

SUMMATION OF DIPOLAR FIELDS IN SIMULATED LIQUID-VAPOUR INTERFACES

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Computer simulations of liquid-vapour interfaces produce configurations of some finite number of atoms or molecules within a central cell. Periodic boundary conditions repeat the central cell to infinity. To extract local fields and optical properties from these configurations it is necessary to sum over dipolar fields to infinity. For N polarizable atoms in the central simulation cell, $\frac{1}{2}N(N-1)$ dipolar sums are required, and N simultaneous linear equations are to be solved to find the self-consistent local fields on each atom. A realistic simulation of a liquid-vapour interface requires a thousand particles or more. Hence an efficient algorithm for the dipolar sums is required. Formulae are given which convert these slowly converging sums to rapidly convergent sums requiring only a few terms. These formulae enable local fields to be computed, for each atom, as a byproduct of the computer simulation. Of particular interest are the fluctuations in the local fields.

1. Introduction

One of the main experimental probes into the structure of liquid-vapour interfaces is polarization-modulation ellipsometry [1]. To lowest order in the interface thickness, the quantity measured is proportional to the integral [2, 3]

$$I = \int dz \left\{ \varepsilon_z + \varepsilon_v - \varepsilon_x(z) - \frac{\varepsilon_t \varepsilon_v}{\varepsilon_z(z)} \right\}, \quad (1)$$

where $\varepsilon_{t,v}$ denote the (optical) dielectric constants of the liquid and vapour phases, and the dielectric functions $\varepsilon_x(z)$ and $\varepsilon_z(z)$ give the response to an external electric field applied respectively along the interface, and perpendicular to the interface. (The interface plane is taken to be normal to the z -axis, and the properties of the system are symmetric with respect to the interchange of x and y coordinates.) It should be noted that (1) is the contribution from a planar stratified interface, and that a further contribution comes from the roughening of the interface by capillary waves [1, 4, 5]. The untangling of these contributions is still under discussion [4, 6], but it appears that the size of

computer simulated systems is too small to allow the surface waves to develop [7, 8].

Even supposing that the integral (1) gives the main contribution to the ellipsometric quantity $\bar{\rho}$ (the imaginary part of r_p/r_s at the angle of incidence where the real part is zero), the problem remains of the relationship of ϵ_x and ϵ_z to the number density $n(z)$ and to the generalized pair correlation function $g(r, z_1, z_2)$. The initial theoretical estimate [9] indicated that some anisotropy may exist at the liquid-vapour interface, making I about 20% smaller than it would be if $\epsilon_x \equiv \epsilon_z$ within the interface (ref. [2], section 7). This estimate was based on a simplified pair correlation function $g(r)$, independent of depth. The same theory, but based on a pair correlation function weighted in proportion to the density at $\bar{z} = (z_1 + z_2)/2$,

$$g(r, z_1, z_2) = \frac{n(\bar{z}) - n_v}{n_\ell - n_v} g_\ell(r) + \frac{n_\ell - n(\bar{z})}{n_\ell - n_v} g_v(r), \quad (2)$$

reversed the sign of the theoretical prediction, making I one or two percent larger than the isotropic value [2]. It is clear that I is sensitive to the pair correlation function, which is not well known. One way of avoiding this weakness of the theory is to use directly the atomic or molecular configurations generated in a computer simulation of the liquid-vapour interface. One does not need to calculate g or the dielectric functions, but can sum directly over the dipolar fields of the atoms, assumed to be polarized by an external field. A possible geometry for the calculation of local fields within the interface is shown in fig. 1.

When the capacitor plates are charged, an external field E^{ext} is imposed on the system. This field acts to polarize the polarizable atoms or molecules: a

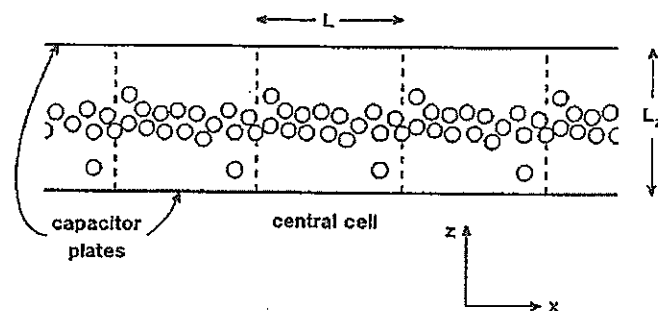


Fig. 1. Side view of a simulation system for calculation of the local fields when the external electric field is applied normal to the interface. The central cell is periodically repeated to infinity in the x and y directions, with period L . The middle part of each cell is occupied by liquid, the upper and lower parts by vapour.

given atom or molecule with polarizability α gets a dipole moment αE^{loc} , where the local field E^{loc} is the vector sum of the external field and of the fields due to all the other dipoles in the fluid,

$$E^{\text{loc}} = E^{\text{ext}} + \sum' E^{\text{dip}}. \quad (3)$$

In nature this equation is "solved" self-consistently: the dipoles adjust in magnitude and orientation so that (3) is satisfied. (More accurately: the electron distributions around each nucleus adjust in response to the external field plus the fields of all the other atoms or molecules.) A complete self-consistent solution is also possible once a computer simulation has produced a set of coordinates for the particles. One could start with a set of trial values of E^{loc} at each atom, and adjust these in magnitude and orientation until (3) is satisfied, using the fact that the field at r due to a dipole p' at r' is

$$|r - r'|^{-5} \{3(r - r')[(r - r') \cdot p'] - p'(r - r')^2\}. \quad (4)$$

Such a self-consistent calculation would be extremely lengthy in systems with a realistic number of particles. What we propose here is a simplified problem: let us assume that all the dipoles point in the direction of the external field, as they do on average, since on average the system as viewed from any atom has cylindrical symmetry about the field direction. In the simplified problem only the dipole magnitudes (or equivalently, the local field magnitudes) have to be adjusted. Eq. (3) then becomes a scalar equation, since all terms in it have non-zero components only along the z direction. We stress that this is by *assumption* in the simplified problem, and true *on average* in an actual planar liquid-vapour interface when the external field is normal to the surface. For N atoms in the central cell of the simulation, (3) holds for each atom, so we have to solve N simultaneous linear equations ($i, j = 1$ to N),

$$E^{\text{loc}}(r_i) = E^{\text{ext}} - \sum_{\substack{\text{all but the} \\ \text{central cell}}} \alpha E^{\text{loc}}(r_i) |r_i - r_i'|^{-3} \\ + \sum_{j \neq i} \sum_{\substack{\text{all} \\ \text{cells}}} \alpha E^{\text{loc}}(r_j) |r_i - r_j|^{-5} \{3(z_i - z_j)^2 - (r_i - r_j)^2\}. \quad (5)$$

The last term on the right of (5) is the field at an atom (centre at r_i) due to other atoms in the central cell and all their periodic repetitions. The second term is the contribution at r_i in the central cell due to the dipolar fields of all the repetitions of the atom at r_i at points r_i' in all cells except the central one.

2. Summation over the cells

In the system under discussion the central cell of the simulation is periodically repeated to infinity in the positive and negative x and y directions. In this section we discuss the transformation of the slowly convergent sums over cells to rapidly convergent sums, using techniques systematized by van der Hoff and Benson [10]. For N particles, there are $\frac{1}{2}N(N-1)$ pairs, and thus $\frac{1}{2}N(N-1)$ cell summations. For a given configuration, these sums need to be evaluated once only; it then remains to solve the N simultaneous linear equations to find the local field acting on each of the atoms.

Consider a particular atom at r_i in the central cell. The last term in (5) contains the sum over all repetitions of an atom at r_j , namely over all of $(x_j + lL, y_j + mL, z_j)$ for positive, zero or negative integer l and m . Define the dimensionless quantities ξ , η and ζ by

$$x_j - x_i = \xi L, \quad y_j - y_i = \eta L, \quad z_j - z_i = \zeta L, \tag{6}$$

where L is the x and y dimension of the central cell. The sums required are (compare ref. [11], eqs. (8) and (10)) L^{-3} times

$$\begin{aligned} S(\xi, \eta; \zeta) &= \sum_{l,m=-\infty}^{\infty} \frac{3\zeta^2 - [(\xi+l)^2 + (\eta+m)^2 + \zeta^2]}{\{(\xi+l)^2 + (\eta+m)^2 + \zeta^2\}^{5/2}} \\ &= -\left(1 + \zeta \frac{\partial}{\partial \zeta}\right) F(\xi, \eta; \zeta), \end{aligned} \tag{7}$$

where

$$F(\xi, \eta; \zeta) = \sum_{l,m=-\infty}^{\infty} \{(\xi+l)^2 + (\eta+m)^2 + \zeta^2\}^{-3/2}. \tag{8}$$

The conversion of these sums to rapidly convergent series proceeds as follows: one first uses the Euler transformation

$$\frac{1}{x^\nu} = \frac{1}{\Gamma(\nu)} \int_0^\infty dt t^{\nu-1} e^{-xt} \quad (\nu > 0) \tag{9}$$

to write

$$\begin{aligned} &\{(\xi+l)^2 + (\eta+m)^2 + \zeta^2\}^{-3/2} \\ &= \frac{1}{\Gamma(3/2)} \int_0^\infty dt t^{1/2} \exp\{-[(\xi+l)^2 + (\eta+m)^2 + \zeta^2]t\}. \end{aligned} \tag{10}$$

Then one of the summations is replaced by its Poisson–Jacobi equivalent (ref. [12], p. 124, Ex. 18)

$$\sum_{-\infty}^{\infty} \exp\{-(\xi + l)^2 t\} = \left(\frac{\pi}{t}\right)^{1/2} \sum_{-\infty}^{\infty} \exp(-\pi^2 l^2/t) \cos 2\pi l \xi. \quad (11)$$

We now have, using $\Gamma(3/2) = \frac{1}{2}\pi^{1/2}$,

$$F(\xi, \eta; \zeta) = 2 \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \cos 2\pi l \xi \int_0^{\infty} dt \exp\{-[(\eta + m)^2 + \zeta^2]t - \pi^2 l^2/t\}. \quad (12)$$

The $l=0$ part of (12) is

$$2 \sum_{-\infty}^{\infty} [(\eta + m)^2 + \zeta^2]^{-1} = \frac{1}{i\zeta} \sum_{-\infty}^{\infty} \{(\eta + m - i\zeta)^{-1} - (\eta + m + i\zeta)^{-1}\}. \quad (13)$$

Now

$$\sum_{-\infty}^{\infty} (z + m)^{-1} = \pi \cot \pi z \quad (14)$$

from the Mittag–Leffler expansion of a cotangent (ref. [12], Section 7.4). Thus the $l=0$ part of $F(\xi, \eta; \zeta)$ is

$$\begin{aligned} \frac{\pi}{i\zeta} \{\cot \pi(\eta - i\zeta) - \cot \pi(\eta + i\zeta)\} &= \frac{(\pi/\zeta) \sinh 2\pi\zeta}{\sinh^2 \pi\zeta + \sin^2 \pi\eta} \\ &= \frac{(2\pi/\zeta) \sinh 2\pi\zeta}{\cosh 2\pi\zeta - \cos 2\pi\eta}. \end{aligned} \quad (15)$$

The other part of (12) is

$$\begin{aligned} 4 \sum_1^{\infty} \cos 2\pi l \xi \sum_{-\infty}^{\infty} \int_0^{\infty} dt \exp\{-[(\eta + m)^2 + \zeta^2]t - \pi^2 l^2/t\} \\ = 8\pi \sum_1^{\infty} l \cos 2\pi l \xi \sum_{-\infty}^{\infty} [(\eta + m)^2 + \zeta^2]^{-1/2} K_1(2\pi l [(\eta + m)^2 + \zeta^2]^{1/2}). \end{aligned} \quad (16)$$

The last step is based on an integral representation of a Bessel function of imaginary argument (ref. [13], p. 183, eq. (15), and using the fact that $K_{-\nu}(z) = K_{\nu}(z)$),

$$\int_0^\infty dt t^{\nu-1} \exp(-m^2 t - \pi^2 l^2 / t) = 2 \left(\pi \left| \frac{l}{m} \right| \right)^\nu K_\nu(2\pi |lm|). \tag{17}$$

The reader may be puzzled by the fact that the symmetry $F(\xi, \eta; \zeta) = F(\eta, \xi; \zeta)$, clear in the defining equation (8), is not at all obvious in the sum of (15) and (16). The equality of $F(\xi, \eta; \zeta)$ and $F(\eta, \xi; \zeta)$ implies an interesting identity between two sums over Bessel functions of imaginary argument. Explicit symmetry between ξ and η is lost when only one of the l, m summations is replaced by its Poisson-Jacobi equivalent to obtain (11). If both summations are so transformed, we obtain the symmetric form

$$F(\xi, \eta; \zeta) = \frac{\pi}{\Gamma(3/2)} \int_0^\infty dt t^{-1/2} e^{-\gamma^2 t} \left\{ 1 + 2 \sum_1^\infty \cos 2\pi l \xi e^{-\pi^2 l^2 t} \right\} \\ \times \left\{ 1 + 2 \sum_1^\infty \cos 2\pi m \eta e^{-\pi^2 m^2 t} \right\}. \tag{18}$$

On using (17) again, and the special form (ref. [13], p80)

$$K_{1/2}(z) = (\pi/2z)^{1/2} e^{-z} \tag{19}$$

we find

$$F(\xi, \eta; \zeta) = \frac{2\pi}{|\zeta|} \left\{ 1 + 2 \sum_1^\infty e^{-2\pi l |\zeta|} \cos 2\pi l \xi + 2 \sum_1^\infty e^{-2\pi m |\zeta|} \cos 2\pi m \eta \right. \\ \left. + 4 \sum_1^\infty \sum_1^\infty \exp\{-2\pi |\zeta| \sqrt{l^2 + m^2}\} \cos 2\pi l \xi \cos 2\pi m \eta \right\}. \tag{20}$$

The single sums in (20) are readily evaluated as the real part of a geometric series:

$$\sum_1^\infty e^{-2\pi l |\zeta|} \cos 2\pi l \xi = \text{Re} \sum_1^\infty e^{-2\pi l (|\zeta| + i\xi)} \\ = \text{Re} \{ e^{2\pi (|\zeta| + i\xi)} - 1 \}^{-1} \\ = \frac{Z \cos 2\pi \xi - 1}{Z^2 - 2Z \cos 2\pi \xi + 1}, \tag{21}$$

where $Z = e^{2\pi |\zeta|}$. Thus this route to the required sum (7) gives

$$\begin{aligned}
S(\xi, \eta; \zeta) &= -\left(1 + \zeta \frac{\partial}{\partial \zeta}\right) F(\xi, \eta; \zeta) \\
&= 8\pi^2 \left\{ Z \left[\frac{Z^2 \cos 2\pi\xi - 2Z + \cos 2\pi\xi}{(Z^2 - 2Z \cos 2\pi\xi + 1)^2} \right. \right. \\
&\quad \left. \left. + \frac{Z^2 \cos 2\pi\eta - 2Z + \cos 2\pi\eta}{(Z^2 - 2Z \cos 2\pi\eta + 1)^2} \right] \right. \\
&\quad \left. + 2 \sum_1^{\infty} \sum_1^{\infty} (l^2 + m^2)^{\frac{1}{2}} Z^{-(l^2+m^2)^{\frac{1}{2}}} \cos 2\pi l \xi \cos 2\pi m \eta \right\}. \quad (22)
\end{aligned}$$

The other route, with an apparently asymmetric $F(\xi, \eta; \zeta)$ formed as the sum of (15) and (16), gives

$$\begin{aligned}
S(\xi, \eta; \zeta) &= \frac{4\pi^2 (\cos 2\pi\eta \cosh 2\pi\zeta - 1)}{(\cos 2\pi\eta - \cosh 2\pi\zeta)^2} \\
&\quad - 8\pi \sum_1^{\infty} l \cos 2\pi l \xi \sum_{-\infty}^{\infty} [(\eta + m)^2 + \zeta^2]^{-3/2} \\
&\quad \times \{[(\eta + m)^2 - \zeta^2] K_1(\lambda) - \zeta^2 \lambda K_0(\lambda)\}, \quad (23)
\end{aligned}$$

where $\lambda = 2\pi l [(\eta + m)^2 + \zeta^2]^{1/2}$.

The explicitly symmetric form (22) has the advantage of being expressed entirely in terms of exponentials and cosines. Its major disadvantage is that the double series converges slowly when $|\zeta|$ is small, and is not defined for zero ζ . The expression (23), in contrast, is well behaved at all ζ . Its asymmetric form can be used to speed the numerical evaluation of $S(\xi, \eta; \zeta) = S(\eta, \xi; \zeta)$: the sum in (23) converges best when $|\eta|$ is close to $\frac{1}{2}$ (in order to make the argument λ of the Bessel functions as large as possible). For example, $S(0.1, 0.5; \zeta)$ is much faster to evaluate than $S(0.5, 0.1; \zeta)$. The Bessel functions K_0 and K_1 may be evaluated by ascending series or asymptotic expansions (ref. [14] formulae 9.6.11, 9.7.2) for small or large argument, or by polynomial approximations (ref. [14], formulae 9.8.5-8).

When $\zeta = 0$ (atoms i and j have $z_i = z_j$), the sum required is

$$S(\xi, \eta; 0) = - \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \{(\xi + l)^2 + (\eta + m)^2\}^{-3/2} = -F(\xi, \eta; 0). \quad (24)$$

From (15) and (16), or from (23), we find

$$S(\xi, \eta; 0) = \frac{-2\pi^2}{\sin^2 \pi\eta} - 8\pi \sum_1^{\infty} l \cos 2\pi l \xi \sum_{-\infty}^{\infty} |\eta + m|^{-1} K_1(2\pi l |\eta + m|). \quad (25)$$

Table I

Values of $S(\xi, \eta; \zeta)$ as defined in eq. (7), together with the central-cell contribution $(2\zeta^2 - \xi^2 - \eta^2)/(\xi^2 + \eta^2 + \zeta^2)^{3/2}$. All numbers have been rounded to five decimals.

ξ	η	ζ	$S(\xi, \eta; \zeta)$	$l, m = 0$ part
0.1	0.2	0.3	10.29978	17.72651
0.1	0.5	0	-22.55606	-7.54293
0.2	0.2	0.3	0.87644	8.39224
0.2	0.3	0.3	-5.44418	2.20249
0.5	0.5	0	-16.51732	-2.82843
0.5	0.5	0.5	-4.17639	0

The special case of $\xi = \frac{1}{2} = \eta$ can be checked against previous results, since this represents a square lattice monolayer, with nearest neighbour distance $L/\sqrt{2}$. The dipolar sum over this lattice is known [10, 11] to be (nearest neighbour distance)⁻³ times S_0 , where

$$-S_0 = 4\zeta(2) + 2\zeta(3) + 16 \sum_1^\infty \sum_1^\infty \frac{l}{m} K_1(2\pi lm) \approx 9.0336217. \tag{26}$$

The sum $S(\xi, \eta; \zeta)$ excludes repetition of the central atom (at r_i) over all the neighbouring cells; this is S_0 . Thus we have the identity

$$L^{-3}S(\frac{1}{2}, \frac{1}{2}; 0) + L^{-3}S_0 = (L/\sqrt{2})^{-3}S_0 \tag{27}$$

or

$$S(\frac{1}{2}, \frac{1}{2}; 0) = (2\sqrt{2} - 1)S_0. \tag{28}$$

This gives another interesting identity relating the Bessel functions K_1 , since from (25)

$$-S(\frac{1}{2}, \frac{1}{2}; 0) = 2\pi^2 + 32\pi \sum_1^\infty (-)^l l \sum_0^\infty (2m + 1)^{-1} K_1(\pi l(2m + 1)). \tag{29}$$

Some representative values of $S(\xi, \eta; \zeta)$ are shown in table I, together with the contribution from the central cell ($l, m = 0$).

3. Evaluation of E^{loc} in some special cases

3.1. $N = 1$: one atom in the central cell

In this simplest case of a square lattice monolayer, (5) reduces to

$$E^{\text{loc}} = E^{\text{ext}} + \alpha L^{-3} S_0 E^{\text{loc}}, \quad (30)$$

so that we regain the result (ref. [11], eq. (13))

$$E^{\text{loc}} = \frac{E^{\text{ext}}}{1 - \alpha L^{-3} S_0}. \quad (31)$$

S_0 differs by about 8% from the corresponding factor $-8\pi/3$ in the Lorentz local field, which is exact in the case of a cubic lattice [15, 16, 11] or a structureless fluid [9]:

$$E_L^{\text{loc}} = \frac{E^{\text{ext}}}{1 + (8\pi/3)\alpha L^{-3}}. \quad (32)$$

3.2. $N = 2$: two atoms in the central cell

Eqs. (5) read, using the dimensionless parameter $\beta = \alpha L^{-3}$,

$$E_1^{\text{loc}} = E^{\text{ext}} + \beta S_0 E_1^{\text{loc}} + \beta S_{12} E_2^{\text{loc}}, \quad (33)$$

$$E_2^{\text{loc}} = E^{\text{ext}} + \beta S_0 E_2^{\text{loc}} + \beta S_{21} E_1^{\text{loc}}. \quad (34)$$

Since $S_{12} = S(\xi, \eta; \zeta) = S_{21}$, this is a symmetric pair, so $E_1^{\text{loc}} = E_2^{\text{loc}}$, with

$$E_{1,2}^{\text{loc}} = \frac{E^{\text{ext}}}{1 - \beta(S_0 + S_{12})}. \quad (35)$$

Note that (5) and this solution rest on the assumption that both local fields have no component perpendicular to the external field. This is true in the special case $\xi, \eta = \frac{1}{2}, \zeta = 0$, for which S_{12} is given by (28). Then

$$E_{1,2}^{\text{loc}} = \frac{E^{\text{ext}}}{1 - \beta 2\sqrt{2} S_0}. \quad (36)$$

This is in accord with (31), since the special case corresponds to a square lattice with nearest neighbour distance $L/\sqrt{2}$.

Eq. (35) is also exact when $\xi, \eta = 0, \zeta \neq 0$ (one atom is directly above the other), in which case the sum required is

$$\begin{aligned} S(0, 0; \zeta) &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{2\zeta^2 - l^2 - m^2}{\{l^2 + m^2 + \zeta^2\}^{5/2}} \\ &= -\left(1 + \zeta \frac{\partial}{\partial \zeta}\right) \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \{l^2 + m^2 + \zeta^2\}^{-3/2}. \end{aligned} \quad (37)$$

From (23) this is given by

$$S(0, 0; \zeta) = \frac{-4\pi^2}{\cosh 2\pi\zeta - 1} - 8\pi \sum_1^{\infty} l \sum_{-\infty}^{\infty} (m^2 + \zeta^2)^{-3/2} \{ (m^2 - \zeta^2) K_1(\lambda) - \zeta^2 \lambda K_0(\lambda) \}, \tag{38}$$

where $\lambda = 2\pi l(m^2 + \zeta^2)^{1/2}$. From (22) we have (with $Z = e^{2\pi|\zeta|}$)

$$S(0, 0; \zeta) = 16\pi^2 \left\{ \frac{Z}{(Z-1)^2} + \sum_1^{\infty} \sum_1^{\infty} (l^2 + m^2) Z^{-(l^2+m^2)^{1/2}} \right\}, \tag{39}$$

thus providing an identity between the sum over Bessel functions in (38) and the sum over exponentials in (39). When $|\zeta| = 1$, $|\Delta z| = L$, (35) must give the same result as obtained in ref. [11], eq. (14) for the two-layer square lattice case,

$$E_{1,2}^{loc} = \frac{E^{ext}}{1 - \beta(S_0 + S_1)} \tag{40}$$

Thus we must have $S(0, 0; 1) = S_1 \approx 0.3274646$ (ref. [11], eq. (12)), as indeed is true. Note that $S_0 + S_1$ differs by only 4% from the Lorentz local field value $-8\pi/3$.

Consideration of this equality suggests another evaluation of the sums $S_n (n = 0, 1, 2, \dots)$ of ref. [11], defined as

$$S_n = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{2n^2 - l^2 - m^2}{\{l^2 + m^2 + n^2\}^{5/2}} \tag{41}$$

Comparison of (41) with (37) and (39) shows that for $n > 0$ these sums may be expressed entirely in terms of elementary functions:

$$S_n = -\left(1 + n \frac{\partial}{\partial n}\right) F(0, 0; n), \tag{42}$$

where from (20)

$$F(0, 0; n) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \{l^2 + m^2 + n^2\}^{-3/2} = \frac{2\pi}{n} \{1 + 4(e^{2\pi n} - 1)^{-1} + 4 \sum_1^{\infty} \sum_1^{\infty} e^{-2\pi n(l^2+m^2)^{1/2}}\}. \tag{43}$$

Thus (compare ref. [11], eq. (11))

$$S_n = 16\pi^2 \left\{ \frac{e^{2\pi n}}{(e^{2\pi n} - 1)^2} + \sum_1^{\infty} \sum_1^{\infty} (l^2 + m^2)^{1/2} \exp\{-2\pi n(l^2 + m^2)^{1/2}\} \right\}. \quad (44)$$

3.3. $N \geq 3$ atoms in the central cell

For $N = 3$ eqs. (5) read

$$\begin{aligned} (1 - \beta S_0)E_1^{\text{loc}} &= E^{\text{ext}} + \beta(S_{12}E_2^{\text{loc}} + S_{13}E_3^{\text{loc}}), \\ (1 - \beta S_0)E_2^{\text{loc}} &= E^{\text{ext}} + \beta(S_{21}E_1^{\text{loc}} + S_{23}E_3^{\text{loc}}), \\ (1 - \beta S_0)E_3^{\text{loc}} &= E^{\text{ext}} + \beta(S_{31}E_1^{\text{loc}} + S_{32}E_2^{\text{loc}}). \end{aligned} \quad (45)$$

Only three sums need to be evaluated, since $S_{ij} = S_{ji}$. The solution for E_1^{loc} is

$$E_1^{\text{loc}} = \frac{(R + T_{13})(R^2 - T_{23}^2) + T_{12}(R + T_{23})^2}{(R^2 - T_{13}^2)(R^2 - T_{23}^2) - T_{12}^2(R + T_{13})^2} E^{\text{ext}}, \quad (46)$$

where $R = 1 - \beta S_0$, $T_{ij} = \beta S_{ij}$. When all the S_{ij} are equal (to S , say) this simplifies to

$$E^{\text{loc}} = \frac{E^{\text{ext}}}{R - 2T} = \frac{E^{\text{ext}}}{1 - \beta(S_0 + 2S)}. \quad (47)$$

For $N > 3$ exact algebraic solution is too cumbersome, and the set of simultaneous equations (5) can be solved numerically, or by approximate analytical methods, as outlined here. We note that (5) can be written in matrix form as

$$(I - \beta M)f = \mathbf{1}, \quad (48)$$

where I is the unit matrix, M is a symmetric $N \times N$ matrix with diagonal elements $M_{ii} = S_0$ and off-diagonal elements $M_{ij} = S_{ij}$, f is a column matrix with elements $f_i = E_i^{\text{loc}}/E^{\text{ext}}$, and $\mathbf{1}$ is a column of ones (cf. ref. [11], appendix B). Provided the largest eigenvalue of M has modulus less than β^{-1} ,

$$f = (I - \beta M)^{-1} \mathbf{1} = \mathbf{1} + \beta M\mathbf{1} + \beta^2 M^2\mathbf{1} + \dots \quad (49)$$

Thus

$$f_i = 1 + \beta \sum_{j=1}^N M_{ij} + \beta^2 \sum_{j=1}^N \sum_{k=1}^N M_{ij}M_{jk} + \dots \quad (50)$$

To lowest order in $\beta = \alpha/L^3$

$$f_i = E_i^{\text{loc}}/E^{\text{ext}} = 1 + \beta \left(S_0 + \sum_{j \neq i} S_{ij} \right) + \dots \quad (51)$$

This leading term is not sufficiently accurate in dense systems. Consider the approximation

$$f_i^{\text{approx}} = \left\{ 1 - \beta \left(S_0 + \sum_{j \neq i} S_{ij} \right) \right\}^{-1} \quad (52)$$

The difference between the "exact" (subject to the validity of (5)) and approximate solutions is

$$f_i - f_i^{\text{approx}} = \beta^2 \sum_{j=1}^N M_{ij} \sum_{k=1}^N (M_{jk} - M_{ik}) + \mathcal{O}(\beta^3).$$

In the liquid phase we expect $\sum_k (M_{jk} - M_{ik})$ to be small, and zero on average, since it is a difference of two sums relating to the fixed atoms i and j over all other atoms k in the system. Near the surface, however, these sums may be quite different, since the distribution of atoms k around atoms i and j can be different if (say) atom i is more in the vapour and atom j more in the liquid phase.

4. Discussion

We have shown how a configuration of N polarizable atoms or molecules generated in a computer simulation can be used to compute the self-consistent local fields acting on each atom, in the approximation that all dipoles point in the same direction. A calculation of the local fields along these lines will give an estimate of the fluctuations in dipolar fields of atoms, both within a "bulk" fluid phase, and (of more importance in ellipsometry) within a liquid-vapour interface. The indications from table I are that fluctuations about the Lorentz value

$$E_L^{\text{loc}}(z) = \frac{E^{\text{ext}}}{1 + (8/3)\pi\alpha n(z)}, \quad (53)$$

(where $n(z)$ is the number density at depth z) will be large. How this affects reflection properties is not yet known. The theory needed is one which starts from the position coordinates of atoms in a layered configuration, and their local fields (to be found as discussed above) and produces reflection amplitudes for the s and p polarizations, as well as a scattered field. Such a theory would

include fluctuations in the magnitudes of the atomic dipoles from the outset, and avoid the pair correlation function and dielectric function, which are not well known. The author hopes to produce this next step in the theoretical understanding of reflection by liquid surfaces in a future paper. In this context we note that the reflection of light by a square lattice of polarizable nonpolar particles has been treated by Vlieger in an important paper [17].

We note finally that the case of the electric field parallel to the liquid-vapour interface does not involve the evaluation of separate dipolar sums: if all the dipoles point at 45° to the x and y directions, the relevant dipolar contribution at r due to a dipole p' at r' is its $(\hat{x} + \hat{y})$ -component

$$|r - r'|^{-5} \left\{ \frac{3}{2}(x - x')^2 + \frac{3}{2}(y - y')^2 - (r - r')^2 \right\} p'. \quad (54)$$

Thus the required dipolar sums are

$$S'(\xi, \eta; \zeta) = \frac{1}{2} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{(\xi + l)^2 + (\eta + m)^2 - 2\zeta^2}{\{(\xi + l)^2 + (\eta + m)^2 + \zeta^2\}^{5/2}} = -\frac{1}{2} S(\xi, \eta; \zeta). \quad (55)$$

Additional discussion of this case may be found in refs. [9, 11].

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