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Optical properties of two-dimensional disordered systems on a substrate

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We calculate the dielectric response of free-standing and supported two-dimensional layers of polarizable entities, such as metallic particles or adsorbed molecules. We take into account dipole-dipole and the image interaction and investigate the effects of disorder within a two-dimensional renormalized polarizability theory. The behavior of the resonances arising from both the single particle's and the substrate's surface plasmon is studied.

I. INTRODUCTION

The macroscopic dielectric function of granular materials made up of a mixture of substances with different individual response functions depends on the morphology of the sample. The most simple effective-medium theory assumes an isotropic but ordered ensemble of small spherical inclusions[1] characterized by its number density. However, it is well known that the actual shapes and sizes of the grains, the topology and connectivity of the sample, its dimensionality, the statistical distribution of the grains, the fractal dimension of grain clusters, and other morphological parameters play an important role in the determination of the macroscopic response functions. The identification of the most relevant parameters and their incorporation into manageable theories,[2,3] as well as their comparison to experiment on well-characterized samples,[4] constitute a very active field of research.

Although most of the work has been directed towards composites systems in three dimensions, the properties of discontinuous films and inhomogeneous media have attracted considerable attention during the last years.[5-9] When the films are very thin and the number of nucleation sites is large enough, very small particles with sizes of a few nanometers or less can be grown at the surface of a substrate. Their electromagnetic properties make them suitable as effective coatings for solar-energy absorbers,[10] and to study surface-enhanced Raman scattering[11] and spectroscopy of atoms and molecules adsorbed on surfaces.[12,13] On the other hand, the optical properties of molecules adsorbed on flat surfaces have been stimulated by a vast amount of experimental results.[14]

In the present paper we focus our attention on the optical response of two dimensional (2D) disordered systems made of polarizable entities, such as small conducting particles or molecules adsorbed on a substrate. We investigate the effects of disorder, taking into account the fluctuations in the dipole moments and the influence of the substrate for supported films.

There are many ways to approach the problem of the macroscopic response of granular materials in both two and three dimensions. The topology may be incorporated by defining suitable random unit cells[15] in such a way that the classical Maxwell-Garnett[1] and Bruggeman[16] theories are recovered as special cases. Some recent efforts aim to incorporate the morphology in simple phenomenological theories with a few parameters, such as a percolation threshold, and an exponent related to the dimensionality and the distribution of depolarization factors.[17] Others workers have obtained formulas that interpolate to finite filling fraction f the effective dielectric function from its behavior near $f=0$ and 1, where topological constrictions are more easily handled.[18]

A different approach to the problem is to generate an ensemble of well-characterized finite or periodically repeated disordered systems through Monte Carlo simulations. The macroscopic response is then obtained by exactly calculating the total polarization of each system and averaging it over the ensemble.[19,20] An advantage of this approach is that it has allowed a direct comparison with approximate analytical formulas, such as those obtained from a truncated cluster expansion,[21] expected to be adequate for small filling fractions.[22] Numerical simulations have also allowed the investigation of the fluctuations of the local field that are responsible of the corrections to the Maxwell-Garnett results in the cermet topology.[23] The dielectric response of fractal media such a porous rocks filled with brine has also attracted much attention.[24] The importance of multipolar[25] and finite-size effects has also been recognized, both for relatively large particles[26] and for clusters with only a small number of atoms,[27] and phenomenological effective-medium formulas[28] have been used to investigate experimentally the size dependence of the dielectric response of the individual constituents.[29]

As for 2D systems, in the most simple calculations the polarizable entities are assumed spherically symmetric, they interact through their dipolar fields, and are arranged in a square lattice.[30–32] Since the interaction among dipoles in a square lattice almost exhausts the lattice sums in 3D cubic lattices, 3D mean-field theories have also been employed for the 2D case.[33] Nevertheless, we must remark that other periodic arrangements, such as the triangular lattice, do not exhaust the 3D lattice sums, even though they retain optical isotropy within the plane. Artificial 2D square crystals made up of small Au particles have actually been fabricated. Their optical properties indicate the importance of the particle shapes and of their indirect interactions through the substrate.[34] Theoretical effort has been devoted to the calculation of the polarizability of single nonspherical particles on a substrate, such as truncated spheres,[35] spheroids,[36] and even arbitrarily shaped particles,[37] taking into account the interaction of each particle with its own image on the substrate. The interaction between anisotropic particles arranged in a square lattice was calculated within the spherical-dipole approximation.[38] Nevertheless, most experiments on 2D systems have been performed on disordered systems.

Experiments on thin granular metallic films near the percolation threshold[39] display a large absorption with only a small-wavelength dependence. This was explained[40] by applying scaling relations to the dominant Joule losses in narrow channels within large clusters. Other approaches to the dielectric response of 2D systems include real-space renormalization techniques[41] and simulations with networks of resistor-inductor-capacitor (RLC) elements distributed stochastically on a square lattice.[42]

For disordered 2D systems it has been recognized that, even within the mean-field and long-wavelength approximations and for densities below the scaling region, the response does depend on the local environment of each particle, that is, on the spatial arrangement of its neighbors. This is unlike the situation in isotropic 3D systems, where the macroscopic response within the mean-field approximation is independent of the statistics of the particle positions. The first statistical theories for disordered 2D systems stressed the importance of the mass autocorrelation functions,[43,44] although they neglected the dipolar fluctuations. They were later generalized to account for particle shapes and particle-substrate interactions,[45] both of which have also been investigated experimentally.[46]

A different approach to the problem assumes a lattice gas of polarizable entities that occupy sites on a fictitious square lattice with a probability dependent on the filling fraction. The interaction between particles was approximated by the dipolar term without substrate effects, and the fluctuations were incorporated through the lattice-gas–coherent-potential approximation (LG-CPA).[47,48]

The purpose of the present paper is to develop a microscopic theory for the optical properties of 2D systems that explicitly accounts for the dipolar fluctuations. As these are related to the local environment of every polarizable entity, we write our results in terms of the position pair distribution functions and we take into account the indirect interactions through the polarization of the substrate. For this purpose we formulate a renormalized polarizability theory (RPT) not unlike the one recently developed for disordered 3D systems.[49] The RPT has been compared to other theories that account for disorder in three dimensions, where it leads to similar results, namely, a red shift and an asymmetric broadening of the resonant structures. Since we concentrate our attention on the effects of disorder, we simplify the mathematics by assuming that each polarizable entity is isotropic, thus ignoring the shape effects mentioned above. Furthermore, we only consider dipole-dipole interactions, although higher multipoles become important at high filling fractions[50] and even at very low filling fractions[51] for systems with aggregation.

The structure of the paper is the following: In Sec. II we develop, within the quasistatic dipolar approximation, the formalism for the effective anisotropic renormalized polarizabilities of disordered 2D systems with and without a substrate. By neglecting the fluctuations and the disorder, we also recover previously obtained formulas. Since our theory is equally suited to granular films as to molecular overlayers, in Sec. III we apply it to two important disordered systems: metallic spheres on an insulating substrate and isotropic molecules deposited on a metallic substrate. Here, we also compare our results with those of other theories and with experiment. Finally, Sec. IV is devoted to conclusions.

II. THEORY

A. Renormalized polarizability theory

We consider a homogeneous and isotropic two-dimensional ensemble of $N \gg 1$ identical polarizable entities centered at random positions $\mathbf{R}_i$ on the X-Y plane at a distance d from the surface of a semi-infinite substrate with dielectric function ϵ_s. The system is in the presence of an external field $\mathbf{E}^{\text{ext}}$ oscillating with frequency ω and wavelength much greater than the typical separation between the entities. Within the dipolar approximation, the induced dipole $\mathbf{p}_i$ at R_i obeys

$$\mathbf{p}_i = \alpha(\omega) \left[\mathbf{E}^{\text{ext}} + \sum_j \mathbf{v}_{ij} \cdot \mathbf{p}_j \right] , \tag{1}$$

where $\alpha(\omega)$ is the isotropic polarizability of each entity, $\mathbf{v}_{ij} = \mathbf{t}_{ij} + \mathbf{t}_{ij}^I \cdot \mathbf{M}$,

$$\mathbf{t}_{ij} = (1 - \delta_{ij}) \nabla_i \nabla_i (1/R_{ij}) \tag{2}$$

is the dipole-dipole interaction tensor in the quasistatic limit, with $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$,

$$t_{ij}^I = \nabla_i \nabla_i (1/R_{ij}^I) \tag{3}$$

is the corresponding dipole-image dipole interaction tensor with $\mathbf{R}_{ij}^I = \mathbf{R}_{ij} - 2d\hat{e}_z$ the vector from the image of the jth particle to the ith particle,

$$\mathbf{M} = A \ \text{diag}(-1, -1, 1) , \tag{4}$$

and $A = (\epsilon_s - 1)/(\epsilon_s + 1)$ is the strength of the image of a unit dipole. Here we assumed a flat surface and we used classical image-field theory, although it is known[31] that the discreteness of the substrate has important effects sometimes.

Using the continuity of the normal component of the displacement field and the tangential component of the electric field, which allows us to identify $\mathbf{E}^{\mathrm{ext}}$ with the macroscopic fields E_x, E_y, and D_z, we have

$$P_x=\frac{1}{4\pi}(\epsilon_x-1)E_x^{\mathrm{ext}}=\chi_x^{\mathrm{ext}}E_x^{\mathrm{ext}} , \tag{5a}$$

$$P_z=\frac{1}{4\pi}(1-\epsilon_z^{-1})E_z^{\mathrm{ext}}=\chi_z^{\mathrm{ext}}E_z^{\mathrm{ext}} , \tag{5b}$$

where ϵ_γ ($\gamma=x,y$) is the anisotropic macroscopic dielectric function, $\chi_\gamma^{\mathrm{ext}}$ is the external susceptibility, and $\mathbf{P}$ is the average dipole moment per unit volume of the layer. Furthermore, due to homogeneity and isotropy of the ensemble in the X-Y plane, $\epsilon_x=\epsilon_y$. Notice that to define $\mathbf{P}$ and therefore ϵ_γ we have to introduce some convenient characteristic width for the 2D system. However, its optical properties are independent of this width as long as it is much smaller than the wavelength.

Now we rewrite Eq. (1) as

$$\mathbf{p}_i=\alpha\left[\mathbf{E}^{\mathrm{ext}}+\sum_j \mathbf{v}_{ij}\cdot\langle\mathbf{p}\rangle+\sum_j \mathbf{v}_{ij}\cdot(\mathbf{p}_j-\langle\mathbf{p}\rangle)\right] . \tag{6}$$

The second term on the right-hand side is the field due to average dipoles occupying random positions, while the third term is the contribution due to the fluctuations of the dipole moments. Within the framework of Ref. 49, we define two renormalized polarizabilities α_x^* and α_z^* to take partially into account the fluctuations through the approximation

$$p_i^x=\alpha_x^*\left[E_x^{\mathrm{ext}}+\sum_j v_{ij}^{xx}\langle p_x\rangle+\sum_j v_{ij}^{xz}\langle p_z\rangle\right] , \tag{7a}$$

$$p_i^z=\alpha_z^*\left[E_z^{\mathrm{ext}}+\sum_j v_{ij}^{zx}\langle p_x\rangle+\sum_j v_{ij}^{zz}\langle p_z\rangle\right] , \tag{7b}$$

where $\langle\mathbf{p}\rangle$ is the ensemble average dipole moment which is independent of position due to the translational invariance of the ensemble. Substituting these equations in Eq. (1) and demanding self-consistency,[49] we obtain the following two coupled equations for α^*:

$$\frac{\alpha_\gamma^*}{\alpha}=1-(\alpha_\gamma^*)^2\left\langle\sum_j v_{ij}^{\gamma\gamma}\right\rangle^2+\alpha_\gamma^*\left\langle\sum_{jk}(\mathbf{v}_{ij}\cdot\alpha^*\cdot\mathbf{v}_{jk})^{\gamma\gamma}\right\rangle , \tag{8}$$

where $\gamma=x,z$.

Now we assume that the three-particle distribution required to average the product of two tensors $\mathbf{v}$ can be replaced by the product of two-particle distribution functions

$$\rho^{(3)}(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)\approx\rho^{(2)}(\mathbf{R}_{12})\rho^{(2)}(\mathbf{R}_{23}) . \tag{9}$$

In the 3D case, this simplifying assumption is known to hold for low filling fractions, although it becomes inadequate for filling fractions $f\approx0.3$. A similar limit of validity is expected in two dimensions. In three dimensions the formalism has already been extended to account properly for three-particle distributions.[52] The corresponding extension in two dimensions will be the object of future research. Equation (8) then becomes

$$\frac{\tilde\alpha_x^*}{\tilde\alpha}=1+\tfrac{1}{4}f_{xx}(\tilde\alpha_x^*)^2+f_{xz}\tilde\alpha_z^*\tilde\alpha_z^* , \tag{10a}$$

$$\frac{\tilde\alpha_z^*}{\tilde\alpha}=1+2f_{zx}\tilde\alpha_x^*\alpha_z^*+\tfrac{1}{4}f_{zz}(\tilde\alpha_z^*)^2 , \tag{10b}$$

where $\tilde\alpha^*\equiv\alpha^*/a^3$ is made dimensionless by introducing the radius of the polarizable entities a. The 2D filling fraction is $f=N\pi a^2/S$, where N is the number of entities on an area S; expressions for the effective filling fractions f_{xx}, f_{zz}, and f_{xz} are given in the Appendix.

Without images, $\epsilon_s=1$, $A=0$, and $f_{xz}=0$, and therefore the equations uncouple yielding two simple quadratic equations. In this case $f_{xx}/f_{zz}=5/2$, which shows that the effect of disorder on the polarizability is more pronounced in the X direction, that is, parallel to the plane. In the presence of a substrate the coefficient f_{xz}, which also contains information on disorder, becomes nonvanishing.

Taking ensemble average of Eqs. (7) we obtain

$$\epsilon_x-1=4\pi\chi_x^{\mathrm{ext}}=\frac{2f\tilde\alpha_x^*}{1-\frac{1}{2}f\tilde\alpha_x^*(g+AG^I)} , \tag{11a}$$

$$1-\epsilon_z^{-1}=4\pi\chi_z^{\mathrm{ext}}=\frac{2f\tilde\alpha_z^*}{1+f\tilde\alpha_z^*(g-AG^I)} , \tag{11b}$$

where we identified the diameter $2a$ as the width of the layer,

$$g\equiv\int_0^\infty\frac{\rho^{(2)}(2ax)}{x^2}dx , \tag{12a}$$

$$G^I\equiv\frac{1}{4fr^3}-g^I , \tag{12b}$$

$$g^I\equiv\int_0^\infty\rho^{(2)}(2ax)\frac{x(x^2-2r^2)}{(x^2+4r^2)^{5/2}}dx , \tag{12c}$$

and $r=d/a$. The first term in G^I comes from the interaction of a dipole with its own image, and the second one from the interaction with the rest of the images.

In summary, within RPT, the renormalized or effective polarizability is calculated from Eqs. (10), which can are then substituted in Eqs. (11) together with Eqs. (12) to obtain the anisotropic electric susceptibility and dielectric function. The formalism above can be rederived from a diagrammatic multiple-dispersion analysis of the dipole-dipole interaction, which shows that it is an extension of mean-field theory to higher filling fractions.[53]

B. Mean-field theory

The mean-field theory (MFT) is obtained by neglecting completely the contributions to the field due to the dipole fluctuations in Eq. (6), and yields

$$\epsilon_x^{\mathrm{MFT}}-1=\frac{2f\tilde\alpha}{1-\frac{1}{2}f\tilde\alpha(g+AG^I)} , \tag{13a}$$

$$1-(\epsilon_z^{\mathrm{MFT}})^{-1}=\frac{2f\tilde\alpha}{1+f\tilde\alpha(g-AG^I)} , \tag{13b}$$

which are identical to Eqs. (11) upon replacement of $\tilde{\alpha}_\gamma^*$ by $\tilde{\alpha}$. Our Eqs. (13) are equivalent to the expressions developed in Refs. 43–45. Those results were used to analyze the optical transmission measurements obtained in Ref. 54 by using correlation functions obtained from electron micrographs of the islands forming the 2D system. The only difference lies in the absence of the explicit self-image term $[1/(4fr^3)$ in $G^I]$ in Ref. 54, which, however, was accounted for by redefining the polarizability of each entity.

C. Ordered system

The analogous expressions for the square lattice with the same filling fraction are[30,38]

$$\epsilon_x^{\text{latt}}-1=\frac{2f\tilde{\alpha}}{1-\frac{1}{2}\tilde{\alpha}(-\xi_0+A\xi_I)(f/\pi)^{3/2}}\;, \tag{14a}$$

$$1-(\epsilon_z^{\text{latt}})^{-1}=\frac{2f\tilde{\alpha}}{1+\tilde{\alpha}(-\xi_0-A\xi_I)(f/\pi)^{3/2}}\;, \tag{14b}$$

where

$$\xi_I=\sum_{i,j=-\infty}^{\infty}\frac{3t^2-(i^2+j^2+t^2)}{(i^2+j^2+t^2)^{5/2}}\;, \tag{15}$$

$\xi_0=-9.0336$, $t=2d/a_l$, and a_l is the lattice constant of the 2D array.

III. APPLICATIONS

Although the theory we have developed is very general, now we choose for convenience the simple hole-correction (HC) distribution function $\rho^{(2)}(2ax)=\Theta(2ax-1)$, where Θ is the unit step function. Also, for definiteness, we choose $d=a$. The systems we study are metallic spheres over an insulator and molecules adsorbed on a metal.

A. Metal spheres on an insulator

We consider a disordered system of metallic spheres of radius a. First we will model the metal by a simple Drude model. The polarizability of a single sphere is

$$\alpha_s=a^3\frac{\epsilon_p-1}{\epsilon_p+2}\;, \tag{16}$$

where R is the radius of the sphere and

$$\epsilon_p=1-\frac{\omega_p^2}{\omega(\omega+i/\tau)} \tag{17}$$

is the Drude dielectric function of the plasma. This yields

$$\tilde{\alpha}_s=\frac{1}{1-[\omega(\omega+i/\tau)/\Omega_s^2]}\;, \tag{18}$$

where $\Omega_s=\omega_p/\sqrt{3}$. Thus, each particle behaves as an isotropic harmonic oscillator with resonance frequency Ω_s and damping constant $1/\tau$.

Figure 1 shows the loss functions $\text{Im}(\epsilon_x)$ and $\text{Im}(-1/\epsilon_z)$ (denoted generically as η in the figures) as a function of ω/ω_p for an ordered square lattice. The system is composed of ordered Drude spheres with damping constant $\hbar/\tau=0.158$ eV, plasma frequency $\hbar\omega_p=6.928$ eV, and filling fraction $f=0.2356$, which correspond to the parameters used in Ref. 47. However, we present results both with and without a quartz substrate with index of refraction $n_s=\sqrt{\epsilon_s}=1.5$. We note that the interaction splits the absorption peak of a single sphere into a blue-shifted perpendicular resonance (⊥) and a red-shifted parallel resonance (‖). Without a substrate, the ⊥ shift is larger than the ‖ one, since in the former case the moment of any given dipole is opposed by the field due to all neighbors [Fig. 2(a)]. If we regard each dipole as an harmonic oscillator, then the effect of the neighbors is to increase its effective restoring force, leading to a blue shift. In the ‖ case, some neighbors oppose and some reinforce

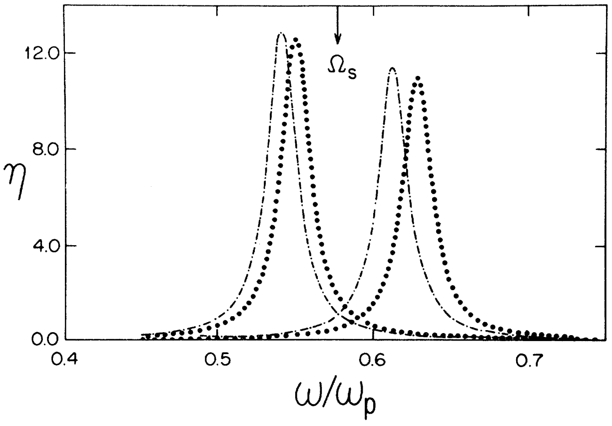

FIG. 1. Loss functions η (imaginary parts of ϵ_x and $-1/\epsilon_z$ for fields parallel and normal to the surface, respectively) calculated for a periodic square array of Drude spheres with (dotted-dashed lines) and without (dotted lines) a substrate of quartz ($n=1.5$) as a function of frequency. Here, $\hbar\omega_p=6.928$ eV, $\hbar/\tau=0.158$ eV, and $f=0.2356$. The resonance frequency of an isolated sphere $\Omega_s\equiv\omega_s/\omega_p=1/\sqrt{3}$ is indicated by a small vertical arrow.

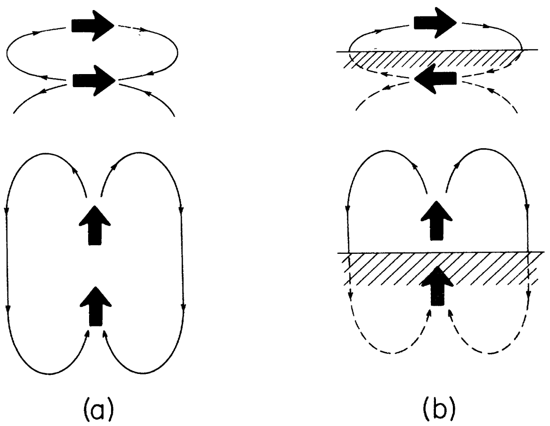
(a) (b)

FIG. 2. Dipole-dipole interaction for different orientations illustrating (a) interactions among neighbors and (b) interactions with images.

the given dipole [Fig. 2(a)]. The net result is a decrease of the effective restoring force and a comparatively small redshift, analogous to that in 3D systems. The presence of a substrate further shifts both peaks to lower frequencies. This is mainly due to the contribution of the self-images which soften, for both orientations, the restoring forces [Fig. 2(b)].

In Fig. 3 we show results for a free-standing 2D disordered system using the parameters of Fig. 1. Our calculations were performed within the 2D mean-field theory (MFT) and the renormalized polarizability theory (RPT) discussed above, as well as the lattice-gas coherent potential approximation (LG-CPA) presented in Ref. 47. It can be seen that the MFT calculation yields two nearly symmetric absorption peaks. Their widths are the same, but their frequency shift from Ω_s is larger than that of the square array, since for a given filling fraction, particles may get closer in the disordered system. The dipolar fluctuations, taken into account within RPT and LG-CPA, induce further redshifts and blueshifts and a considerable asymmetric broadening with a long tail towards Ω_s. These effects are more pronounced for the $\|$ resonance. Recall that in the $\perp$ case the interaction with all neighbors induces a blueshift, while in the $\|$ case some induce a blueshift and others a redshift, increasing the width.[47] The radial distribution function of a lattice gas has structure, including a δ-function peak at the first-neighbor distance $2a$, unlike the HC distribution. Since in two dimensions nearby dipoles are much more important than those farther away, the LG-CPA yields larger shifts and widths than RPT.

In Fig. 4 we show the effects of a substrate with $n=1.5$ on the disordered system discussed above. The MFT peaks are both redshifted with respect to the free-standing case due to the interaction with the images, as in Fig. 1. Furthermore, fluctuations broaden the peaks and shift them towards the red ($\|$) and blue ($\perp$) ends of the spectrum. However, these shifts and broadenings are larger for the $\perp$ case and weaker for the $\|$ case than those corresponding to the free-standing system, which can be understood by considering each dipole and its own image as one interacting entity. In the $\|$ case, the real and the image dipoles point in opposite directions, weakening the interaction among neighbor entities, contrary to the $\perp$ case [Fig. 2(b)].

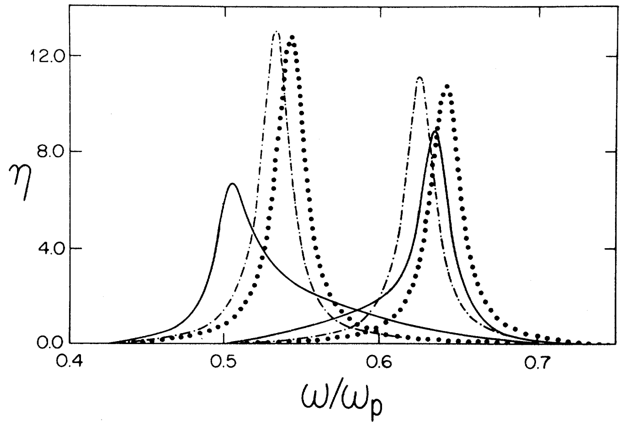

FIG. 4. Loss functions η calculated with different theories for a disordered system of Drude spheres on a substrate with $n=1.5$. The parameters are the same as in Fig. 1. We show results of the RPT (solid lines) and MFT (dotted-dashed lines). For reference, we also included the plot of MFT without images (dotted lines).

To compare our results with experiment,[38] we have calculated the absorption spectrum for small silver spheres of radius $a=90$ Å randomly located on the surface of a film of polyvinyl alcohol with filling fraction $f=0.275$ (Fig. 5). The $\|$ and $\perp$ contributions to the absorptance were sorted out as discussed in Ref. 38 and give two peaks similar to the experimental ones. However, they

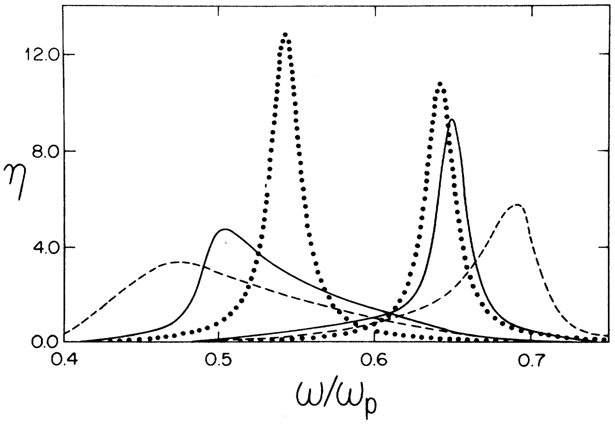

FIG. 3. Loss functions η calculated with different theories for a free-standing disordered system of Drude spheres. The parameters are the same as in Fig. 1. The results obtained from MFT, RPT, and LG-CPA are indicated by dotted, solid, and dashed lines, respectively.

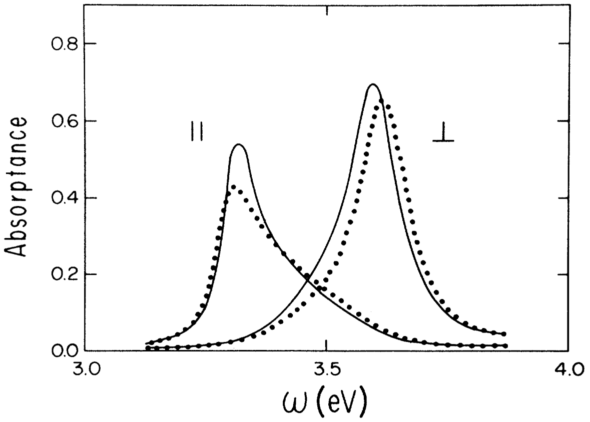

FIG. 5. Calculated absorption spectrum of disordered silver spheres on polyvinyl alcohol for parallel ($\|$) and perpendicular ($\perp$) modes with (dotted lines) and without (solid lines) substrate.

are centered around 3.5 eV, whereas in the experiment they are centered around 3.1 eV. Furthermore, the calculated heights are approximately 3 times larger, and their width and separation are correspondingly smaller. In the experimental setup[38] there was a broad distribution of sizes and shapes and a large uncertainty in a and f. Our theory can be generalized to polydispered samples[55] and predicts in three dimensions wider resonances. Other sources of discrepancy may be nonspherical shapes,[35-37] higher-order multipoles,[50,51] more structure in the pair-distribution function, and corrections due to higher-order distributions.[52]

B. Molecules on a metal

We consider now a disordered system of optically isotropic molecules of C-Cl_4 adsorbed on a substrate characterized by a Drude dielectric constant. We chose $f=0.3$, $w_p\tau=10$, $\alpha=10.475$ Å^3, and $a=2.715$ Å, which are consistent with the bulk density $\rho=1.59$ g/cm^3 of C-Cl_4 and its nondispersive dielectric constant in the visible $\epsilon_B=2.141$. In Fig. 6 we exhibit the differential reflectance ΔR_p of the adsorbate covered with respect to the clean metal surface for p polarization calculated using a perturbative formalism.[30-32] We chose as angle of incidence θ, the Brewster angle of the vacuum-bulk C-Cl_4 interface $\theta_B=\tan^{-1}(\sqrt{\epsilon_B})$. As discussed in Ref. 56, at this angle, a continuous film would not be optically observable. Therefore, any change of reflectivity when wetting the surface would be due to the interaction of the first monolayer with its image. We obtain a single peak at the surface plasma frequency[56] Ω_{sp}, which is slightly broadened by the fluctuations.

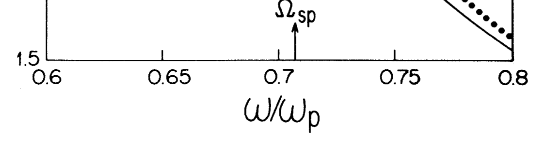

FIG. 6. Relative change of reflectance $-\Delta R_p$ as a function of frequency ω for a layer of C-Cl_4 adsorbed on a Drude metal with $f=0.3$ and $\theta=\theta_B=55.6°$. The results of MFT and RPT with images are indicated by dotted and solid lines, respectively. The surface plasma frequency of the flat metallic surface $\Omega_{sp}=1/\sqrt{2}$ is indicated by a small vertical arrow.

IV. CONCLUSIONS

We have developed a renormalized polarizability theory[49] to calculate the dielectric response of 2D isotropic disordered systems of identical polarizable entities, applicable to both free-standing and supported layers. This is a microscopic statistical theory whose starting point is the set of coupled equations for the polarization of individual dipoles. These equations were solved and ensemble averaged making use of well-defined approximations, the dipole and field fluctuations were explicitly accounted for, and the statistical properties of the system were incorporated through its density and functionals of its pair-distribution functions. It should be remarked that, given the polarizability of the particles or their microscopic dielectric response and size, and their statistical distribution, our theory predicts definite results with no adjustable parameters, in contrast to phenomenological theories. Our work can be considered an extension of previously developed formalisms that either assumed that the system was ordered[30-32,38] or neglected the dipolar fluctuations.[43,44] As such, it is the first theory that accounts for fluctuations and for interactions with the substrate in 2D disordered systems.

For free-standing systems, the parallel and perpendicular renormalized polarizabilities satisfy uncoupled quadratic equations, whose coefficients depend on functionals of the two-particle distribution function. These equations become coupled when the presence of a substrate is incorporated through the induced image fields. To illustrate our formalism, we calculated the optical properties of metallic spheres over a dispersionless insulator and dispersionless molecules on a metal, choosing the simple hole-correction distribution function. We found resonances in the loss functions $\mathrm{Im}(\epsilon_x)$ and $\mathrm{Im}(-1/\epsilon_z)$ in the absorption and in the optical reflectance, and we identified the effects of disorder and image fields.

Our results show that the dipole-dipole interaction splits the surface-plasmon resonance of individual spheres, shifting the $\|$ mode towards lower and the $\perp$ mode towards higher frequencies. The mean-field theory (MFT) for a disordered system yields a larger splitting than that for a square array. Our RPT increases it further, and leads to a fluctuation-induced asymmetric broadening of both resonances, with a stronger effect on the $\|$ resonance. This broadening is, however, smaller than that predicted by the LG-CPA.[48] The inclusion of images shifts both peaks to lower frequencies. Furthermore, it increases the effects of disorder on the $\perp$ and decreases it on the $\|$ resonance. All of these results can be simply understood by examining the dipolar fields due to neighbors and images. When the substrate is conducting, a resonance appears in the differential reflectance spectrum, which is best observed at the Brewster angle of the overlayer. This feature is slightly broadened by disorder.

We also presented a comparison with one experiment.[38] However, 2D numerical simulations will constitute a better testing ground for the theory, due to the difficulties in sample preparation and in characterizing all the relevant parameters, such as the distribution functions, experimentally. Although we presented calculations for the simple hole-correction distribution function $\rho^{(2)}$, our results are sensitive to the choice of $\rho^{(2)}$. We remark that in two dimensions, this dependence is not only in our RPT but even within MFT, unlike the 3D case.[49]

The RPT can be extended to include size dispersion,[55] other particle shapes, and three-body distributions, as well as quadrupole and higher multipole interactions expected to be important for large densities.[52] It can also be derived within the context of multiple-dispersion theory.[53]

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APPENDIX

The coefficients of the coupled equations in Eq. (10) are given, in terms of $r=d/a$, by

$$f_{xx}=\tfrac{5}{4}f\int_0^{\infty}\rho^{(2)}(2ax)\left[\frac{1}{x^5}-2A\frac{x^2-\frac{1}{5}r^2}{x^2(x^2+r^2)^{5/2}}\right.$$

$$\left.+A^2\frac{x(x^4-\frac{2}{5}r^2x^2+\frac{2}{5}r^4}{(x^2+r^2)^5}\right]dx\ ,$$

$$f_{zz}=\tfrac{1}{2}f\int_0^{\infty}\rho^{(2)}(2ax)\left[\frac{1}{x^5}+2A\frac{x^2-2r^2}{x^2(x^2+r^2)^{5/2}}\right.$$

$$\left.+A^2\frac{x(x^4-4r^2x^2+4r^4)}{(x^2+r^2)^5}\right]dx\ ,$$

and

$$f_{xz}=-\tfrac{9}{16}fA^2\int_0^{\infty}\rho^{(2)}(2ax)\frac{r^2x^3}{(x^2+r^2)^5}dx\ .$$

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