>). The corresponding 10–90 thickness of the interface is  $(2 \log 5)\lambda$ , i.e. about 1.3 atomic diameters. In the interface term we have used

$$g(r) = g_v(r) = \exp[-u(r)/T], \quad (18)$$

with the interatomic potential given by

$$u(r) = 4v \left[ \left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^6 \right]. \quad (19)$$

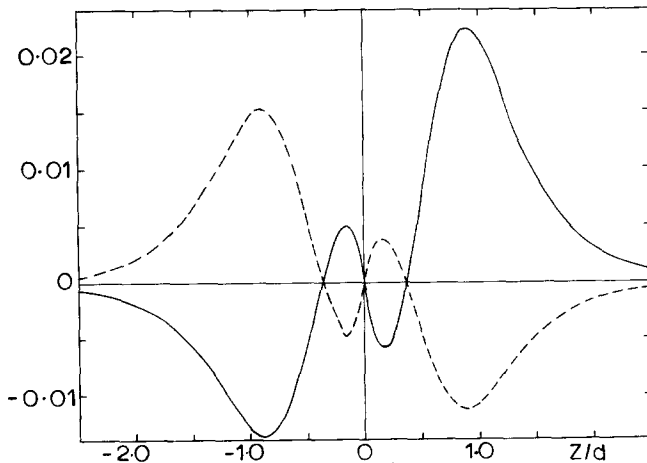


Fig. 3. Local fields plotted as departures from those for structureless fluids. Continuous curve is  $(E^{\text{loc}}(z) - E_{\text{L}}^{\text{loc}}(z))/E^{\text{ext}}$  (perpendicular case); broken curve is  $(E^{\text{loc}}(z) - E_{\text{st}}^{\text{loc}}(z))/E^{\text{ave}}$  (parallel case).

As in refs. 2 and 6 we use  $4v/T = 5.69$ , this being the average for Ar, Kr and Xe at their triple points. For the product of density with polarizability we have used  $\alpha n_1 = 0.03444$ , appropriate to liquid argon near its triple point ( $n_1 = 0.02126 \text{ \AA}^{-3}$ <sup>7</sup>) and  $\alpha = 1.62 \text{ \AA}^3$ <sup>8</sup>): these values give a Clausius–Mossotti dielectric constant of 1.506, in agreement with experiment<sup>9</sup>).

### 3. Average field, dielectric function, and potentials

In the previous section we related the local field to the external field. To determine the dielectric function we need to relate these to the average field, in order to use the electrostatic definition

$$\epsilon^{-1}(z) = \frac{E^{\text{ave}}(z)}{E^{\text{ext}}}. \quad (20)$$

The average field is the average of the microscopic field over all positions at a given depth  $z$ , whereas the local field is the electric field at the centre of an atom in the fluid, excluding the contribution from its own dipole.

To calculate the average field we shall find the potential at an arbitrary position at depth  $z_1$ , and differentiate with respect to  $z_1$ . Since the potential at  $r_1$  due to a dipole  $p_2$  at  $r_2$  is  $r_{12} \cdot p_2 / r_{12}^3$ , which is  $z_{12} p_2 / r_{12}^3$  when  $p_2$  points in the  $z$ -direction, we have

$$\begin{aligned} U^{\text{ave}}(z_1) &= -z_1 E^{\text{ext}} + \alpha \int_{z_b}^{z_1} dz_2 n(z_2) E^{\text{loc}}(z_2) z_{12} \iint_{-\infty}^{\infty} dx_2 dy_2 r^{-3} \\ &= -z_1 E^{\text{ext}} + 2\pi\alpha \int_{z_b}^{z_1} dz_2 n(z_2) E^{\text{loc}}(z_2) z_{12} \int_{|z_{12}|}^{\infty} dr r^{-2} \\ &= -z_1 E^{\text{ext}} + 2\pi\alpha \int_{z_b}^{z_1} dz_2 n(z_2) E^{\text{loc}}(z_2) \text{sgn } z_{12}. \end{aligned} \quad (21)$$

Since

$$\frac{\partial}{\partial z_1} \text{sgn } z_{12} = 2\delta(z_{12}), \quad (22)$$

$$E^{\text{ave}} = -\frac{\partial U^{\text{ave}}(z_1)}{\partial z_1} = E^{\text{ext}} - 4\pi\alpha n(z_1) E^{\text{loc}}(z_1). \quad (23)$$

This has been proved with no approximations other than those involved in setting up eq. (3). Baym and Brown<sup>10</sup>) have given an elegant proof of (23) for a homogeneous fluid by Fourier transform methods. From (20) and (23) we have the static dielectric constant in terms of  $E^{\text{loc}}/E^{\text{ext}}$ :

$$\epsilon^{-1}(z_1) = 1 - 4\pi\alpha n(z_1) E^{\text{loc}}(z_1) / E^{\text{ext}}. \quad (24)$$

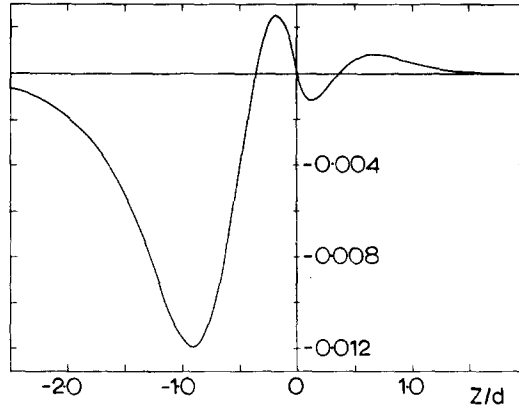


Fig. 4. Dielectric function for the perpendicular case, plotted as a departure from the structureless fluid value:  $\epsilon(z) - \epsilon_{CM}(z)$ .

Using our calculations of  $E^{loc}$  of the previous section, we find that the departure of  $\epsilon(z)$  from the Clausius–Mossotti form at the local density (eq. (6)) is small, at the most 1% (see fig. 4). This small departure may nevertheless have an appreciable effect on the surface thickness calculated from ellipsometric measurements<sup>11</sup>).

While the potential is a useful quantity for calculating the average field, it cannot be used for calculating the local field, as the following argument shows. Suppose we have a local potential function  $U^{loc}(r_1)$ , meaning “potential at  $r_1$ , given that there is an atom centred on  $r_1$ ”. Differentiation of this function gives

$$-\nabla_1 U^{loc}(r_1) = -\lim_{\Delta r_1 \rightarrow 0} \left\{ \begin{aligned} &(\text{potential at } r_1 + \Delta r_1, \text{ given atom at } r_1 + \Delta r_1) \\ &- (\text{potential at } r_1, \text{ given atom at } r_1) \end{aligned} \right\} / \Delta r_1.$$

This is not the local field, which is

$$-\lim_{\Delta r_1 \rightarrow 0} \left\{ \begin{aligned} &(\text{potential at } r_1 + \Delta r_1, \text{ given atom at } r_1) \\ &- (\text{potential at } r_1, \text{ given atom at } r_1) \end{aligned} \right\} / \Delta r_1.$$

Thus

$$E^{loc}(r_1) \neq -\nabla_1 U^{loc}(r_1), \quad (25)$$

and so this local potential function cannot be used to calculate the local field.



#### 4. Dipoles oriented parallel to the surface

For this case we adopt the geometry of fig. 2 in ref. 1: the liquid half-fills a container, the sides of which (at  $x = \pm X$ ) are capacitor plates which when charged provide the external field which orients the atomic dipoles parallel to the surface. The liquid-vapour interface is again near  $z = 0$ , and extends to  $\pm\infty$  in the  $y$ -direction. This case is more complicated than that for dipoles perpendicular to the surface, because the external field is no longer constant: the density of charges on the capacitor plates will vary with depth. There will also be fringing of the external field (i.e. it will have a non-zero  $z$ -component); this fringing, as we shall see below, is cancelled exactly by fringing in  $E^{\text{dip}}$ ; the field due to the atomic dipoles. The local field  $E^{\text{ext}} + E^{\text{dip}}$  will thus be parallel to the surface at all points. To calculate  $E^{\text{ext}}$  and  $E^{\text{dip}}$  we shall assume that  $E_x^{\text{loc}}$  is a function of  $z$  only, and that  $E_z^{\text{loc}} = 0$ , and show that this local field is self-consistent.

We begin by calculating the field due to the atomic dipoles [cf. (3)]:

$$E^{\text{dip}}(z_1, x_1) = \alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{-X}^X dx_2 \int_{-\infty}^{\infty} dy_2 r^{-5} [3(\hat{p}_2 \cdot \mathbf{r})\mathbf{r} - r^2 \hat{p}_2] g(r, z_1, z_2). \quad (26)$$

By our assumption about  $E^{\text{loc}}$ ,  $\hat{p}_2 = \hat{x}$ ; the  $x$  and  $z$  components of (26) therefore have  $3x_{12}^2 - r^2$  and  $3x_{12}z_{12}$  in the integrand. In  $E_x^{\text{dip}}$ , the integral over  $x_2$  and  $y_2$  can be written as

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy r^{-5} (3x^2 - r^2) g(r, z_1, z_2) - \left\{ \int_{X-x_1}^{\infty} + \int_{X+x_1}^{\infty} \right\} dx \int_{-\infty}^{\infty} dy r^{-5} (3x^2 - r^2) \quad (27)$$

(we have put  $g = 1$  in the second term since  $r \geq |x_{12}|$  and we avoid wall effects by keeping  $|x_1|$  less than  $X$  by at least a correlation length). Now (cf. eq. (A.4) of ref. 1)

$$\begin{aligned} \int_X^{\infty} dx \int_{-\infty}^{\infty} dy r^{-5} (3x^2 - r^2) &= -2 \int_X^{\infty} dx \left[ 1 + x \frac{\partial}{\partial x} \right] \int_0^{\infty} dy r^{-3} \\ &= -2 \int_X^{\infty} dx \left[ 1 + x \frac{\partial}{\partial x} \right] (x^2 + z^2)^{-1} = \frac{2X}{X^2 + z^2}. \end{aligned} \quad (28)$$

In the first term of (27) we use the  $x$ - $y$  symmetry to replace  $3x_{12}^2 - r^2$  by  $-(3z_{12}^2 - r^2)/2$ . Thus

$$\begin{aligned}
 E_x^{\text{dip}}(z_1, x_1) = & -\pi\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{|z_{12}|}^{\infty} dr r^{-4} (3z_{12}^2 - r^2) g(r, z_1, z_2) \\
 & - 2\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \left\{ \frac{X - x_1}{(X - x_1)^2 + z_{12}^2} + \frac{X + x_1}{(X + x_1)^2 + z_{12}^2} \right\}.
 \end{aligned} \tag{29}$$

The second term is the fringing term. Before showing that this is cancelled by the fringing term in the external field, we shall consider  $E_z^{\text{dip}}$ : we have

$$\int_{-X}^X dx_2 x_{12} r^{-5} g(r, z_1, z_2) = - \int_{-X-x_1}^{X-x_1} dx x r^{-5} g(r, z_1, z_2) = \int_{X-x_1}^{X+x_1} dx x r^{-5} \tag{30}$$

(we have put  $g = 1$  again). Thus, after elementary integration,

$$\begin{aligned}
 E_z^{\text{dip}}(z_1, x_1) = & 2\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) z_{12} \{ [(X - x_1)^2 + z_{12}^2]^{-1} \\
 & - [(X + x_1)^2 + z_{12}^2]^{-1} \}.
 \end{aligned} \tag{31}$$

We shall now calculate  $E^{\text{ext}}$  from  $E^{\text{ave}}$ , using potentials as in section 3. Analogously to (21), we have

$$\begin{aligned}
 U^{\text{ave}} = & U^{\text{ext}} + \alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{-X}^X dx_2 \int_{-\infty}^{\infty} dy_2 x_{12} r^{-3} \\
 = & U^{\text{ext}} + 2\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{X-x_1}^{X+x_1} dx \frac{x}{x^2 + z_{12}^2}.
 \end{aligned} \tag{32}$$

Now  $U^{\text{ave}} = -x_1 E^{\text{ave}}$  where  $E^{\text{ave}}$  is the  $x$ -component of the average field, and is independent of  $x_1$  and  $z_1$  (this solution satisfies the boundary conditions on  $U^{\text{ave}}$ , and by uniqueness is thus the correct solution). Thus

$$\begin{aligned}
 E_z^{\text{ext}}(z_1, x_1) = & -\frac{\partial U^{\text{ext}}}{\partial z_1} = \frac{\partial}{\partial z_1} \alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \log \frac{(X + x_1)^2 + z_{12}^2}{(X - x_1)^2 + z_{12}^2} \\
 = & -2\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) z_{12} \\
 & \times \{ [(X - x_1)^2 + z_{12}^2]^{-1} - [(X + x_1)^2 + z_{12}^2]^{-1} \}.
 \end{aligned} \tag{33}$$

This cancels exactly with (31), showing that the dipoles experience no field in the  $z$  direction. Differentiating (32) with respect to  $x_1$ , we obtain

$$E_x^{\text{ext}}(z_1, x_1) = E^{\text{ave}} + 2\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \left[ \frac{X - x_1}{(X - x_1)^2 + z_{12}^2} + \frac{X + x_1}{(X + x_1)^2 + z_{12}^2} \right]. \quad (34)$$

The second term cancels exactly with the second term in (29), leaving no fringing in the local field:

$$\begin{aligned} E_x^{\text{loc}} &= E_x^{\text{ext}} + E_x^{\text{dip}} \\ &= E^{\text{ave}} - \pi\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{|z_{12}|}^{\infty} dr r^{-4} (3z_{12}^2 - r^2) g(r, z_1, z_2). \end{aligned} \quad (35)$$

For this geometry, the average field has emerged as the useful quantity, in place of the external field:  $E^{\text{ave}}$  is directly linked to the potential difference across the capacitor plates, and is not subject to fringing.

Returning to (35), we note that the second term on the right is  $-\frac{1}{2}$  times the second term in (4), and so we can use the results of the perpendicular case to immediately write down the results for the parallel case. Using (5) in (35) we obtain

$$\begin{aligned} E^{\text{loc}}(z_1) &= E^{\text{ave}} + \frac{4}{3}\pi\alpha n(z_1) E^{\text{loc}}(z_1) \\ &\quad - \pi\alpha \int_{-\infty}^{\infty} dz_2 n(z_2) E^{\text{loc}}(z_2) \int_{|z_{12}|}^{\infty} dr r^{-4} (3z_{12}^2 - r^2) [g(r, z_1, z_2) - 1]. \end{aligned} \quad (36)$$

The structureless fluid approximation to  $E^{\text{loc}}$  is thus

$$\frac{E^{\text{ave}}}{1 - (4/3)\pi\alpha n(z_1)}. \quad (37)$$

Since the last term in (36) is purely an interface term, as before, the local field within either bulk phase is given by

$$E_{1,v}^{\text{loc}} = \frac{E^{\text{ave}}}{1 - (4/3)\pi\alpha n_{1,v}}. \quad (38)$$

Deep inside either phase (on the scale of  $X$ ), (34) gives

$$E_{1,v}^{\text{ext}} = E^{\text{ave}} - 4\pi\alpha n_{1,v} E_{1,v}^{\text{loc}}. \quad (39)$$

Together with (38) this shows that the local field takes the Lorentz value (11) deep in either phase.

When  $E^{\text{loc}}(z_2)$  is approximated by  $E^{\text{loc}}(z_1)$  in the last term of (36),

$$E^{\text{loc}}(z_1) = E^{\text{ave}} \left/ \left\{ 1 - (4/3)\pi\alpha n(z_1) + \pi\alpha \int_0^\infty dr r^{-4} \int_{-r}^r dz (3z^2 - r^2)n(z_1 + z)[g(r, z_1, z_1 + z) - 1] \right\} \right. \quad (\text{A} \cdot 0)$$

Using the exponential profile, and  $g$  as defined by (18) and (19), gives the results for  $E^{\text{loc}}$  shown in fig. 3.

### Appendix A

$$\text{Proof of } \int_{|z|}^\infty dr r^{-4}(3z^2 - r^2) = -(4/3)\delta(z) \quad (\text{A} \cdot 1)$$

This integral is zero for  $z \neq 0$  and singular at  $z = 0$ . To see that the singularity is a delta function we consider

$$I = \int_{-L}^L dz f(z) \int_{|z|}^\infty dr r^{-4}(3z^2 - r^2) = \sum_{n=0}^\infty \frac{f^{(n)}(0)}{n!} \int_{-L}^L dz z^n \int_{|z|}^\infty dr r^{-4}(3z^2 - r^2). \quad (\text{A} \cdot 2)$$

Now

$$\begin{aligned} \int_{-L}^L dz z^n \int_{|z|}^\infty dr r^{-4}(3z^2 - r^2) \\ = \int_0^L dr r^{-4} \int_{-r}^r dz z^n (3z^2 - r^2) + \int_L^\infty dr r^{-4} \int_{-L}^L dz z^n (3z^2 - r^2). \end{aligned} \quad (\text{A} \cdot 3)$$

This is zero for  $n$  odd. For  $n = 0$  the first term is zero, the second is  $-4/3$ . For  $n$  even and non-zero (A·3) equals

$$2 \int_0^L dr r^{n-1} \left( \frac{3}{n+3} - \frac{1}{n+1} \right) + 2 \int_L^\infty dr r^{-4} \left( \frac{3L^{n+3}}{n+3} - \frac{r^2 L^{n+1}}{n+1} \right) = 0.$$

Thus  $I = -(4/3)f(0)$ , which proves (A·1). (We have used symmetric limits  $\pm L$  in (A·2) for simplicity; arbitrary limits give the same result.)

### Appendix B

$$\text{Evaluation of } K(r, z_1) = \int_{-r}^r dz (3z^2 - r^2)\theta(z_1 + z)$$

For the exponential profile,  $\theta(z)$  is equal to

$$\operatorname{sgn} z(1 - e^{-|z|/\lambda}) = \frac{d}{dz}(|z| + \lambda e^{-|z|/\lambda}). \quad (\text{B}\cdot 1)$$

Using

$$|z| = \frac{1}{2} \frac{d}{dz}(z^2 \operatorname{sgn} z), e^{-|z|/\lambda} = \lambda \frac{d}{dz}[\operatorname{sgn} z(1 - e^{-|z|/\lambda})] \quad (\text{B}\cdot 2)$$

and

$$\operatorname{sgn} z[z^2 + 2\lambda^2(1 - e^{-|z|/\lambda})] = \frac{d}{dz} \left[ \frac{1}{3}|z|^3 + 2\lambda^2|z| + 2\lambda^3 e^{-|z|/\lambda} \right],$$

we find, on successive integration by parts,

$$K(r, z_1) = J(r + z_1) - J(r - z_1), \quad (\text{B}\cdot 3)$$

where

$$J(z) = (2r^2 + 6\lambda^2)(|z| + \lambda e^{-|z|/\lambda}) - 3r \operatorname{sgn} z[z^2 + 2\lambda^2(1 - e^{-|z|/\lambda})] + |z|^3.$$

**Note added in proof.** A general definition of the dielectric function, used in the generalization of Maxwell's equations to dielectric media [see for example Landau and Lifshitz<sup>12</sup>], §68] is

$$\epsilon(z) = 1 + 4\pi\alpha n(z)E^{\text{loc}}(z)/E^{\text{ave}}(z).$$

In the perpendicular case, this reduces to (20). In the parallel case,  $E^{\text{ave}}(z)$  is independent of  $z$ . Using (37) for  $E^{\text{loc}}(z)$  yields the Clausius–Mossotti form of the dielectric function, so for a structureless fluid, and [see (38)] deep inside either phase,  $\epsilon_{\perp}(z)$  and  $\epsilon_{\parallel}(z)$  are identical. To first order in the interface term in (13),

$$\epsilon_{\parallel}(z) - \epsilon_{\text{CM}}(z) = -\frac{1}{2}[\epsilon_{\perp}(z) - \epsilon_{\text{CM}}(z)].$$

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