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Calculating the surface potential of unionized monolayers

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A quantitative model is presented which enables contributions to the surface potential of a monolayer at the air-water interface to be determined from known values of group dipole moments. Based on the Lennard-Jones and Dent approach, the model shows that the head- and tail-group moments in a condensed, long-chain, *n*-alkanoic acid monolayer may be assumed to be noninteracting so long as the monolayer-forming molecule is more than about 0.5 nm in length, thus confirming one of the main tenets of the model by Demchak and Fort [J. Colloid Interface Sci. **46**, 191 (1974)]. By the same token, it is shown that imaging effects in the subphase are only important for the head group and negligible for the tail group of a molecule more than about 0.5 nm long. The present model shows that the local field acting on dipoles in the monolayer can be described in terms of a relative permittivity for the monolayer. An upper bound of between 1.98 and 2.24 is established for the local relative permittivity of the hydrophobic chain region of alkanoic acids. The major contribution to the local field which leads to these values is from the "layers" of methylene groups forming the hydrophobic region of the monolayer. For the case of the distal methyl groups of an alkanoic acid, consideration of only the mutual induced depolarization of in-plane methyl dipoles leads to a local relative permittivity as low as 1.18. Thus, it is shown that even though horizontally directed methylene-group moments cannot make a direct contribution to the surface potential of a condensed monolayer, they do make a significant indirect contribution via their local field.

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I. INTRODUCTION

The surface potential ΔV of a floating monolayer, defined as the difference in potential between a monolayer-covered surface and a clean water surface, has been the subject of much interest and debate since the turn of the century. While measuring ΔV is relatively simple [1] interpretation of the result is still a matter of conjecture except perhaps when the technique is used to investigate the Gouy-Chapman double layer [2] associated with the ionized monolayers. When the monolayer is unionized the usual approach is to apply the Helmholtz equation (HE) which relates the surface potential to an average dipole moment for the monolayer-forming molecules.

In its original form HE is derived by analogy between the monolayer and a parallel-plate capacitor *in vacuo* whose plates carry the positive and negative charges forming the dipoles. From sufficiently far away these discrete charges may be viewed as sheets of smeared out charge of surface density $\sigma = nq$. For a parallel-plate capacitor *in vacuo* $E = \sigma/\epsilon_0 = \Delta V/d$ thus $\Delta V = nqd/\epsilon_0$ so that HE is given by

$$\Delta V = \frac{\mu_\perp}{A\epsilon_0}\,, \tag{1}$$

where $\mu_\perp = qd$ is the average component of the molecular dipole moment normal to the plane of the monolayer, $A = 1/n$ is the average area available per molecule, and ϵ_0 is the permittivity of free space. Thus ΔV is seen to be dependent upon both the packing density n and orientation of the molecules in the monolayer.

Dipole moments calculated by substituting experimental values of ΔV in Eq. (1) are usually much lower than those obtained for the same molecules in bulk. Various reasons have been proposed for this discrepancy. Adam, Danielli and Harding [3] suggested that the permittivity of the monolayer may differ from that of free space. Harkins and Fischer [4] reject this approach primarily because of the application of a macroscopic concept to an essentially microscopic situation. Furthermore, it was pointed out by Macdonald and Barlow [5] that insofar as the introduction of a relative permittivity ϵ is at all valid it must be n dependent hence the use of bulk relative permittivity values is precluded.

Other possible explanations advanced for the discrepancy between HE and experiment include (i) the presence of mutual induced depolarization within the monolayer which, as will be demonstrated herein, is tantamount to assuming a local permittivity, (ii) reorientation of water molecules in such a way as to oppose the dipole moment of the monolayer, and (iii) the assumed orientation of molecular dipoles in the condensed monolayer is incorrect [1].

The first major development of HE was by Davies and Rideal [6], who suggested that the contributions to $\mu_\perp$ from the hydrophylic head group, the hydrophobic tail group, and the underlying water subphase could be treated independently so that the single homogeneous capacitor model of HE may be replaced by a three-layer capacitor. This model was refined further by Demchak and Fort (DF) [7] by the assignment of a local permittivity ϵ_i to each of the three layers (Fig. 1). Thus

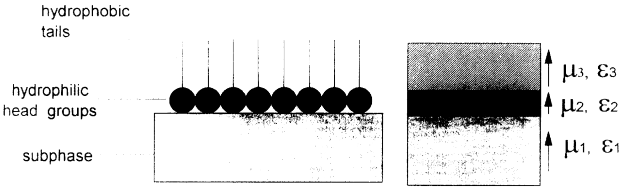

FIG. 1. The Demchak and Fort [7] three-layer-capacitor model of a condensed monolayer at the air-water interface.

$$\Delta V=\frac{1}{A\epsilon_0}\left\{\frac{\mu_1}{\epsilon_1}+\frac{\mu_2}{\epsilon_2}+\frac{\mu_3}{\epsilon_3}\right\}, \tag{2}$$

where μ_1/ϵ_1 is the contribution to ΔV arising from the polarization and change in orientation of the subphase molecules due to the presence of the monolayer and assumed approximately constant for all unionized close-packed insoluble monolayers, μ_2/ϵ_2 the contribution from the dipoles associated with the hydrophilic head-group region, and μ_3/ϵ_3 the contribution of dipoles associated with the hydrophilic tail region of the monolayer. Into ϵ_2 and ϵ_3 were incorporated all factors which caused the dipole moments of the functional head and tail groups within the environment of the monolayer to deviate from the values they would otherwise have in the isolated molecules. Based on measurements carried out on a series of substituted difunctional *p*-terphenyl compounds Demchak and Fort suggested $\epsilon_2=7.6$ and $\epsilon_3=5.3$. It was shown by Oliveira *et al.* [8] that $\epsilon_2=6.4$ and $\epsilon_3=2.8$ were more appropriate values for monolayers composed of long-chain aliphatic compounds. The DF model incorporating these new values together with a contribution Ψ_0, to account for the diffuse double layer potential, was then applied to phospholipid monolayers [9] and used to explain the surface-potential–area (ΔV-A) isotherm of stearic acid [10]. The model was also applied to aqueous solutions of acetic acid, chloroacetic, dichloroacetic, and trichloroacetic acid and alcohols by Dynarowicz and Paluch [11].

In a recent paper Schuhmann [12] provided some theoretical justification for the Demchak and Fort model by showing that the surface potential of a plane array of identical dipoles depended only on the relative permittivity ϵ of the medium in which the dipoles were localized and was independent of the permittivities of the semi-infinite phases on either side of the array, i.e., Eq. (1) was obeyed irrespective of the subphase material. Schuhmann interpreted this to mean that imaging effects in the semi-infinite phases make no contribution to the measured surface potential of a monolayer and proceeded to extend the model to a multilayer (or foliated) dipole array, from which Eq. (2) was obtained. The major criticism of Schuhmann's work and indeed of the whole DF approach is that it is assumed *a priori* that dipole layers possess relative permittivities which are greater than unity.

In a slightly different approach, Vogel and Mobius (VM) [13] prefer to consider the monolayer as a two-layer capacitor in which μ_α is an effective dipole moment at the monolayer-water interface and μ^ω the effective moment at the monolayer-air interface. For an *unionized* monolayer the DF and VM models are easily compared by the equalities

$$\mu_\alpha=\left[\frac{\mu_1}{\epsilon_1}+\frac{\mu_2}{\epsilon_2}\right] \quad\text{and}\quad \mu^\omega=\frac{\mu_3}{\epsilon_3} \tag{3}$$

so that instead of identifying a local permittivity, the problem becomes one of identifying the factors that cause the group dipole moments in a monolayer to depart from their values in isolated molecules.

Based on the application of classical electrostatics we develop in the following a quasimicroscopic mathematical model to describe the surface potential of a monolayer. The functional group moments are described by point charge distributions in free space. The subphase is assumed to be a continuous dielectric medium with an abrupt boundary to the monolayer. The model shows that local relative permittivities greater than unity arise naturally from a consideration of mutual, induced depolarization which occurs when interacting, *polarizable* dipoles are assembled in a two-dimensional (2D) array. It is also shown for such a system that (i) the calculation of the local relative permittivity is essentially a calculation of the local field acting on dipoles, (ii) imaging in the subphase does contribute to the surface potential of a monolayer, contrary to the claim by Schuhmann [12], and (iii) the DF equation is a valid description of a condensed monolayer.

II. APPARENT RELATIVE PERMITTIVITY OF A MONOLAYER

As a starting point for deducing an expression for the *relative permittivity* of a monolayer a plane infinite array of identical, vertically oriented, point dipoles is considered [Fig. 2(a)]. The array is assumed located in free space so that no appeal is made, *a priori,* to a local permittivity. The packing density n is assumed uniform and the mode of packing hexagonal [Fig. 2(b)], which is the configuration of maximum nearest-neighbor separation distance and hence of minimum electrostatic interaction energy *for any given packing density.* With the point dipole moments constrained to remain vertical, orientational polarization is ruled out. The dipoles are assumed to depolarize from a moment μ for a single isolated dipole to a value m in the environment of the array. The depolarizing field is calculated by removing the dipole at the origin of the z axis to create a cavity. The field E_0 acting at the origin, where the magnitude of $\mathbf{E}_z$ is maximum, is then calculated, thus enabling the depolarization of an isolated dipole of moment μ inserted into the cavity to be determined. Figure 2 illustrates the relevant parameters.

For purely electronic polarization, α, we have to first order

$$\mathbf{m}=\boldsymbol{\mu}+\alpha\mathbf{E}_0 \tag{4}$$

and from HE

$$\Delta V=\frac{m}{A\epsilon_0}=\frac{\mu}{A\epsilon\epsilon_0}, \tag{5}$$

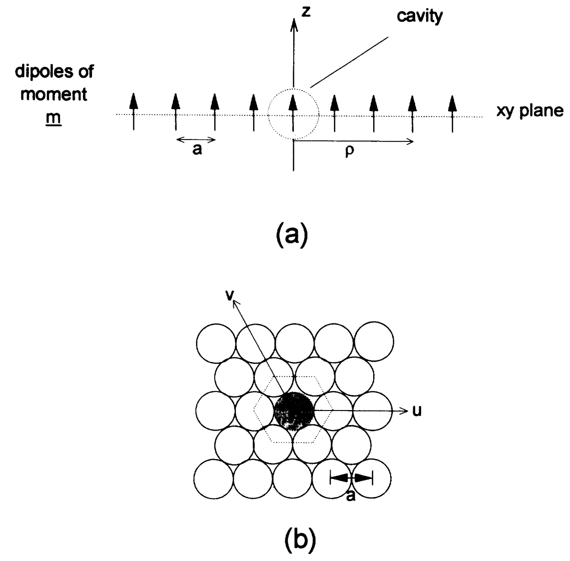

FIG. 2. (a) The model used for calculating the local field experienced by dipoles forming part of an infinite 2D array. The "cavity" is formed by removing the shaded dipole at the origin of the array in (b).

where ϵ is an apparent relative permittivity accounting for the depolarization of the dipoles from μ to m and defined by (5) as the ratio

$$\epsilon = \frac{\mu}{m} \, . \tag{6}$$

The field due to a single point dipole of moment m in the plane $z=0$ is given by

$$\mathbf{E}_0 = -\frac{m}{4\pi\epsilon_0 \rho^3}\mathbf{k} \, , \tag{7}$$

where ρ is the radial distance in the plane and $\mathbf{k}$ the unit vector in the z direction. Summing for the infinite array, the total field at the origin is given by

$$\mathbf{E}_0 = -\frac{m}{4\pi\epsilon_0 a^3} \sum_{u=-\infty}^{\infty} \sum_{v=-\infty}^{\infty} \frac{1}{(u^2+v^2-uv)^{3/2}}\mathbf{k} \, , \tag{8}$$

where a is the nearest-neighbor separation distance and u,v are integers not simultaneously zero. The double summation has been evaluated by Topping [14] as 11.0342. If α is given in units of $4\pi\epsilon_0$ Å^3 as per Israelachvili [15] and a is in Å, then

$$\epsilon = \frac{\mu}{m} = \left[1 + \frac{11.0342\alpha}{a^3} \right] . \tag{9}$$

Thus ϵ is seen to be a function of a and, therefore, of n as suggested by Macdonald and Barlow [5].

Equation (8) assumes that the length of dipole m is small compared with the separation distance a, so that the point dipole approximation is valid about the origin. If not, the array may be subdivided into inner and outer domains, the exact form for $\mathbf{E}_0$ being used near the origin and the point dipole form elsewhere. Using the symmetry of a hexagonal array we have then

$$\mathbf{E}_0 = -\frac{m}{4\pi\epsilon_0 a^3} \left\{ 3 \sum_{u=1}^{N} \sum_{v=0}^{N} \frac{1}{[u^2+v^2-uv+(l/a)^2]^{3/2}} + \left[11.0342 - 3 \sum_{u=1}^{N} \sum_{v=0}^{N} \frac{1}{(u^2+v^2-uv)^{3/2}} \right] \right\} \mathbf{k} \, , \tag{10}$$

where l is the dipole half length and integer N is chosen according to the degree of accuracy required, so that the apparent relative permittivity is now also a function of the dipolar length $2l$.

Assuming for the moment that the terminal methyl groups in a long-chain fatty acid monolayer neither affect, nor are affected by, the carboxyl head groups and subphase, then the methyl groups may be treated as a uniform dipole array isolated in free space and Eq. (10) is applicable. Smyth [16] gives the dipole moment of the methyl group as 400 mD. Within a condensed monolayer, in which the molecules are vertical, this moment is inclined at an angle of 35° to the vertical, so that $\mu = 330$ mD. Israelachvili [15] gives the electronic polarizability of a C—H bond as $0.65 \times 4\pi\epsilon_0$ Å^3. As an upper limit, α for the CH_3 group may then be taken as $1.95 \times 4\pi\epsilon_0$ Å^3 which upon substituting into Eq. (9) enables ϵ and m to be determined (see Fig. 3 for dipolar separations in the range $2 < a < 8$ Å). Also shown in Fig. 3 are plots calculated from Eq. (10) for $N = 10\,000$ in which the dipole half length l is taken as (i) 0.45 Å and (ii) 0.9 Å, values which are not unreasonable compared with 1.095 Å, the

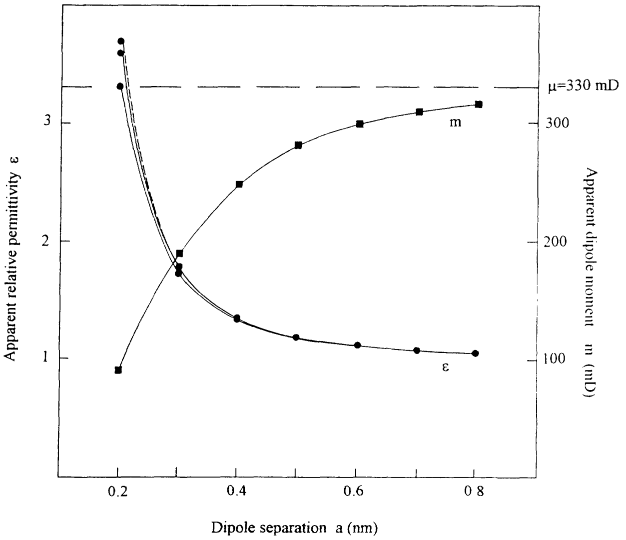

FIG. 3. Effect of dipole separation on the apparent dipole moment m and apparent relative permittivity ϵ of a 2D array of polarizable dipoles of initial magnitude $\mu = 330$ mD. It is assumed that the dipoles are located in free space. (- - -) point dipole case; (–●–) for $l = 0.45$ Å and 0.9 Å, upper and lower curves, respectively.

length of a C—H bond. Clearly the point dipole solution [Eq. (9)] introduces little error unless $a < 3$ Å, values which are physically unrealizable in a condensed fatty acid monolayer. For $a = 4.9$ Å, the minimum nearest-neighbor separation distance in such a monolayer, it is seen that m is approximately 280 mD with a corresponding value for ϵ of about 1.18. Although this value for ϵ is significantly less than the 2.8 suggested by Oliviera *et al.* [8] for the tail group of fatty acids, nevertheless, this simple model provides for the first time, as far as we are aware, a theoretical justification for the inclusion of a local relative permittivity greater than unity in the Helmholtz equation. Since capacitance measurements have shown [17] that the limiting value for the relative permittivity of a compact monolayer can be taken as that of a paraffin, i.e., approximately 2, it is clear that the above analysis significantly underestimates the local or "cavity" field acting on the methyl groups.

In reality the dipole μ inserted into the vacancy represents an oriented methyl group of physical extent. Assuming a maximum radius for the group equal to the length of a C—H bond (1.095 Å) and calculating the vertical field component at 1.095 Å along a trigonal axis, i.e., along either the u or v axis, gives

$$|\mathbf{E}_0| = \frac{11.8569m}{4\pi\epsilon_0 a^3} ,$$

an increase of about 6.9% on the value given by (8) which is clearly insufficient to account for the above discrepancy between theoretical and experimental values of ϵ. The task then is to ascertain whether it is reasonable to consider that the methyl group array may be treated in isolation as assumed above and if this is not the case, to identify those factors that contribute to the local field acting on the methyl groups.

III. THE LOCAL POTENTIAL AND FIELD

The potential along the z axis due to a single point dipole of moment m located in free space in the plane $z = 0$ at a distance ρ from the origin is given by

$$V_z = \frac{m}{4\pi\epsilon_0} \frac{z}{(\rho^2+z^2)^{3/2}} \tag{11}$$

and that due to a real dipole of length $2l$ by

$$V_z = \frac{m}{4\pi\epsilon_0 2l} \left\{ \frac{1}{[\rho^2+(z-l)^2]^{1/2}} - \frac{1}{[\rho^2+(z+l)^2]^{1/2}} \right\} . \tag{12}$$

For an *infinite* array Gomer [18] employs direct summation of Eq. (12) for dipoles extending to a distance $\rho = Na$, and integration of Eq. (11) for distances greater than Na, that is, for the outer domain

$$V_z = \frac{2\pi m}{4\pi\epsilon_0 A} \int_{Na}^{\infty} \frac{z\rho d\rho}{(\rho^2+z^2)^{3/2}} , \tag{13}$$

where A is the average area per dipole. Clearly for this procedure the outer boundary of the inner domain is hexagonal and the inner boundary of the outer domain circular, so that for $N \geq 6$ the outer integral begins to miss dipoles. Modifying the method of Gomer to make the boundaries identical, and noting the symmetry about the reflective axes of a hexagon, then integral (13) is replaced by

$$V_z = \frac{12mn}{4\pi\epsilon_0 A} \times \int_{x=(\sqrt{3}/2)Na}^{x=\infty} \left\{ \int_{y=0}^{y=x/\sqrt{3}} \frac{zdy}{(x^2+y^2+z^2)^{3/2}} \right\} dx \tag{14}$$

giving, for $z \geq l$ for an infinite hexagonally packed array with the dipole at the origin included,

$$V_z = \frac{m}{4\pi\epsilon_0} \left[\frac{1}{z^2-l^2} + \frac{3}{2la} \sum_{u=1}^{N} \sum_{v=0}^{N} \left\{ \frac{1}{\{u^2+v^2-uv+[(z-l)/a]^2\}^{1/2}} - \frac{1}{\{u^2+v^2-uv+[(z-l)/a]^2\}^{1/2}} \right\} + \frac{12}{\sqrt{3}a^2} \left[\pi - 2\arctan\left\{ 3 \left[1 + \left[\frac{Na}{z} \right]^2 \right] \right\}^{1/2} \right] \right] , \tag{15}$$

where the first two terms account for the discrete dipoles and the third term is the solution to Eq. (14). Clearly, since N is finite, in the limit $z \to \infty$ the first term and the double summation vanish and remembering that the area per molecule is given by $A = \sqrt{3}a/2$ then

$$\Delta V = (V|_z - V|_{-z}) = \frac{m}{A\epsilon_0}$$

and form (5) of HE is recovered. Differentiating (15) for the local field gives

$$E_z = \frac{m}{4\pi\epsilon_0} \left[\frac{2z}{(z^2-l^2)^2} + \frac{3}{2la^3} \sum_{u=1}^{N} \sum_{v=0}^{N} \left[\frac{z-l}{\{u^2+v^2-uv+[(z-l)/a]^2\}^{3/2}} - \frac{z+l}{\{u^2+v^2-uv+[(z+l)/a]^2\}^{3/2}} \right] - \left\{ \frac{6N^2}{[\frac{3}{4}(Na)^2+z^2][(Na)^2+z^2]^{1/2}} \right\} \right] \tag{16}$$

so that E_z vanishes as $z \rightarrow \infty$.

Figure 4 shows plots of normalized $V_z' = V_z(2A\epsilon_0/m)$ computed from Eq. (15) for $N=10$ and 100. The corresponding plots for $N=1000$ and 10 000 were indistinguishable from that for $N=100$. It is seen that V_z tends to $m/2A\epsilon_0$ as $z \rightarrow \infty$, which, in view of the symmetry of the problem is consistent with HE. Computation of E_z from Eq. (16) gives results critically dependent upon the value of N regardless of which integral term, (13) or (14), is used. It is concluded that this is a computational error arising from the integration, which ignores the discrete nature of the dipoles. Hence for more accurate calculations a computational method which retains the discrete nature of the array is required.

Summations of the kind encountered above, while conditionally convergent, converge in a manner that is extremely slow. [For example, computation of Eq. (16) with $N=10\,000$ took in excess of 24 h using FORTRAN77 in double precision on a 486DX personal computer]. However, such summations may be made rapidly convergent by means of the Poisson summation formula [19]. Lennard-Jones and Dent [20] derive, for an infinite regular array of point charges whose net charge is zero, the general equation

$$V(r)=\frac{1}{4\pi\epsilon_0}\frac{2\pi}{|\mathbf{a}_1\mathbf{a}_2|}\sum_k\sum_{u,v}q_k\frac{e^{-|\mathbf{k}_{u,v}||\mathbf{z}|}}{|\mathbf{k}_{u,v}|}e^{i[\mathbf{k}_{u,v}\cdot(\mathbf{r}-\mathbf{r}_k)]} ,$$

where

$$\mathbf{k}_{u,v}=2\pi(u\mathbf{b}_1+v\mathbf{b}_2) ,$$

$\mathbf{b}_1$ and $\mathbf{b}_2$ are reciprocal vectors given by

$$\mathbf{b}_{1x}=\frac{a_{2y}}{|\mathbf{a}_1\mathbf{a}_2|},\quad \mathbf{b}_{1y}=\frac{-a_{2x}}{|\mathbf{a}_1\mathbf{a}_2|} ,$$

$$\mathbf{b}_{2x}=\frac{-a_{1y}}{|\mathbf{a}_1\mathbf{a}_2|},\quad \mathbf{b}_{2y}=\frac{a_{1x}}{|\mathbf{a}_1\mathbf{a}_2|} ,$$

where $|\mathbf{a}_1\mathbf{a}_2|=a_{1x}a_{2y}-a_{2x}a_{1y}$, and $\mathbf{r}_k$ is the vector locating charge q_k with reference to some point within a unit cell, the charge distribution being doubly periodic with respect to the vectors $\mathbf{a}_1,\mathbf{a}_2$.

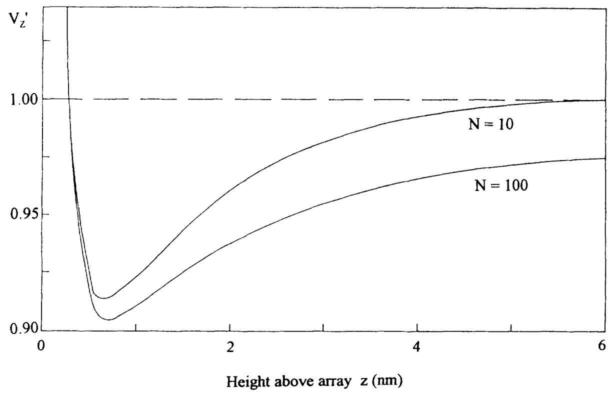

FIG. 4. Normalized potential, $V_z'=V_z(2A\epsilon_0/m)$, plotted as a function of height z above an infinite 2D array of dipoles of moment m. The calculation is based on Gomer [18]. For distances from the origin that are greater than $\rho=Na$, where $a=4.9$ Å is the assumed dipole separation, the dipole array is assumed to be an infinite continuum (see text for details).

For the case in hand the unit cell is a rhombus, $\mathbf{a}_1$ in the direction of x and $\mathbf{a}_2$ along the trigonal axis v, so that $\mathbf{a}_1=(a,0)$ and $\mathbf{a}_2=(-a/2,a\sqrt{3}/2)$. For a sheet of positive charges q with each charge located at the origin of a unit cell so that $\mathbf{r}_k=0$, the real part of the potential is given by

$$V(q)=\frac{q}{4\pi\epsilon_0}\frac{4\pi}{\sqrt{3}a^2}\times\sum_{u,v}\frac{e^{-Xz}}{X}\cos\left[\frac{2\pi}{a}\left\{ux+\frac{(u+2v)y}{\sqrt{3}}\right\}\right]+C^+ ,$$

where

$$X=\frac{4\pi}{\sqrt{3}a}(u^2+v^2+uv)^{1/2}$$

and constant C^+ accounts for the fact that the net charge per unit cell is not zero. Locating a sheet of charges q^+ at $z=l$ and a further sheet of charges q^- at $z=-l$ an infinite dipolar array symmetric about $z=0$ is simulated, and for vertical orientation we have

$$V(m)=\frac{m}{4\pi\epsilon_0}\frac{2\pi}{\sqrt{3}a^2l}\times\sum_{u,v}\frac{e^{-Xz}}{X}2\sinh(Xl)\times\cos\left[\frac{2\pi}{a}\left\{ux+\frac{(u+2v)y}{\sqrt{3}}\right\}\right]+C$$

in which the constant C is established by the condition that $V_z(z\rightarrow\infty)=m/2A\epsilon_0$ giving, for $z>l$,

$$V(m)=\frac{m}{2A\epsilon_0}\left\{\sum_{u,v}\frac{e^{-Xz}}{Xl}\sinh(Xl)\times\cos\left[\frac{2\pi}{a}\left\{ux+\frac{(u+2v)y}{\sqrt{3}}\right\}\right]+1\right\} \tag{17}$$

and

$$\mathbf{E}_z(m)=\frac{m}{4\pi\epsilon_0}\frac{2\pi}{\sqrt{3}a^2l}\times\sum_{u,v}e^{-Xz}2\sinh(Xl)\times\cos\left[\frac{2\pi}{a}\left\{ux+\frac{(u+2v)y}{\sqrt{3}}\right\}\right]\mathbf{k} . \tag{18}$$

Figure 5(a) shows the plots for V_z' computed from Eq. (17). For the z axis passing through a dipole (P_1) it is seen that V_z' neither falls below unity nor oscillates in the manner predicted by the Gomer method. Interestingly, when the integral term in Eq. (15) is ignored so that the potential of a *finite* array is computed then as seen in Fig. 5(b) the solution tends towards that obtained from the Lennard-Jones and Dent (LJD) approach as the size of the array increases. (It should be noted though that for large z the potential must fall to zero in the case of a finite array.) For the z axis passing through points P_2 and P_3, Eq. (17) predicts that V_z' is always less than unity but tends asymptotically to unity with increasing z.

Figure 6 shows a 3D plot of the normalized field $E_z' = E_z(4\pi\epsilon_0 \text{ Å}^3/m)$ at $z = 1.2615$ Å over a square of side a containing three dipoles m. Very large positive fields exist above each dipole but these fall quickly to small negative values on moving away from the dipole. In Fig. 7 are given semilogarithmic plots of the dimensionless field E_z' versus z for three cases (a) above a dipole, P_1, (b) midway between two dipoles, P_2, and (c) equidistant from three dipoles, P_3. Clearly for curves P_2 and P_3, E_z' is negative hence $\log_{10}|E_z'|$ is shown. These plots illustrate the very steep field gradients in the neighborhood of the dipole sheet indicating that only near-neighbor effects will influence the cavity field and hence m.

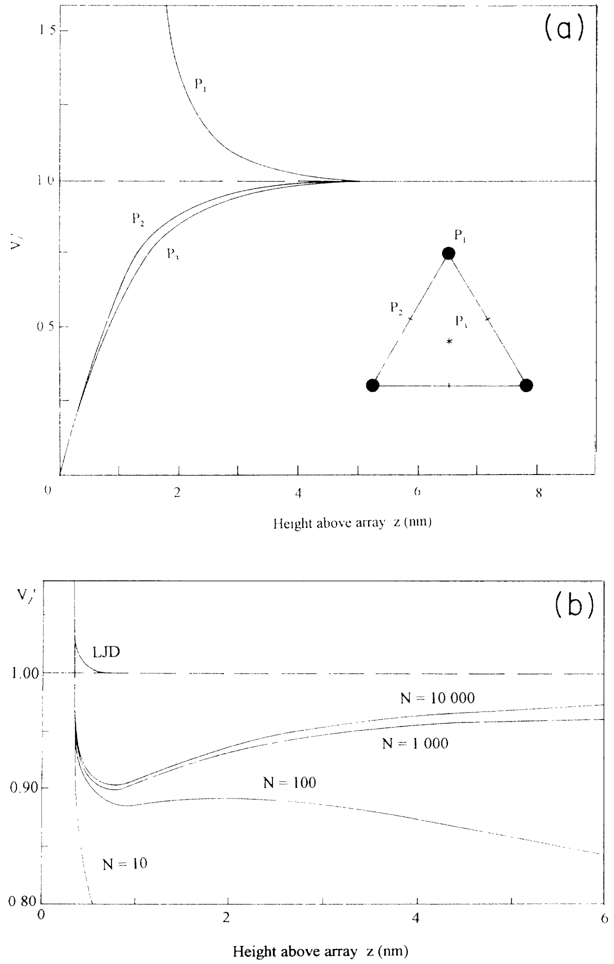

FIG. 5. (a) Normalized potential, $V_z' = V_z(2A\epsilon_0/m)$, plotted as a function of height z above an infinite 2D array of dipoles of moment m, based on the Lennard-Jones and Dent [19] approach ($a = 4.9$ Å). P_1, P_2, and P_3 were calculated for the z axis immediately above a dipole, midway between two dipoles and equidistant from three dipoles as shown in the inset diagram. (b) Normalized potential, $V_z' = V_z(2A\epsilon_0/m)$, plotted as a function of height z above a *finite*, $N \times N$ array of discrete dipoles of moment m. Also shown for comparison (LJD) is plot P_1 from (a). In both cases $a = 4.9$ Å.

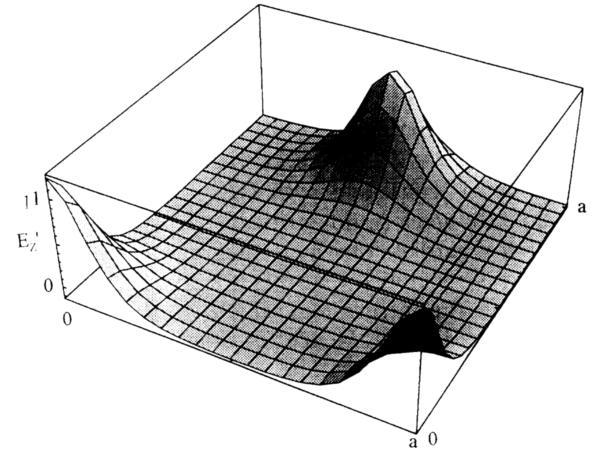

FIG. 6. 3D plot of the normalized electric field $E_z' = E_z 4\pi\epsilon_0 \text{ Å}^3/m$ at a height $z = 1.2615$ Å above a hexagonal array of dipoles of moment m. Note the field reversal between the dipoles.

For example, from Eq. (8) the normalized cavity field, arising from in-plane methyl dipoles is 9.306×10^{-2}. If now a second, parallel array of dipoles of similar magnitude is brought within 3 Å of the first, its contribution to the normalized cavity field will be almost negligible, being only about 0.1% of that arising from the in-plane methyl dipoles of the first array. For a fatty acid, the second array is composed of COOH groups and depending on the conformation of this moiety, the vertical component of the dipole moment will lie between −640 and +3560 mD [7], with values of +820 [21] or 990 mD [8,9] being the most likely. Thus it is concluded that interaction between the distal moieties of an n-alkanoic acid will

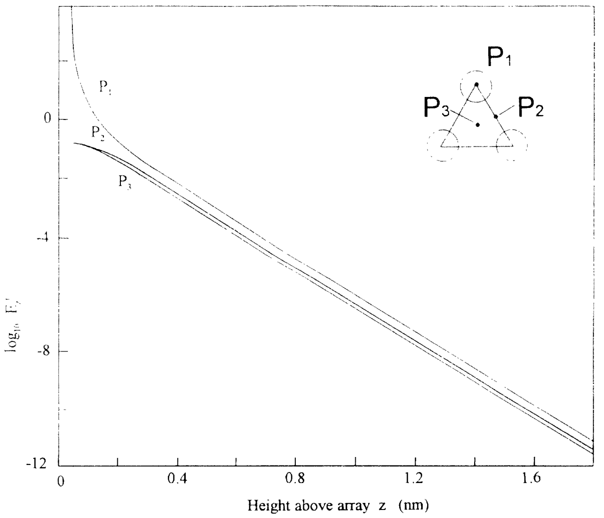

FIG. 7. Decrease in the normalized field $E_z' = E_z 4\pi\epsilon_0 \text{ Å}^3/m$ with height z above an infinite 2D array of dipoles of moment m. Note that for curves P_2 and P_3 the fields are negative.

be negligible if the head and tail groups are separated by more than about four or five methylene units.

This rapid attenuation of the field normal to the plane of a dipolar array provides strong support for the DF model which assumes that the contributions of head- and tail-group dipoles are independent and noninteracting.

IV. DIPOLE ARRAY ABOVE A SUBPHASE

Contrary to the conclusion of Schuhmann [12], it is to be expected that the presence of an adjacent subphase (or solid substrate) will contribute to ΔV because polarization of the subphase or, equivalently, imaging of the dipolar array within the subphase must change the depolarizing field in the cavity. Furthermore, the potentials above and below the subphase interface will include some component due to the imaging. Schuhmann [12] assumed that the dipolar array was immersed in a region of local permittivity ϵ_2 sandwiched between two semi-infinite regions of permittivity ϵ_1 and ϵ_3 with abrupt interfacial boundaries. These boundaries, acting as mirrors, lead to a first-order infinity of images per dipole. Since we make no appeal in this analysis to a macroscopic permittivity in the vicinity of the array, the system presented here is equivalent to setting $\epsilon_2=\epsilon_3=1$ which, removing one boundary, produces only one image per dipole. The system with the relevant parameters is illustrated in Fig. 8(a).

Using the Fourier-Bessel transform of inverse distance, then for the positive charge at $z_0=d+l$

$$V_1^+ = \frac{q}{4\pi\epsilon_0}\int_0^\infty F(k)J_0(k\rho)e^{k(z-z_0)}dk\ , \quad z\le 0$$

and

$$V_2^+ = \frac{q}{4\pi\epsilon_0}\left\{\int_0^\infty J_0(k\rho)e^{-k|z-z_0|}dk + \int_0^\infty G(k)J_0(k\rho)e^{-k(z-z_0)}dk\right\},\quad z\ge 0\ ,$$

where F and G are functions of k, an eigenvalue of the Laplacian. The boundary conditions are $V_1=V_2$ and $\epsilon_1\partial V_1/\partial z=\partial V_2/\partial z$ evaluated at $z=0$.

As shown by Smyth [16], these conditions are satisfied if equalities are written for the integrands, from which

$$F=\frac{2}{\epsilon_1+1} \quad \text{and} \quad G=-\frac{\epsilon_1-1}{\epsilon_1+1}e^{-2k(d+l)}\ .$$

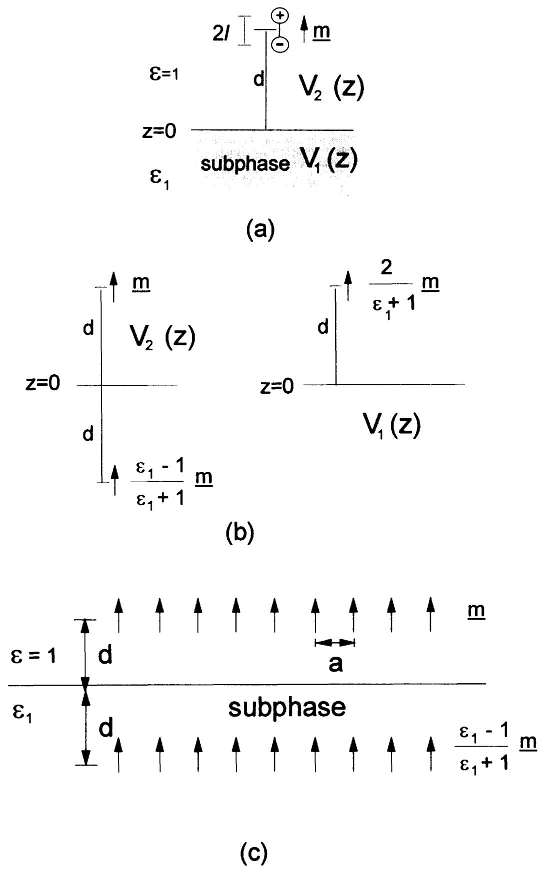

FIG. 8. (a) Dipole of moment m located in free space at a height d above a subspace of relative permittivity ϵ_1. The potentials $V_1(z)$ in the subphase and $V_2(z)$ above the subphase arising from this dipole may be determined using the system of dipoles shown in (b). The local field acting on dipoles in an infinite 2D array above a subphase is calculated using the two arrays in (c).

For the negative charge, q and l are replaced by $-q$ and $-l$ yielding by inspection for $z\le 0$

$$V_1(z)=\frac{q}{4\pi\epsilon_0}\frac{2}{\epsilon_1+1}\left\{\frac{1}{[\rho^2+(z-d-l)^2]^{1/2}}-\frac{1}{[\rho^2+(z-d+l)^2]^{1/2}}\right\} \tag{19}$$

and for $z\ge 0$

$$V_2(z)=\frac{q}{4\pi\epsilon_0}\left[\frac{1}{[\rho^2+(z-d-l)^2]^{1/2}}-\frac{1}{[\rho^2+(z-d+l)^2]^{1/2}}+\frac{\epsilon_1-1}{\epsilon_1+1}\left[\frac{1}{[\rho^2+(z+d-l)^2]^{1/2}}-\frac{1}{[\rho^2+(z+d+l)^2]^{1/2}}\right]\right]\ . \tag{20}$$

The charge distributions represented by Eqs. (19) and (20) are sketched in Fig. 8(b).

Clearly $V_1(z)$ is negative and it is interesting to note that the presence of the subphase increases the potential $V_2(z)$ for $z>d$ above that which it would otherwise be if the dipole were located in free space. Expanding the bracketed terms and proceeding to the point dipole limit Eqs. (19) and (20) reduce to

$$V_1(z)=\frac{-m}{4\pi\epsilon_0}\frac{2}{\epsilon_1+1}\frac{|z-d|}{[\rho^2+(z-d)^2]^{3/2}} \tag{21}$$

for $z \ll 0$, and

$$V_2(z)=\frac{m}{4\pi\epsilon_0}\left\{\frac{z-d}{[\rho^2+(z-d)^2]^{3/2}}+\frac{\epsilon_1-1}{\epsilon_1+1}\frac{z+d}{[\rho^2+(z+d)^2]^{3/2}}\right\} . \qquad (22)$$

for $z \gg d$.

Integrating over the plane $z=d$ containing the array of uniformly distributed point dipoles, the total potential is given by

$$\begin{aligned} V_1(z)&=\frac{-m}{2A\epsilon_0}\frac{2}{\epsilon_1+1}\int_0^\infty \frac{|z-d|\rho d\rho}{(\rho^2+|z-d|^2)^{3/2}} \\ &=\frac{-m}{2A\epsilon_0}\frac{2}{\epsilon_1+1} . \end{aligned} \qquad (23)$$

Similarly

$$V_2(z)=\frac{m}{2A\epsilon_0}\frac{2\epsilon_1}{\epsilon_1+1} . \qquad (24)$$

Equations (23) and (24) are independent of both z and d and constant for a given packing density. It should be stressed though, that the expressions are only valid for large z and for infinite arrays. If the upper limits of the radial integrals are made finite then, as expected, the potentials vanish as the magnitude of z tends to infinity.

For the potential difference across the monolayer we have then

$$\Delta V=V_2(z)-V_1(z)=\frac{m}{A\epsilon_0} \qquad (25)$$

and form (5) of HE is recovered, confirming the solution given by Schuhmann [17]. This result apparently indicates that the presence of the subphase does not affect the potential difference across the array. However, as seen from the second term of Eq. [19], the subphase image of dipole **m** is a component of $V_2(z)$. Hence the cavity field will be modified from that of an array located in free space. Thus, contrary to the conclusion arrived at by Schuhmann [17], the moment **m** and hence the apparent relative permittivity ϵ will also be modified.

Since potentials are additive it is clear that as many arrays as wished may be incorporated in the model so that for monolayers of molecules possessing two or more functional polar groups Eq. (25) may be generalized to give

$$\Delta V=\frac{1}{A\epsilon_0}\sum_i m_i, \quad \text{with} \quad m_i=\frac{\mu_i}{\epsilon_i} . \qquad (26)$$

Equation (26) is, of course, the DF equation since it describes the potential across a foliated array where the dipoles representing the functional groups lie in planes or layers one above the other.

According to Demchak and Fort [7] the quantity μ_1/ϵ_1 describes the contribution to ΔV from polarization of the subphase due to the presence of the monolayer. As seen above, Eq. (20) includes the effect *on the monolayer* of subphase polarization due to the *presence of the monolayer,* and Eq. (19) accounts for the effect within the subphase whence, upon subtraction, the overall effect of imaging should already be incorporated within ΔV. If this is the case then μ_1/ϵ_1 is redundant except insofar as a spontaneous reorganization of water molecules may occur in the presence of the monolayer thus effectively producing a change in the reference potential. In other words, even after accounting for imaging effects the potential of a water surface below a monolayer may differ from that of pure water owing to a change in the organization of the water molecules at or near the surface.

To calculate the contribution made by imaging effects to the apparent dipole moment **m** in Eq. (25) we must calculate the local cavity field in the presence of the subphase. This is composed of two terms (i) from the array of real dipoles, **m**, and (ii) from the array of image dipoles $\mathbf{m}(\epsilon_1-1)/(\epsilon_1+1)$ in the subphase [Fig. 8(c)]. These contributions may be determined from Eqs. (10) and (18), respectively. In Table I the magnitudes of these contributions to the cavity field are shown in normalized form for an array of vertically oriented methyl-group dipoles located at different heights above a water surface ($\epsilon_1=80$).

Apart from the factor $(\epsilon_1-1)/(\epsilon_1+1)$ the contributions of the image dipoles are identical to those in Fig. 7 for $d=2z$. Noting that the vertical distance between the methylene groups in a condensed fatty acid monolayer is 1.2615 Å, it is obvious that even when only four methylene moieties separate the head and tail groups the contribution of the image dipole is negligible. Thus imaging is only important for dipoles in, or immediately adjacent to the head group. It should be noted, also, that the image contribution is of opposite sign to that from the real dipoles and acts so as to *increase* the cavity field and hence to *decrease* the apparent permittivity of the monolayer.

V. THE POLARIZING EFFECT OF THE HYDROCARBON CHAIN

No consideration has been given thus far to the polarizing effect of the methylene groups which constitute the hydrocarbon chain. It is generally assumed that within a fully condensed monolayer the methylene groups are horizontally directed so that their dipole moments make no contribution to the experimentally measured surface potential. However, these dipoles will contribute to a *local* potential and thus to a *local* field which must have a polarizing effect on the distal methyl and carboxyl groups. To calculate the magnitude of the field arising from this

TABLE I. Contributions to the normalized cavity field calculated for the in-plane methyl dipoles and for their images in the subphase. Values are given for the methyl array located at three different heights above a water surface.

Height above subphase (nm)	Normalized cavity field From CH_3 layer	From images
0.5	-9.31×10^{-2}	3.88×10^{-13}
1.0	-9.31×10^{-2}	1.44×10^{-19}
1.5	-9.31×10^{-2}	5.35×10^{-26}

source, we assume that in a fully condensed monolayer the molecules are highly organized [Fig. 9(a)] so that for each CH_2 array the resolved horizontal moments are unidirectional and coplanar with the resolved vertical moments of the CH_3 groups as shown in Fig. 9(b). The model thus supposes that every molecule is stationary and possesses no rotation, vibration, or random orientation about its long axis. Within these constraints, the vertical component of the field acting at the cavity in the array of methyl groups due to each layer of methylene groups was calculated using the Lennard-Jones and Dent approach [Eq. (18) with $C=0$ in the expression for potential]. Figure 9(b) shows the relevant parameters. For the odd-numbered layers $N=2n-1$ and, neglecting reaction effects, the polarizing field $\mathbf{E}_P$ at the vacancy is given by

$$\mathbf{E}_P=\frac{\mu_{\mathrm{CH}_2}}{4\pi\epsilon_0}\frac{4\pi}{\sqrt{3}a^2L}\sum_{n=1}^{n}\sum_{u}e^{-X[l+s(2n-1)]}\times\left\{\cos\left[\frac{2\pi}{a}[u(x-L)]\right]-\cos\left[\frac{2\pi}{a}(ux)\right]\right\}\mathbf{k} \qquad (27)$$

and for even-numbered layers $N=2n$,

$$\mathbf{E}_P=\frac{\mu_{\mathrm{CH}_2}}{4\pi\epsilon_0}\frac{4\pi}{\sqrt{3}a^2L}\sum_{n=1}^{n}\sum_{u}e^{-X[l+s(2n)]}\times\left\{\cos\left[\frac{2\pi}{a}(ux)\right]-\cos\left[\frac{2\pi}{a}[u(x-L)]\right]\right\}\mathbf{k}. \qquad (28)$$

The sum of Eqs. (27) and (28) then gives the total cavity field arising from N methylene layers, neglecting reaction effects, so that Eq. (4) now becomes

$$\mathbf{m}=\boldsymbol{\mu}+\alpha_0(\mathbf{E}_0+\mathbf{E}_P)\ . \qquad (29)$$

For n-alkanes $s=1.2615$ Å, $l=0.4485$ Å, and H—C—H bond angle is 110°. Assuming that the methylene group may be considered as two C—H bonds of moment 400 mD and length 1.095 Å symmetrically located about the x axis then the projection onto this axis gives $L=0.6281$ Å, $\mu_{\mathrm{CH}_2}=460$ mD and $x=-0.8833$ Å (N odd) and $x=L$ (n even). Table II gives the normalized contribution $E_p[(4\pi\epsilon_0\ \text{Å}^3)/\mu_{\mathrm{CH}_2}]$ to the vertical component of the local field acting on the methyl groups from each of the first eight layers of CH_2 groups. It appears that only the first four layers make a significant contribution. Therefore, taking $\alpha_{\mathrm{CH}_3}=1.95\times4\pi\epsilon_0$ Å^3 as before, then

$$m=\mu_{\mathrm{CH}_3}-1.95(9.30\times10^{-2}m+0.1482\mu_{\mathrm{CH}_2}) \qquad (30)$$

from which it is seen that the dominating depolarization effect comes from the methylene groups rather than the mutual depolarization of the methyl groups. Inserting

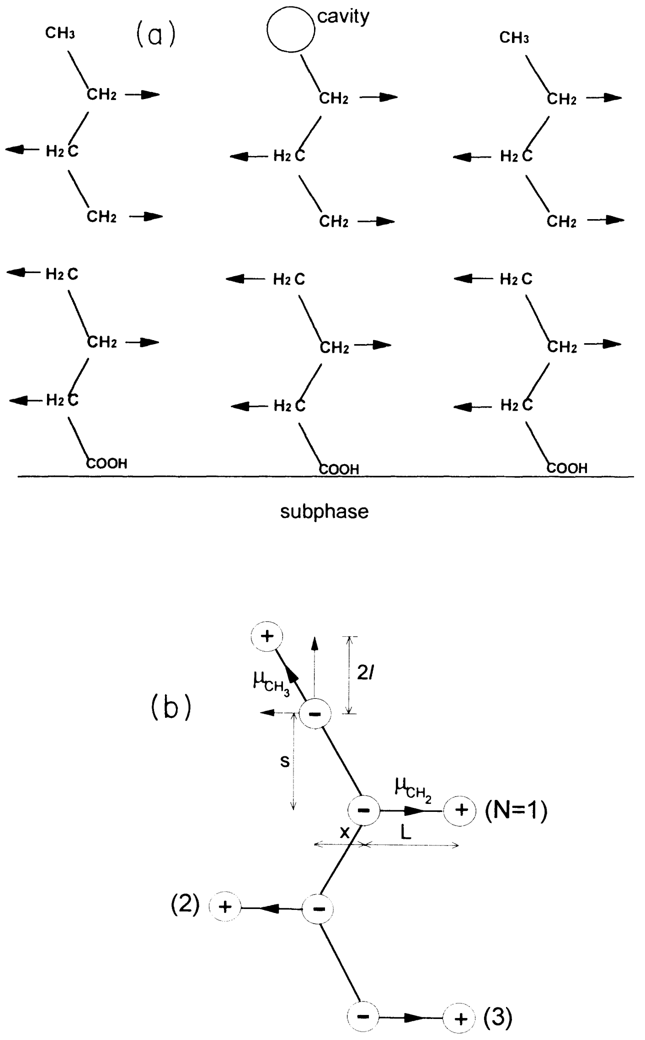

FIG. 9. (a) Regular array of long-chain alkanoic acid molecules at the air-water interface. (b) This sketch gives the relevant parameters used for calculating the contribution of the CH_2 groups to the local field experienced by the distal CH_3 groups in the array.

TABLE II. Contributions to the normalized cavity field from each of the methylene "layers" immediately below the distal methyl groups.

N	E'_P
1	−0.137 6
2	−0.008 402
3	−0.002 891
4	0.000 174 6
5	−0.000 068 26
6	−0.000 004 134
7	−0.000 001 627
8	−0.000 000 098 57

the appropriate dipole moments $\mu_{\mathrm{CH}_3}=330$ mD and $\mu_{\mathrm{CH}_2}=460$ mD in Eq. (30) we have

$$m=167 \text{ mD}$$

whence by Eq. (6)

$$\epsilon=\mu_{\mathrm{CH}_3}/m=1.98 \ .$$

This latter value is in excellent agreement with the macroscopic relative permittivity of a paraffin but it should be noted that reaction effects, which would further modify the depolarization field, have been ignored.

Departure from the assumed idealized dipole alignments would also modify the depolarizing field. In the limiting case it may be assumed that each molecule is orientated about its long axis in such a way that the moments of the methylene groups within each array statistically cancel. For such a case, each methyl group would experience only the depolarizing effect of the CH_2 groups of its own molecule. Thus the contribution to the local field acting at the methyl groups would be given by

$$\mathbf{E}_p=\frac{\mu_{\mathrm{CH}_2}}{4\pi\epsilon_0}\frac{1}{L}\left\{\frac{z}{[z^2+(x-L/2)^2]^{3/2}}-\frac{z}{[z^2+(x+L/2)]^{3/2}}\right\}\mathbf{k} \ , \qquad (31)$$

where $z=l+s(2n-1)$ for N odd and $z=l+2ns$ for N even. The computed contributions for the first four methylene groups are given in Table III. The effect of randomizing the methylene contribution but retaining that from the methyl-group dipoles (these are vertical so rotating the molecule does not change the array contribution) is to depolarize the methyl group from 330 to 147 mD which corresponds to a local relative permittivity, $\epsilon=2.24$. Assuming that the inclusion of reaction fields would lower the permittivity, then for a fully condensed fatty acid monolayer ($a=4.9$ Å) of chain length greater than about eight methylene units approximate upper bounds for the apparent relative permittivity of the methyl-group array are found to be 1.98 and 2.24 depending on the individual organization of the molecules within the hexagonal lattice.

VI. CONCLUSIONS

It has been shown that the surface potential of a condensed monolayer at the air-water interface may be described in terms of interacting dipolar arrays. The model shows that the multilayer-capacitor model of Demchak and Fort is a valid description of the monolayer but the most important feature of the model is that it establishes that the origin of the local relative permittivity of a condensed monolayer is the induced depolarization of dipoles in the electric fields of their neighbors. For the case of the distal methyl groups of a fatty acid monolayer we have derived explicit expressions for this local field based on the Lennard-Jones and Dent approach. Calculations based on the theory show that the major contribution to the local field is from the dipoles associated with the first four layers of methylene groups despite the fact that these are horizontally directed. Mutual depolarization of the methyl groups makes a further small contribution. Since we have neglected reaction fields, we have established that the upper bound for the relative permittivity of the hydrophobic chain region lies between 1.98 and 2.24, an eminently satisfactory value—the relative permittivities of n-alkanes from C_5 to C_{10} increase from 1.844 to 1.991. Further increase in chain length to C_{12} increases the relative permittivity by only 1.2% to 2.015 [22].

TABLE III. Contributions to the normalized cavity field for the first four methylene units bonded to a methyl group. It is assumed here that contributions from the methylene groups of neighboring molecules cancel (see text).

N	E_P'
1	$-0.152\,8$
2	$-0.011\,4$
3	$-0.009\,1$
4	$-0.001\,0$

So long as other polar groups, e.g., the COOH head groups in a fatty acid monolayer, are more than about 5 Å away, their contribution to the local field experienced by the methyl groups is negligible. A corollary of this is that imaging effects in the subphase are also negligible unless dipole arrays are close to the subphase surface. This has been confirmed experimentally by Mobius and Vogel [13], who showed that the surface potential of condensed monolayers formed from long-chain n-alkanoic acids was independent of chain length (within about 10 mV) for the series C_{14} to C_{22}. In contrast, Evans and Ulman [23] interpreted their results as showing an increase in surface potential from about 500 to about 700 mV for the series of n-alkalyl thiols from C_6 to C_{22} chemisorbed onto a gold substrate. Interestingly, the error bars in their work are so wide that the surface potential for the C_{11} to C_{22} thiols could be considered independent of chain length and equal to 650±70 mV. If the data for the C_{20} and C_{22} thiols are ignored then the surface potential appears to saturate at about 620±40 mV for thiols longer than C_{11}. According to the model developed here, no change in surface potential should have been observed for compounds with more than about eight methylene units. (This would provide four methylenes to interact with each distal group and would ensure that reaction effects on the methylene groups at one end of the molecule would not influence the groups at the other.) It should be noted also that the contribution of the methylene chains to the local cavity field at the ends of the molecule will depend sensitively on their exact positions and orientation in the array relative to the terminal groups. It is possible, therefore, that the large error bars in the work of Evans and Ulman may indicate differences in film quality or differences in the molecular packing from sample to sample.

Further development of the present model is now under way. First, the assumption regarding the polarization of the methyl group is an oversimplification. Any improvements must consider the tensorial nature of this parameter. Account should also be taken of the reaction fields set up when the methylene groups depolarize the methyl groups. Finally, and most importantly, it will be necessary to deal with the more complex problem of the head-group–water interface. This will require a model to be developed which describes the hydrogen bonding interactions between the carboxyl head group of the fatty acid and the underlying subphase molecules.

ACKNOWLEDGMENT

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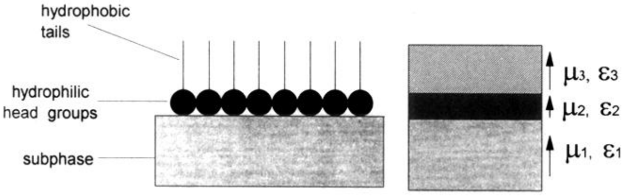


FIG. 1. The Demchak and Fort [7] three-layer-capacitor model of a condensed monolayer at the air-water interface.

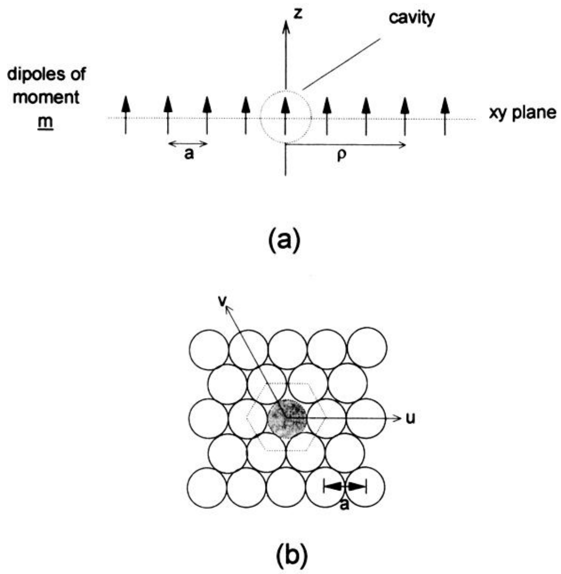


FIG. 2. (a) The model used for calculating the local field experienced by dipoles forming part of an infinite 2D array. The "cavity" is formed by removing the shaded dipole at the origin of the array in (b).

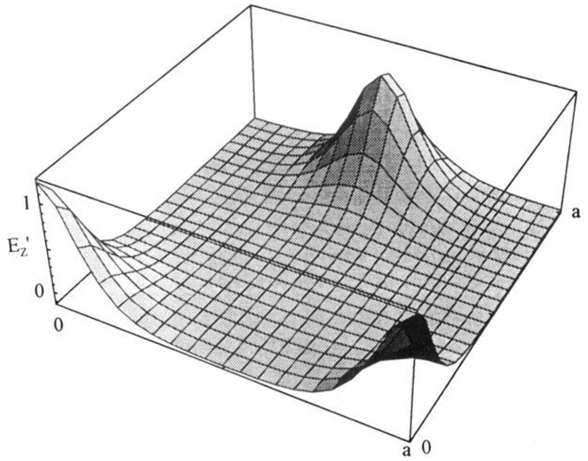
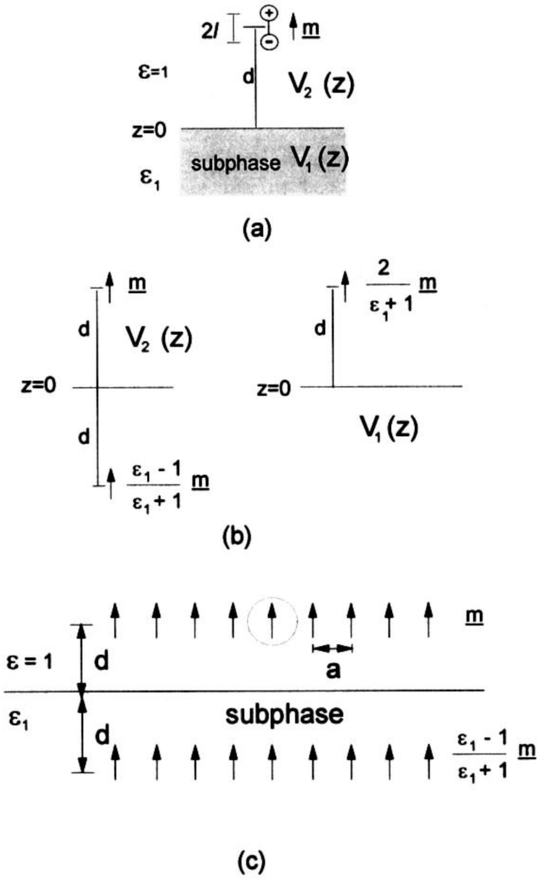


FIG. 6. 3D plot of the normalized electric field $E_z' = E_z 4\pi\epsilon_0 \text{ Å}^3/\text{m}$ at a height $z = 1.2615$ Å above a hexagonal array of dipoles of moment m. Note the field reversal between the dipoles.



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