

## Electromagnetic response of a dipole-coupled ellipsoidal bilayer

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We derive an expression for the polarizability of an ellipsoidally shaped cell-like structure at field frequencies where membrane molecular resonances (vibrational and electronic) are important. We first present analytical results for the dielectric function of a *flat*, dipole coupled, bilayer consisting of molecules with one prominent resonance frequency. Due to the nature of the dipole coupling the dielectric function is different for the field being parallel or perpendicular to the bilayer normal with two new resonance frequencies  $\omega = \tilde{\omega}_{0\parallel}$  and  $\omega = \tilde{\omega}_{0\perp}$ . We then combine this anisotropic bilayer dielectric function with the analytical solution of Gauss equation for an ellipsoid with an anisotropic coating (the coating dielectric function being different parallel and perpendicular to the coating normal) in order to find the polarizability of an *ellipsoidal* bilayer membrane. In particular, we find that for a thin-walled (compared to the size of the cell) membrane the resonance frequencies of the polarizability are the same as for a flat bilayer (independent of the cell shape). However, our analytic result for the geometric weights for the oscillator strengths is sensitive to the shape; the geometric weight for the  $\omega = \tilde{\omega}_{0\perp}$  ( $\omega = \tilde{\omega}_{0\parallel}$ ) peak is largest when the external field is along the largest (smallest) axis. The geometric weights are shown to be constrained by three sum rules.

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### I. INTRODUCTION

Over the past decades, there has been an increasing interest among physicists and chemists in biological and mesoscopic systems. Important objectives have been to extend physicists' models to meet quantum chemists' detailed calculations, relate shape to electronic response properties, to provide criteria for intelligent selection of large-scale expensive calculations, and to explore applicability/extension of classical concepts to nanoscale objects. A potentially highly fruitful extension is to provide a fundamental understanding of many biological systems via new interpretive couplings. One such field is perturbing biological systems such as cells with electromagnetic fields.

In this study we are primarily interested in modeling the electromagnetic response of cell-like structures at frequencies where the molecules forming the membrane have vibrational [1] or electronic [2] transitions (i.e., typically 0.1–3 eV). At these high frequencies the ions in the cytoplasm cannot follow the rapidly varying field and the cytoplasm effectively behaves as a dielectric. The cell *membrane* then determines the response of the cell. The cell membrane consists to a large extent of lipid molecules and different proteins embedded or attached forming a bilayer molecular aggregate. It is well known that for molecular aggregates the local field effect is important [2–4]. Furthermore, cells are in general of nontrivial shape, which affects their response properties. It is the aim of this study to include both local field and shape effects into a frequency dependent polariz-

ability of cell-like structures (assuming, as we do throughout this study, that we can ignore magnetic effects so that the electromagnetic response is determined by the electric field component of the external field).

The paper is organized as follows. In Sec. II the dielectric function of a flat bilayer of polarizable molecules (a cell membrane) is derived. In particular, we show that the local field effect causes the dielectric function of the bilayer to be anisotropic. In Sec. III we recapitulate results for the polarizability of an ellipsoidal particle with an anisotropic coating, where the coating dielectric function is different parallel and perpendicular to the coating normal [12]. Finally in Sec. IV we combine the results of Secs. II and III in order to obtain an analytic expression for the polarizability of a dipole coupled ellipsoidal bilayer membrane.

### II. DIPOLE-COUPLED FLAT BILAYER

In this section we derive an expression for the dielectric function of a flat bilayer, including the induced dipole coupling (the local field) between the constituting molecules. Due to the nature of the local field the electric responses perpendicular and parallel to the bilayer normal are different, even if the molecules in the bilayer are isotropic.

Let us consider the interaction between a set of polarizable molecules and an external time-varying electric field,  $\vec{E}_0(\vec{r}, t) = \vec{E}_0 \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$  where  $\vec{k}$  is the wave vector ( $|\vec{k}| = 2\pi/\lambda$  where  $\lambda$  is the wavelength) and  $\omega$  the frequency of the field. We consider, for the ease of presentation, a bilayer of polarizable molecules situated on a “cubic” lattice (see Fig. 1) with the lattice vectors described by

$$\vec{r}(l_x, l_y, l_z) = a(l_x \hat{x} + l_y \hat{y}) + dl_z \hat{z}, \quad (1)$$

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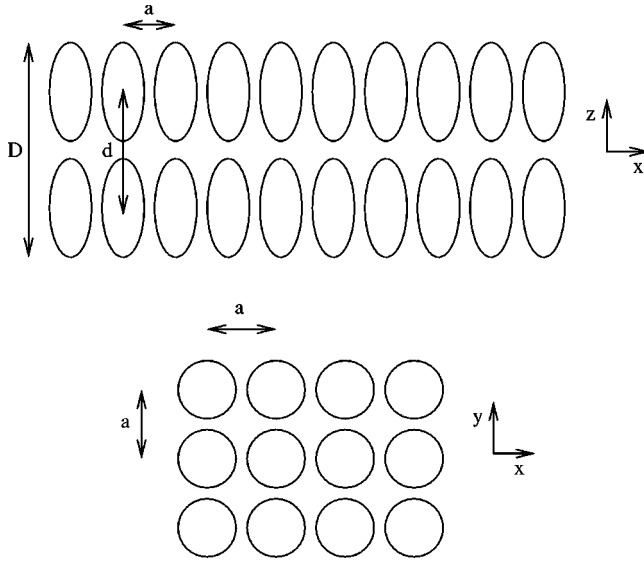


FIG. 1. Model geometry. Top: A side view of a bilayer of molecules. The distance between the “center-of-mass” positions of the molecules is  $a$  within each layer. The interlayer distance is  $d$ . The membrane thickness is denoted by  $D$ . Bottom: Top view of the bilayer. The bilayer extends to infinity in the  $x$  and  $y$  directions.

where  $a$  is the distance between molecules in each layer and  $d$  is the interlayer distance.  $l_x$  and  $l_y$  are integers, such that  $-\infty < l_x, l_y < \infty$ . For  $l_z$  we have  $l_z = 0, 1$ , where  $l_z = 0$  ( $l_z = 1$ ) corresponds to the lower (upper) layer in Fig. 1. Each molecule “feels” a local electric field  $\vec{E}_{\text{loc}}$  which is the superposition of the external field and the induced dipolar field from all the other molecules in the system. For the induced dipole moment of the molecule at position  $\vec{r}$  [see Eq. (1)] we write  $\vec{p}(\vec{r}, t) = \vec{p}(\vec{r}) \exp[i(\vec{k} \cdot \vec{r} - \omega t)]$ , and similarly for the local field. In the linear regime the induced dipole moment  $\vec{p}(\vec{r})$  is proportional to the local field  $\vec{E}_{\text{loc}}(\vec{r})$ , i.e.,

$$\vec{p}(\vec{r}) = 4\pi\epsilon_0\epsilon_m\vec{\gamma} \cdot \vec{E}_{\text{loc}}(\vec{r}), \quad (2)$$

where  $\vec{\gamma}$  is the polarizability (a  $3 \times 3$  tensor) of the molecule,  $\epsilon_0$  is the permittivity of vacuum, and  $\epsilon_0\epsilon_m$  is the dielectric function of the medium in which the molecules are situated. Since the local field depends on the induced dipole moments in the system the above equation gives a self-consistency equation for the dipole moments in the system. Using a standard expression for the nonretarded ( $c \rightarrow \infty$ ) dipolar field [3,4] we find that Eqs. (1) and (2) become

$$p_\mu(l_x, l_y, l_z) = 4\pi\epsilon_0\epsilon_m\gamma_{\mu\nu}E_{0,\nu} + \frac{\gamma_{\mu\nu}}{a^3} \times \sum_{l'_x, l'_y, l'_z} D_{\nu\gamma}(l_x, l'_x, l_y, l'_y, l_z, l'_z) \times p_\gamma(l'_x, l'_y, l'_z),$$

$$D_{\mu\nu} = \left\{ \frac{-\delta_{\mu\nu}}{[(l_x - l'_x)^2 + (l_y - l'_y)^2 + \Delta_z^2(l_z - l'_z)^2]^{3/2}} + \frac{3\Delta_\mu\Delta_\nu(l'_\mu - l_\mu)(l'_\nu - l_\nu)}{[(l_x - l'_x)^2 + (l_y - l'_y)^2 + \Delta_z^2(l_z - l'_z)^2]^{5/2}} \right\} \times e^{i[k_x a(l'_x - l_x) + k_y a(l'_y - l_y) + k_z d(l'_z - l_z)]}, \quad (3)$$

where  $\mu, \nu = x, y, z$ ,  $\Delta_z = d/a$ ,  $\Delta_x = \Delta_y = 1$ , and  $E_{0,\nu}$  is the  $\nu$  component of the external field. Summations over repeated vector indices are left implicit and we have above canceled out the  $\exp[i(\vec{k} \cdot \vec{r} - \omega t)]$  dependences. Because of translational invariance along the bilayer planes we have  $\vec{p}(l_x, l_y, l_z) = \vec{p}(l'_x, l'_y, l_z)$ . We can therefore, without loss of generality, let  $\vec{p}(l_x, l_y, l_z) = \vec{p}(0, 0, l_z) = \vec{p}(l_z)$ , i.e., the problem is reduced to finding the induced dipole moments in the upper and lower layers, respectively, which in general are different. However, for the case of large wavelength compared to the nearest neighbor distance between molecules  $k_x a, k_y a, k_z d \ll 1$  we find that the equations for the dipole moment in the upper and lower layers are identical, and hence  $\vec{p}(l_z = 0) = \vec{p}(l_z = 1) = \vec{p}$ . For the case of electromagnetic fields in the optical range, the wavelength is  $\sim 400\text{--}800$  nm, whereas the typical distance between molecules is  $< 1$  nm for the systems we consider. The above assumption is then well justified. Furthermore, assuming that the molecular polarizability is diagonal with components  $\gamma_x = \gamma_y = \gamma_\perp$  and  $\gamma_z = \gamma_\parallel$  [the subscript  $\perp$  ( $\parallel$ ) denotes polarizability component perpendicular (parallel) to the molecular symmetry axis, see Fig. 1] and using the fact that sums over functions that are odd with respect to  $l_x$  or  $l_y$  vanish we find ( $\mu = \perp$  or  $\parallel$ )

$$p_\mu = 4\pi\epsilon_0\epsilon_m\tilde{\gamma}_{\mu\mu}E_{0,\mu}, \quad (4)$$

where the renormalized polarizability is

$$\tilde{\gamma}_{\mu\mu} = \frac{\gamma_{\mu\mu}}{1 - \gamma_{\mu\mu}I_\mu/a^3} \quad (5)$$

with  $I_\parallel = \chi_0 + \chi_I$ ,  $I_\perp = -I_\parallel/2$  and  $\chi_0$  and  $\chi_I$  are dimensionless dipole sums defined by (a prime denotes that the term  $l_x = l_y = 0$  should be excluded)

$$\begin{aligned} \chi_0 &= - \sum'_{l_x, l_y = -\infty}^{\infty} \frac{1}{(l_x^2 + l_y^2)^{3/2}} \approx -9.0336 \dots, \\ \chi_I &= \sum_{l_x, l_y = -\infty}^{\infty} \frac{3\Delta^2/(l_x^2 + l_y^2 + \Delta^2) - 1}{(l_x^2 + l_y^2 + \Delta^2)^{3/2}} \\ &= 16\pi^2 \sum_{l_x=0}^{\infty} \sum_{l_y=1}^{\infty} (l_x^2 + l_y^2)^{1/2} \exp[-2\pi\Delta(l_x^2 + l_y^2)^{1/2}]. \end{aligned} \quad (6)$$

We have used the results in Refs. [5,6] in order to rewrite the expression for  $\chi_I$  into a more rapidly converging sum. Notice

that the dipole sum  $\chi_I$  is positive and depends on the dimensionless quantity  $\Delta \equiv \Delta_z = d/a$ , i.e., the ratio between the interlayer distance and the intralayer distance between molecules in each layer. Also notice that the different vector components of the induced dipole moments decouple (for “long” wavelengths as assumed here), i.e., if the external field is parallel or perpendicular to the molecular symmetry axis then the induced dipole moments are also in the same direction.

It is interesting to compare our results to the results for the nonretarded response of a monolayer of molecules above a metal surface [5]. Since molecules above a metal surface induce image dipoles in the metal this system is also effectively a dipole coupled bilayer. The expression (for infinite metal dielectric function, i.e., an impurity-free ideal metal at low frequencies) for the induced dipole moments parallel to the layer normal  $p_{\parallel}$  is identical to ours [see Eq. (5)], whereas the expression for  $p_{\perp}$  differs;  $p_{\perp}$  in the metallic case is same as given by Eq. (5) but now with  $I_{\perp} = -\chi_0/2 + \chi_I/2$ , i.e., there is a plus sign in front of the  $\chi_I/2$  term (whereas we have a minus sign). These results are due to the fact that an induced dipole moment parallel (perpendicular) to the metal surface normal induces an image dipole moment that is in the same (opposite) direction. In our case (for long wavelength compared to intermolecular distances) the induced dipole moments in the upper and lower layers are identical, independent of the polarization direction of the external field.

Let us now assume that the molecular polarizability takes the form ( $\mu = \perp$  or  $\parallel$ )

$$\gamma_{\mu\mu} = \gamma_{0\mu} \frac{\omega_{0\mu}^2}{\omega_{0\mu}^2 - \omega^2 - i\omega\Gamma_{\mu}}, \quad (7)$$

where  $\gamma_{0\mu}$  is the static polarizability of the molecules,  $\omega_{0\mu}$  is a resonance frequency, and  $\Gamma_{\mu}$  is a damping parameter [4,5]. Inserting this expression for the polarizability into Eq. (5) we find

$$\begin{aligned} \tilde{\gamma}_{\mu\mu} &= \gamma_{0\mu} \frac{\omega_{0\mu}^2}{\tilde{\omega}_{0\mu}^2 - \omega^2 - i\omega\Gamma_{\mu}}, \\ \tilde{\omega}_{0\mu}^2 &= \omega_{0\mu}^2 \left( 1 - \frac{\gamma_{0\mu} I_{\mu}}{a^3} \right), \end{aligned} \quad (8)$$

where  $I_{\parallel} = \chi_0 + \chi_I$ ,  $I_{\perp} = -I_{\parallel}/2$  as before, and  $\chi_0$  and  $\chi_I$  are given by Eq. (6). This model for the renormalized molecular polarizability is most appropriate close to a resonance as contributions from other frequencies can be ignored. We notice that for  $\gamma_{0\perp} = \gamma_{0\parallel}$  the two new resonance frequencies satisfy the sum rule

$$\frac{\tilde{\omega}_{0\parallel}^2}{\omega_{0\parallel}^2} + 2 \frac{\tilde{\omega}_{0\perp}^2}{\omega_{0\perp}^2} = 3 \quad (9)$$

independent of the interaction between the molecules. The electric response of the system in the perpendicular direction is different from the response in the parallel direction. This

holds even if the constituting molecules in the bilayer are assumed isotropic and is then therefore solely caused by the local field effect. For isotropic molecules the strength of the anisotropy is determined by the dimensionless dipole coupling parameter  $\gamma_0/a^3$ . It is only when this parameter is small we obtain an isotropic bilayer response. Notice that if  $\tilde{\omega}_{0\parallel}$  is redshifted then  $\tilde{\omega}_{0\perp}$  is blue shifted. We also notice that  $\chi_0$  and  $\chi_I$  have opposite signs [see Eq. (6)]. Therefore for the case when  $|\chi_0| > \chi_I$  ( $|\chi_0| < \chi_I$ ) the frequency  $\tilde{\omega}_{0\parallel}$  ( $\tilde{\omega}_{0\perp}$ ) is blue shifted.

The above result for the polarization allows us to identify the macroscopic relative dielectric function parallel (perpendicular)  $\epsilon_{\parallel}$  ( $\epsilon_{\perp}$ ) to the molecular symmetry axis [or equivalently parallel (perpendicular) to the bilayer *normal*]. Introducing the dipole density  $\vec{P} = \vec{p}/v_0$ , where  $v_0 = a^2 D/2$  (see Fig. 1) is the unit cell volume per molecule ( $D$  is the effective layer thickness [7] and in general  $D \neq d$ ) and using the continuity of the normal component of the displacement field as well as the continuity of the tangential component of the total electric field it is straightforward to show that [5]

$$\begin{aligned} \epsilon_{\perp} - 1 &= \frac{4\pi\tilde{\gamma}_{\perp}}{v_0}, \\ 1 - \epsilon_{\parallel}^{-1} &= \frac{4\pi\tilde{\gamma}_{\parallel}}{v_0}. \end{aligned} \quad (10)$$

In the next two sections we will investigate the electric response of a dipole coupled ellipsoidal shell (cell membrane). The above result for the (local) dielectric functions of the bilayer will be used in the solution of the Gauss equation. We want to point out that there is some arbitrariness in the choice of the effective layer thickness  $D$  (not to be confused with the interlayer center-of-mass distance  $d$ , see Fig. 1).  $D$  is taken as the distance between two “sharp” boundaries separating the membrane from its surroundings. Since molecules do not have a well-defined size one must be careful to choose these sharp boundaries in such a way that the macroscopic fields are the same as the averaged microscopic fields as given by the induced microscopic dipole moments and the external field [7]. We will in the subsequent sections primarily be concerned with thin-walled membranes,  $D/L \ll 1$ , where  $L$  is the typical size of the cell. As we will see,  $D$  does not appear explicitly in the expression for the cell polarizability. We therefore need not concern ourselves with a discussion about the appropriate choice of an effective layer thickness. However, for systems where  $D/L$  is not necessarily small one must be more careful.

The results obtained in this section will remain qualitatively the same whether one considers a monolayer, bilayer, or a multilayer. The appearance of two resonances is, for isotropic molecules, a manifestation of the dipole-dipole interactions, whose net contribution is different in the normal and parallel directions. Therefore the general conclusions drawn in terms of the shifted (or modified) resonance frequencies will remain the same irrespective of the number of layers. In particular, we point out that the monolayer response is obtained from the results in this section simply by

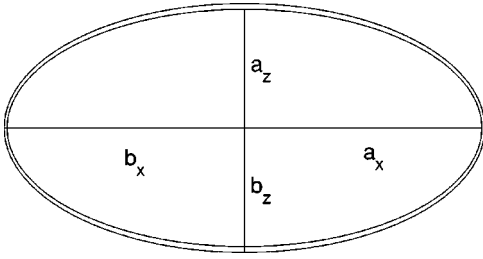


FIG. 2. A cut through a coated ellipsoid. The principal semi-axes perpendicular to the paper are of length  $b_y$  (the outer ellipsoid) and  $a_y$  (the inner ellipsoid). We assume that the inner and outer surfaces are confocal:  $b_v^2 = a_v^2 + t$  and that  $a_x \geq a_y \geq a_z$ . The shape of the coated ellipsoid is completely specified by the ellipticity of the inner surface  $e_i^2 \equiv 1 - a_x^2/a_z^2$  and the ellipticity of the outer surface  $e_o^2 \equiv 1 - b_x^2/b_z^2$  and  $s \equiv (b_x^2 - b_y^2)/(b_x^2 - b_z^2)$ . For the case of a thin coating the ellipticities are related:  $e_i^2 = e_o^2(1 + \bar{\delta})$  where  $\bar{\delta} \equiv t/b_x^2$  is the relative coating thickness. The ellipsoidal shell has relative dielectric function  $\epsilon_{\parallel}$  in the normal direction and  $\epsilon_{\perp}$  in the tangential direction. The relative dielectric function of the inner ellipsoid is  $\epsilon_i$ .

setting  $\chi_I = 0$  (together with the appropriate modification of the unit cell volume per molecule  $v_0$ ).

### III. POLARIZABILITY FOR AN ELLIPSOID WITH AN ANISOTROPIC COATING

In this section we present the analytical expression for the polarizability of an ellipsoidal particle with an anisotropic coating (the coating dielectric function is different parallel and perpendicular to the coating normal).

We consider the coated ellipsoidal particle in an external electric field  $\vec{E}_0$ , with the lengths of the principal semi-axes of the inner and outer ellipsoids as  $a_v$  and  $b_v$  ( $v = x, y, z$ ), see Fig. 2. In a standard fashion [8] we assume that the inner and outer surfaces are confocal:  $b_v^2 = a_v^2 + t$  and that  $a_x \geq a_y \geq a_z$ . The shape of the coated particle is completely specified [9] by the ellipticity of the inner surface  $e_i^2 \equiv 1 - a_z^2/a_x^2$ , the ellipticity of the outer surface  $e_o^2 \equiv 1 - b_z^2/b_x^2$  ( $e_i^2 = e_o^2 = 0$  for a sphere), and  $s \equiv (b_x^2 - b_y^2)/(b_x^2 - b_z^2)$ . We notice that  $e_i^2$ ,  $e_o^2$ , and  $s$  all are in the range  $[0, 1]$ . We denote the relative dielectric function (i.e., dielectric function in units of  $\epsilon_0 \epsilon_m$ , where  $\epsilon_0 \epsilon_m$  is the dielectric function of the medium in which the particle is immersed) of the inner ellipsoid by  $\epsilon_i$ . The coating has relative dielectric function  $\epsilon_{\parallel}$  in the normal direction and  $\epsilon_{\perp}$  in the tangential direction, i.e.,

$$\vec{\epsilon}_{\text{coat}} = \epsilon_{\parallel} \hat{\xi} \hat{\xi} + \epsilon_{\perp} (\hat{\eta} \hat{\eta} + \hat{\zeta} \hat{\zeta}). \quad (11)$$

The standard ellipsoidal coordinates are denoted by  $\xi$ ,  $\eta$ , and  $\zeta$  [10] and  $\hat{\xi}$  above is a unit vector perpendicular to the ellipsoidal surface  $\xi = \text{const}$ . Similarly  $\hat{\eta}$  and  $\hat{\zeta}$  are unit vectors perpendicular to the hyperboloid surfaces  $\eta = \text{const}$  and  $\zeta = \text{const}$ , respectively. We assume that  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are given by the result for a flat bilayer from the preceding section [see Eqs. (8) and (10)]; the implicit assumption underlying Eq.

(11) is then that the membrane molecular symmetry axes are oriented along the ellipsoidal cell membrane normal (as is typically the case for real cells). Use of the form of dielectric function as contained in Eq. (11) is expected to be rigorous if the bilayer thickness  $D$  is much smaller than the typical linear size  $L$  of the cell, i.e., if  $D/L \ll 1$  [11]; if this criterion is not fulfilled one expects significant redistribution of molecules (compared to the flat bilayer) which can cause, for instance, radial inhomogeneities. For cells typically  $D/L \sim 0.001$  and we can therefore safely apply the local dielectric function from the preceding section to the present case.

We now consider the response in the nonretarded limit. For the applied potential we write  $\Phi_{0v} = -vE_0$ , i.e., the external field  $E_0$  is constant and in the  $v$  direction ( $v = x, y, \text{ or } z$ ). In the nonretarded limit the potential  $\Phi$  satisfies Gauss equation given by

$$\vec{\nabla} \cdot [\vec{\epsilon}(\omega) \cdot \vec{\nabla} \Phi] = 0. \quad (12)$$

This problem has been treated in detail and is published elsewhere [12]. We here only summarize the results. We introduce  $q \equiv e_i^2/(1 + \xi/a_x^2)$ , where  $\xi$  is the usual ‘‘radial’’ ellipsoidal coordinate [10]. We have that  $\xi \geq -a_z^2$  [10] and hence  $0 \leq q \leq 1$ . The inner (outer) surface corresponds to  $q = e_i^2$  ( $q = e_o^2$ ). For the case of a thin coating, the ellipticities are related:  $e_i^2 = e_o^2(1 + \bar{\delta})$ , where  $\bar{\delta} \equiv t/b_x^2$  is the relative coating thickness ( $\bar{\delta} \sim D/L \ll 1$ ). We will use this relation in the following section in order to make an expansion in the relative coating thickness  $\bar{\delta}$  for the ellipsoid polarizability. The solution of Gauss equation for the coating region is then ( $v = x, y$  or  $z$ )

$$\Phi = B_v v H_v(u_-, s; q) q^{(1-u_-)/2} + C_v v H_v(u_+, s; q) q^{(1-u_+)/2}, \quad (13)$$

where the asymmetry in the dielectric function of the coating ( $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ ) enters through  $u$  defined as

$$u = u_{\pm} = -\frac{1}{2} \pm \frac{1}{2} (1 + 8\epsilon_{\perp} \epsilon_{\parallel}^{-1})^{1/2}, \quad (14)$$

and  $B_v$  and  $C_v$  are constants that are determined by the boundary conditions. The function  $H_v(u, s; q)$  satisfies Heun’s equation [12–14]. In general, Heun’s equation does not have compact solutions in terms of known standard functions. However, it does have series solutions around the singular points [13, 14]. We will here use the series expansion around  $q = 0$  (valid for  $|q| < 1$ ) which is (leaving the  $v$  dependence of coefficients implicit)

$$H_v(u, s; q) = \sum_{m=0}^{\infty} k_m(u, s) q^m, \quad (15)$$

where the expansion coefficients satisfy the recurrence relation [15]

$$\begin{aligned} & (m+1)(m+\gamma)k_{m+1} \\ & - \{[(1+s)(m-1+\gamma) + \delta_v + s\epsilon_v]m + s\lambda_v\}k_m \\ & + s(m-1+\alpha_v)(m-1+\beta)k_{m-1} = 0 \end{aligned} \quad (16)$$

TABLE I. Parameters in Heun's equation in terms of  $u = 1/2(-1 \pm [1 + 8\varepsilon_{\perp}\varepsilon_{\parallel}^{-1}]^{1/2})$ , where  $\varepsilon_{\parallel}$  ( $\varepsilon_{\perp}$ ) is the relative dielectric function in the direction parallel (perpendicular) to the ellipsoid coating normal. The shape parameter  $s$  is defined in Sec. III.

$v$	$x$	$y$	$z$
$\alpha_v$	$-u/2$	$1-u/2$	$1-u/2$
$\beta$	$(1-u)/2$	$(1-u)/2$	$(1-u)/2$
$\gamma$	$1/2-u$	$1/2-u$	$1/2-u$
$\delta_v$	$1/2$	$1/2$	$3/2$
$\epsilon_v$	$1/2$	$3/2$	$1/2$
$\lambda_v$	$(u-1)u(s+1)/(8s)$	$(u-1)[2s(u-1)+u]/(8s)$	$(u-1)[2(u-1)+su]/(8s)$

with  $k_0=1$  and  $k_{-1}=0$ . The parameters are given in terms of  $u$  in Table I. The above series is not defined for  $\gamma = -m$  where  $m$  is a positive integer. For the inner ellipsoid as well as for the surroundings the dielectric function  $\vec{\epsilon}$  is taken as constant and scalar and Gauss equation reduces to Laplace equation in these regions, for which the solution can be found in textbooks [8,10]. The potential in all space is obtained by imposing the conditions that the potential and the normal component of the displacement field are continuous at the boundaries as well as requiring that the solution  $\Phi \rightarrow \Phi_{0v} = -vE_0$  ( $v=x, y, z$ ) at infinity. We are here primarily interested in the resulting polarizability  $\vec{\alpha}$  of the coated ellipsoid.

A complete knowledge of the polarizability for a coated ellipsoid requires the knowledge of  $H_v(u, s; q)$  and a second function  $r_v(u, s; q)$  ( $v=x, y$  or  $z$ ) defined by

$$r_v(u, s; q) = 1 - f_v(s; q) \left\{ 1 - u + 2q \frac{\partial}{\partial q} \ln[H_v(u, s; q)] \right\}, \quad (17)$$

where  $f_x(s; q) = 1$ ,  $f_y(s; q) = 1 - sq$ , and  $f_z(s; q) = 1 - q$ . With the above definitions the polarizability of an ellipsoid with an anisotropic coating is

$$\alpha_{vv} = \frac{V_o}{4\pi n_v^o} \frac{I_v(\kappa = -1)}{I_v(\kappa = 1/n_v^o - 1)}, \quad (18)$$

where

$$I_v(\kappa) = [r_v^o(u_+) + \kappa \varepsilon_{\parallel}^{-1}] [r_v^i(u_-) - \varepsilon_i \varepsilon_{\parallel}^{-1}] - \rho_v [r_v^o(u_-) + \kappa \varepsilon_{\parallel}^{-1}] [r_v^i(u_+) - \varepsilon_i \varepsilon_{\parallel}^{-1}], \quad (19)$$

and  $V_o = 4\pi b_x b_y b_z / 3$  is the outer volume of the ellipsoid. We have above introduced the shorthand notation  $r_v^i(u_{\pm}) \equiv r_v(u_{\pm}, s; e_i^2)$  and  $r_v^o(u_{\pm}) \equiv r_v(u_{\pm}, s; e_o^2)$ .  $n_v^o = n_v(s; e_o^2)$  is the standard depolarization factor for the  $v$  direction for the outer surface [10] where explicitly

$$n_v(s; q) = \frac{1}{2} [f_x f_y f_z]^{1/2} H_v(-2, s; q) = \frac{1}{2} [f_x f_y f_z]^{1/2} \int_0^1 \frac{t^{1/2}}{(1-qt)^{\delta_v} (1-qrt)^{\epsilon_v}} dt \quad (20)$$

with  $f_v \equiv f_v(s; q)$  and  $\delta_v$  and  $\epsilon_v$  are given in Table I. We have also introduced

$$\rho_v \equiv \left( \frac{e_o}{e_i} \right)^{(u_+ - u_-)} \frac{H_v^o(u_-) H_v^i(u_+)}{H_v^o(u_+) H_v^i(u_-)}, \quad (21)$$

where  $H_v^o(u_{\pm}) \equiv H_v(u_{\pm}, s; e_o^2)$  and  $H_v^i(u_{\pm}) \equiv H_v(u_{\pm}, s; e_i^2)$ . The geometry of the particle enters through the geometric entities  $n_v^o$ ,  $r_v^i(u_{\pm})$ , and  $r_v^o(u_{\pm})$ . These quantities can straightforwardly be generated on a computer using the recurrence relation, Eq. (16). The standard isotropic depolarization factor  $n_v^o$  depends only on the shape ( $s$  and  $e_o^2$ ), whereas  $r_v^i(u_{\pm})$  and  $r_v^o(u_{\pm})$  couple the geometry to the dielectric asymmetry of the coating. For the case of spheroids (two of the principal axes are equal)  $H_v(u, s; q)$  and  $r_v(u, s; q)$  are expressible in terms of hypergeometric functions [12]. For an anisotropic coated *sphere* ( $q \rightarrow 0$ ) we notice from Eq. (17) that  $r_v^i(u) = r_v^o(u) = u$  and the expression for the polarizability reduces to the result obtained in Ref. [11]. For an isotropic coating  $\varepsilon_{\parallel} = \varepsilon_{\perp}$  the polarizability reduces to the standard result given in, for instance, Ref. [8].

#### IV. POLARIZABILITY OF AN ELLIPSOIDAL BILAYER MEMBRANE

In this section we combine the result for an ellipsoid with an anisotropic coating (Sec. III) with the results for a dipole coupled flat bilayer obtained in Sec. II in order to obtain the polarizability of an *ellipsoidal bilayer membrane* (a cell).

By combining the results from the previous two sections it is possible to find the polarizability for a dipole coupled ellipsoidally shaped bilayer membrane. We let  $\varepsilon_i = 1$  (i.e., assume that the inside dielectric constant equals the one outside) in Eq. (18) and combine this expression for the polarizability with the bilayer dielectric function, Eqs. (8) and (10). We are here primarily interested in  $\alpha_{vv}(\omega)$  as a func-

tion of shape for a thin-walled membrane,  $\bar{\delta} \ll 1$ . In this limit it is possible to obtain analytic results for the polarizability. We proceed by making an expansion  $I_v(\kappa) \approx I_v^0(\kappa) + I_v^1(\kappa) + \dots$  [see Eq. (19)], where  $I_v^0(\kappa)$  is zeroth order in the relative membrane thickness  $\bar{\delta}$  and  $I_v^1(\kappa)$  is first order in  $\bar{\delta}$ . While deriving below the expansion we will use the fact that the ellipticities of the outer and inner ellipsoidal surfaces are related:  $e_i^2 = e_o^2(1 + \bar{\delta})$  for a thin coating (see the preceding section). We straightforwardly obtain the zeroth order result [see Eq. (19)]

$$I_v^0(\kappa) = -\varepsilon_{\parallel}^{-1} [(r_v^o(u_+) - r_v^o(u_-))(\kappa + 1)]. \quad (22)$$

We notice (for  $\varepsilon_i = 1$  as we assume here) that the numerator of the polarizability, Eq. (18), is zero [ $I_v^0(\kappa = -1) = 0$ ] to zeroth order in  $\bar{\delta}$ , we must therefore approximate the numerator by its first order term in  $\bar{\delta}$ . The zeroth order term for denominator is nonzero and we therefore approximate the denominator by this term. We thus write Eq. (18) accordingly,

$$\alpha_{vv} \approx \frac{V_o}{4\pi n_v^o} \frac{I_v^1(\kappa = -1)}{I_v^0(\kappa = 1/n_v^o - 1)}. \quad (23)$$

We proceed by deriving an expression for  $I_v^1(\kappa)$ , by expanding  $I_v(\kappa)$  to first order in  $\bar{\delta}$  using the fact that  $\rho_v \approx 1 - (\bar{\delta}/2)[r_v^o(u_+) - r_v^o(u_-)]/f_v^o$ . This expansion requires that we assume  $|u|\bar{\delta} \ll 1$  or equivalently  $\bar{\delta} \ll (\Gamma/\omega_0)^{1/2}$  near a resonance, where  $\Gamma$  is the damping constant introduced in Eq. (7). We thus assume that the relative membrane thickness is smaller than the square root of the relative damping constant. Since we assume that we are close to a sharp resonance frequency ( $\varepsilon_{\parallel}^{-1}$  or  $\varepsilon_{\perp}$  large, i.e., small damping,  $\Gamma/\omega_0 \ll 1$ ) we can then proceed by approximating the function  $r_v(u, s; q)$  by its large  $u$  expansion given by [12]

$$r_v(u, s; q) = uR_v(s; q),$$

$$R_v(s; q) = \left( \frac{F(s; q)f_v(s; q) - 1}{2} \right)^{1/2}, \quad (24)$$

where  $q \neq 1$  and

$$F(s; q) \equiv \frac{1}{f_x(s; q)} + \frac{1}{f_y(s; q)} + \frac{1}{f_z(s; q)} \quad (25)$$

with  $f_x(s; q) = 1$ ,  $f_y(s; q) = 1 - sq$ , and  $f_z(s; q) = 1 - q$  as before [notice that  $r_v(u, s; q)$  is proportional to  $u$  for large  $u$ ]. Furthermore, keeping only the highest order terms in  $\varepsilon_{\perp}$  and  $\varepsilon_{\parallel}$  and neglecting terms  $\sim \sqrt{\varepsilon_{\perp}}$  and  $\sim \sqrt{\varepsilon_{\parallel}}$  [this again requires the assumption  $\bar{\delta} \ll (\Gamma/\omega_0)^{1/2}$ ] we find

$$I_v^1(\kappa) \approx -\varepsilon_{\parallel}^{-1} [(r_v^o(u_+) - r_v^o(u_-)) \frac{\bar{\delta}}{2f_v^o} [\varepsilon_{\perp} 2(R_v^o)^2 + \varepsilon_{\parallel}^{-1} \kappa]], \quad (26)$$

where  $R_v^o \equiv R(s; e_o^2)$  and  $f_v^o \equiv f(s; e_o^2)$ . Equation (26) combined with Eqs. (22) and (23) gives the polarizability of the

ellipsoid. This expression can be further simplified by noticing that for a thin coating [such that  $\bar{\delta}/(1 - e_o^2) \ll 1$ ] we have  $V_o F_o \bar{\delta}/2 \approx V_o - V_i = V_{\text{coat}}$ , where  $V_{\text{coat}}$  is the coating volume and  $V_i = 4\pi a_x a_y a_z/3$  is the volume of the inner ellipsoid and  $F_o \equiv F(s; e_o^2)$ . We finally introduce the explicit expression for  $\varepsilon_{\perp}$  and  $\varepsilon_{\parallel}^{-1}$  [Eqs. (8) and (10)] for a flat bilayer and use the fact that the coating volume can equally well be written  $V_{\text{coat}} = Nv_0$ , where  $v_0$  is the unit cell volume per membrane molecule as before and  $N$  is the number of molecules in the membrane, and find ( $v = x, y$  or  $z$ )

$$\alpha_{vv} = N \left[ g_{v\perp} \frac{\gamma_{0\perp} \omega_0^2}{\tilde{\omega}_{0\perp}^2 - \omega^2 - i\omega\Gamma_{\perp}} + g_{v\parallel} \frac{\gamma_{0\parallel} \omega_0^2}{\tilde{\omega}_{0\parallel}^2 - \omega^2 - i\omega\Gamma_{\parallel}} \right], \quad (27)$$

where we have only included the resonant part to obtain the polarizability. Notice that the resonance frequencies  $\tilde{\omega}_{0\perp}$  and  $\tilde{\omega}_{0\parallel}$  are the same as for a flat bilayer [see Eq. (8)] and that cell polarizability  $\alpha_{vv}$  is proportional to the number of molecules  $N$  in the bilayer. The geometric weights for the oscillator strengths are given by

$$g_{v\perp} = \frac{2(R_v^o)^2}{F_o f_v^o} = 1 - \frac{1}{F_o f_v^o},$$

$$g_{v\parallel} = \frac{1}{F_o f_v^o}. \quad (28)$$

The result for the polarizability of a dipole coupled ellipsoidal bilayer membrane (a cell) as contained in Eqs. (27) and (28) is the main result of this study [16]. We again point out that these equations are based on the following assumption: the damping is small (i.e., the membrane molecules have ‘‘sharp’’ resonances), but not ‘‘too small’’ in comparison to the membrane curvature,  $\bar{\delta} \sim D/L \ll (\Gamma/\omega_0)^{1/2} \ll 1$ , where  $D$  is the membrane thickness and  $L$  is a typical linear size of the ellipsoid. The results are illustrated in Fig. 3, where we also give the results using the full expression for the polarizability [Eq. (18) together with the bilayer dielectric function, Eqs. (8) and (10)]. The agreement with the above approximative result and the exact result is excellent. We notice some general features. As already noted, the positions of the resonances are practically the same as for a flat bilayer, i.e., the peak positions are unaffected by the curvature of the bilayer as long as  $\bar{\delta} \ll (\Gamma/\omega_0)^{1/2}$ . If this condition is not satisfied, the induced dipole moments are sufficiently large to allow dipole interactions over distances for which the membrane is not flat. The geometric weight for the oscillator strength is a measure of how many induced dipoles effectively contribute to the extinction cross section ( $\sim \omega \text{Im}[\alpha_{vv}(\omega)]$ ). When the external field is directed along the long axis there are more (less) local area elements with a normal oriented perpendicular (parallel) to the field [and hence more (less) induced dipoles in the field direction] compared to the case when the field is along the short axis. The geometric weight for the  $\omega = \tilde{\omega}_{0\perp}$  ( $\omega = \tilde{\omega}_{0\parallel}$ ) peak is therefore largest when the field is along the largest (smallest) principal axis [see Eq. (28)]. We

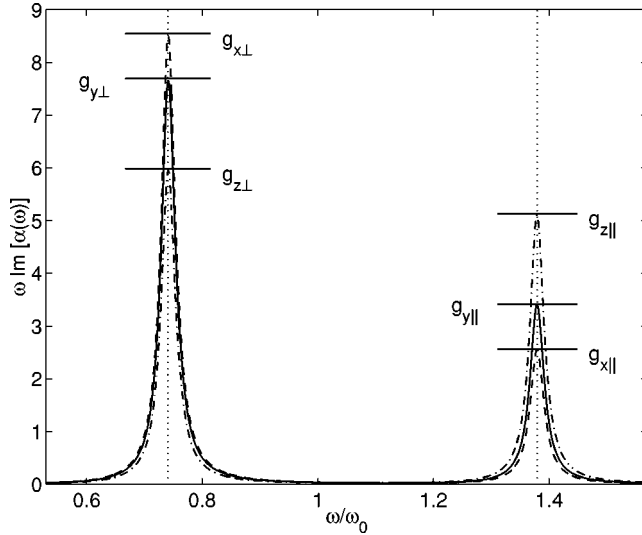


FIG. 3. The extinction cross section  $\sim \omega \text{Im}[\alpha_{vv}(\omega)]$ , where  $\alpha_{vv}(\omega)$  is the polarizability for an ellipsoidally shaped bilayer. The dashed line corresponds to the external field being along the long axis ( $x$  axis), the solid line corresponds to a situation where the external field is along the middle axis ( $y$  axis). For the dash-dotted line the field is along the short ( $z$  axis). The vertical lines correspond to the resonance frequencies for a flat dipole coupled bilayer. Notice that the position of the peaks are located at the same place as for a flat bilayer. The peak positions are thus unaffected by the curvature of the layer. The horizontal lines correspond to the analytic expression for the geometric weight for the oscillator strengths, Eq. (28). The geometric weight for the  $\omega = \tilde{\omega}_{0\perp}$  ( $\omega = \tilde{\omega}_{0\parallel}$ ) peak is largest when the field along the largest (smallest) axis. The shape of the ellipsoid was taken to be  $e_o^2=0.5$ ,  $s=0.5$ , and  $\bar{\delta}=0.002$ . The ratio between intermolecular distance within each layer and distance between molecules in different layers is taken as  $d/a=2$ . The electromagnetic response of the molecules was characterized by the static isotropic polarizability value  $\gamma_0/a^3=0.1$  and the damping parameter is  $\Gamma/\omega_0=0.03$ .

notice that in the spherical limit  $e_o^2 \rightarrow 0$  we have  $g_{v\perp} \rightarrow 2/3$  and  $g_{v\parallel} \rightarrow 1/3$ . The geometric weights satisfy the general sum rules:

$$\begin{aligned} g_{x\parallel} + g_{y\parallel} + g_{z\parallel} &= 1, \\ g_{x\perp} + g_{y\perp} + g_{z\perp} &= 2. \end{aligned} \quad (29)$$

These sum rules state that the rotationally averaged extinction spectrum ( $\sim \omega \text{Im}[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$ ) does not depend on the shape. One must thus align the cells if one wants information about shape using extinction measurements. We also easily obtain the sum rule

$$g_{v\perp} + g_{v\parallel} = 1. \quad (30)$$

This sum rule states that for a field incident along the  $v$  axis of an aligned cell the extinction integrated over all frequencies  $\sim \int d\omega \omega \text{Im}[\alpha_{vv}(\omega)]$  is independent of the shape.

We would like to emphasize that the shape of the cell can be inferred by measuring the peak heights in the extinction (or absorption) spectra for a single isolated cell. The ratios of the peak heights, as our theory shows, can then be utilized to

obtain the geometrical shape of the cell. These ratios can also be used to infer the orientation of the applied field.

We have in this study assumed that the dielectric function of the ellipsoidal bilayer is given by the result for a dipole coupled molecular aggregate where the molecules are situated on a *cubic bilayer* lattice. Real cell membranes are usually found in a two-dimensional fluid state. One should therefore investigate how disorder affects the dielectric functions. This is currently under investigation. We also here point out that the results from this section can straightforwardly be modified in order to obtain the polarizability of an ellipsoidally shaped monolayer or multilayer. The only effect of changing the number of layers is to modify the resonance frequencies  $\tilde{\omega}_{0\perp}$  and  $\tilde{\omega}_{0\parallel}$  (see discussion at the end of Sec. II). The expressions for the geometric weights  $g_{v\perp}$  and  $g_{v\parallel}$ , however, remain the same.

## V. CONCLUSIONS

In this study we have derived an electromagnetic response function for a cell-like structure at field frequencies where molecular resonances (vibrational and electronic) are important (i.e., typically at energies  $\sim 0.1-3$  eV). The basis for this investigation was that a cell membrane is, due to local field effects, typically dielectrically anisotropic. Furthermore, cells are in general not spherical. We have therefore combined results for the electromagnetic response of a flat dipole coupled bilayer with the solution of Gauss equation for an ellipsoid with an anisotropic coating (the coating dielectric function being different parallel and perpendicular to the coating normal) in order to obtain polarizability  $\alpha_{vv}(\omega)$  ( $v=x,y,z$ ) for an *ellipsoidal bilayer membrane*. For a thin-walled bilayer the result is given in Eqs. (27) and (28). Some general features are: the positions of the peaks of  $\text{Im}[\alpha_{vv}(\omega)]$  are the same as for a flat bilayer,  $\omega = \tilde{\omega}_{0\parallel}$  and  $\omega = \tilde{\omega}_{0\perp}$  [see Eq. (8)]. The geometric weight for the oscillator strengths of the peaks are, however, sensitive to the shape. The geometric weight for the  $\omega = \tilde{\omega}_{0\perp}$  ( $\omega = \tilde{\omega}_{0\parallel}$ ) peak is largest when the field is along the largest (smallest) axis. The geometric weights are shown to satisfy three sum rules.

We hope that the results obtained in this study will be useful for cell characterization. The imaginary part of the polarizability is directly accessible to experiments through extinction (or absorption) measurements. The result for the cell polarizability as given by Eqs. (27) and (28) can thus be used to interpret the results of such measurements in terms of molecular polarizabilities, intermolecular distances, cell shape, etc. Furthermore, our results could be applied, with only minor modifications, to other coated anisotropic structures of nontrivial shape that exhibit resonances. Examples of such structures include fullerenes or ellipsoidal nanoparticles with ultrathin coatings.

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- [16] While deriving the dielectric function for the flat bilayer in Sec. II [see Eqs. (8) and (10)] only the dipolar interaction between membrane molecules was included. However, a possible frequency dependence of the background was ignored; if included, it only renormalizes the characteristic parameters (the resonance frequency and damping constants) in the membrane dielectric functions. As a result, in the final expression for the cell polarizability, Eq. (27), one would have renormalized resonance frequencies and damping constants, but the general results for the geometric weights  $g_{v\perp}$  and  $g_{v\parallel}$  remain unaltered.