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LATERAL INTERACTIONS IN SMALL PARTICLE SYSTEMS

B.N.J. Persson

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, U.S.A.

Résumé - Nous discutons, dans cet exposé, une théorie générale des propriétés optiques des systèmes de petites particules. Nous considérons d'abord les propriétés vibrationnelles de mélanges isotopiques de molécules en interaction dipolaire adsorbées selon une structure ordonnée sur une surface métallique. Les propriétés de ce système sont calculées en utilisant l'approximation du potentiel cohérent (APC). Ensuite, nous analysons les propriétés optiques de systèmes de petites particules métalliques à deux et trois dimensions. Un modèle de gaz de réseau est utilisé pour simuler une distribution quasi aléatoire de particules et l'APC est appliquée à l'obtention d'une solution au problème du désordre. Pour tous les systèmes étudiés le désordre introduit, dans le spectre d'absorption, une structure caractéristique qui est en bon accord avec l'expérience.

Abstract - In this review I will discuss a general theory for the optical properties of small particle systems. I first consider the vibrational properties of isotopic mixtures of dipole interacting molecules adsorbed in an ordered structure on a metal surface. The properties of this system are calculated using the coherent potential approximation (CPA). Next I discuss the optical properties of two and three dimensional systems of small metallic particles. A lattice gas model is used to simulate nearly randomly distributed particles and the CPA is applied to obtain a solution of the disorder problem. For all studied systems the disorder introduces characteristic structure in the absorption spectra which compares favourably with experiments.

I COLLECTIVE VIBRATIONAL MODES IN OVERLAYERS

The lateral interaction between adsorbed molecules is of great importance in describing the static and dynamic properties of adsorbed layers. With the use of isotopic mixtures of varying composition at a constant coverage it is possible to study the effect of dynamical interaction while the static interaction is kept constant. In this way it has been determined that the main vibrational coupling between the CO molecules in the c(2x2) overlayer of CO on Cu(100) is due to the dipole-dipole interaction¹. For H in the p(1x1) structure on Pd(100) the dipole-dipole coupling gives a negligible contribution and the relevant coupling seems instead to be an indirect coupling mediated by the metal conduction electrons.³ These conclusions have been derived from studies of how the frequencies and intensities of various vibrational modes depend on the composition of isotopic mixtures.

I will not present any extensive discussion of lateral interactions in overlayers here but merely refer the reader to the original works^{1,2} and also to a recent review⁴. I will discuss, however, how the disorder occurring in an isotopic mixture can be accounted for by use of the Coherent Potential Approximation (CPA) and I will compare theoretical results with experiment in order to illustrate how accurate the CPA is in the present context.

Consider a substitutionally disordered overlayer. That is, assume that two types of molecules, denoted by A and B, are randomly distributed over the lattice sites of a two-dimensional Bravais lattice. In an external electric field (which, at infrared frequencies, is normal to the metal surface) a dipole moment p_i will be induced in particle i:

$$p_i = \alpha_i (E(\vec{x}_i) - \sum_{j \neq i} U(\vec{x}_i - \vec{x}_j) \cdot \vec{p}_j) \quad (1)$$

where $-U(\vec{x}_i - \vec{x}_j) \vec{p}_j$ is the dipole field at particle i from particle j plus its image in the metal. If all the molecules were identical, then (1) is trivially solved by plane waves owing to the translational invariance. However, for an isotopic mixture, $\alpha_i = \alpha_A$ or $\alpha_i = \alpha_B$ depending on if a molecule of type A or B occupies lattice site i. Eq. (1) can now only be solved approximately. A good approximate solution is obtained with the so-called coherent potential approximation (CPA). The basic picture behind the CPA is appealing and simple and I will present a short discussion of it here⁵.

Fig. 1

Figure 1a shows a possible configuration of a substitutionally disordered monolayer with two types of molecules A and B. Physical quantities of interest, such as the polarizability of the monolayer, are not those of a particular configuration, but those averaged over the ensemble of possible configurations. Therefore this ensemble is replaced by a system schematically drawn in Fig. 1b, i.e., a periodic system with the same "ensemble average" polarizability α at each site. According to the CPA, α is determined in a self-consistent way by the following procedure: Assume that each site except for the origin is occupied by the "average" molecule and the origin by molecule A or B, as shown in Fig. 2. Then we calculate the induced dipole moment (due to a given external electric field)

Fig. 2

of the molecule at the origin, denoted by p_A or p_B . Finally we calculate the induced dipole moment p of the molecule at the origin when this is occupied by an "average" molecule. α is then obtained from

$$c_A p_A + c_B p_B = p, \quad (2)$$

where c_a is the concentration of molecules A and c_B of molecules B ($c_A + c_B = 1$). Later, in connection with small metallic particles, I will discuss the nature of the "average" polarizability α .

Hollins and Pritchard¹ have performed infrared reflection spectroscopy (IRS) measurements on ordered $^{12}\text{C}^{16}\text{O}$ - $^{13}\text{C}^{16}\text{O}$ layers on Cu(111) at a coverage $\theta = 1/3$. Figure 3 shows the center frequency and the heights of the absorption peaks (associated with the C - O stretch vibration). The solid lines are the theoretical results obtained from the CPA theory.

Fig. 3

Fig. 4

Ryberg² has performed IRS measurements on ordered $^{12}\text{C}^{16}\text{O}$ - $^{12}\text{C}^{18}\text{O}$ layers on Cu(100) at a coverage $\theta = 0.5$. Figure 4 shows the center frequency and the heights of the absorption peaks as a function of composition. The solid lines are the theoretical results obtained from the CPA theory. Obviously, there is a good agreement between theory and experiment, and the CPA seems to be an excellent approximation in the present context.

II SYSTEMS OF RANDOMLY DISTRIBUTED PARTICLES

A Introduction

The optical properties of small metallic particle systems have attracted considerable interest during the last few years for several reasons. First, in the search of an effective coating for solar energy absorbers, a promising group of materials has been found that consist of small metallic particles embedded in a dielectric host⁶. Second, it was discovered in 1974 that Raman scattering from molecules adsorbed on small silver particles is greatly enhanced⁷.

Consider a system of small metallic particles. In an external electric field the particles will be polarized, i.e., the external field induces dipoles (and also higher multipoles). Within the dipole-approximation the equation determining the dipole moment $\vec{p}_i$ induced in particle i at $\vec{x}_i$ is

$$\vec{p}_i = \vec{\alpha}_i \cdot (\vec{E}_{\perp}(\vec{x}_i) - \sum_{j \neq i} \vec{U}(\vec{x}_i - \vec{x}_j) \cdot \vec{p}_j) \quad (3)$$

where $\vec{E}_{\perp}$ is the transverse part of the total electric field $\vec{E}$. This equation together with Maxwell's equations are the basic equations. In what follows, I will show how Eq. (3) can be solved approximately for two and three dimensional systems of randomly distributed particles.

B Two - Dimensional Particle Systems

Consider a square lattice (lattice constant a) and assume that all the lattice sites are occupied by identical particles with polarizability

$$\alpha(\omega) = \frac{\alpha_0}{1 - \frac{\omega(\omega + i\Gamma)}{\Omega^2}}$$

Thus each particle behaves as an isotropic harmonic oscillator with resonance frequency $\Omega (= \omega_p/\sqrt{3}$ for a Drude particle) and damping constant Γ . Due to the dipole-dipole coupling between the particles, the system will have collective polarization modes which, owing to the periodicity of the system, are easily obtained from Eq. (3). In the long wavelength limit ($qa \ll 1$) there will be two different eigenmodes with frequencies $\Omega_{\parallel}$ and $\Omega_{\perp}$ corresponding to charge oscillations parallel and normal to the plane of particles, respectively. One finds that $\Omega_{\parallel} < \Omega$ and $\Omega_{\perp} > \Omega$ while both modes have the same damping constant Γ as an isolated particle. It is very easy to understand why the $\perp$ -mode is blue-shifted and the $\parallel$ -mode is red-shifted, see Fig. 5.

Fig. 5 - For the $\perp$ mode the electric field at particle 0 from all the surrounding particles (e.g., particle 1 and 2) will be of opposite direction to the dipole $\vec{p}$ and this leads to a blue shift $\Omega_{\perp} > \Omega$. For the $\parallel$ mode particles 1 and 2 will again give a contribution of opposite direction but particles 3 and 4 will give a contribution which is in the same direction as $\vec{p}$ and since the strength of the latter fields is double that from particles 1 and 2, the net field will have the same direction as $\vec{p}$, leading to a red shift $\Omega_{\parallel} < \Omega$.

If a p-polarized electromagnetic wave is incident upon the particle system the absorption spectra will be as shown in Fig. 6.

Fig. 6

The two absorption peaks correspond to excitation of the $\parallel$ and $\perp$ modes (note: an s-polarized incident wave can only excite the $\parallel$ -mode) and both peaks have the same full width at half maximum Γ .

The discussion above is for an ordered system of particles but it is important to understand the optical properties of this system before treating the case of randomly distributed particles as will be done now⁸. Consider a square lattice with lattice constant $a=2R$. We distribute spherical particles of radius R (denoted by A) randomly on the lattice points until a fraction c of the lattice sites are occupied. This generates almost a random distribution of particles with the constrain that the particles do not penetrate each other. We can calculate the optical properties of this system using the CPA by introducing an effective particle (polarizability $\vec{\alpha}$) at each lattice site. α is determined by an equation analagous to Eq. (2) but with $p_B = 0$

$$c\vec{p}_A = \vec{p} \quad (4)$$

Equation (4) gives an integral equation for $\vec{\alpha}(\omega)$ which can be solved by iteration. The analytical structure of the resulting $\vec{\alpha}(\omega)$ is quite different from that of $\alpha_A(\omega)$. $\alpha_A(\omega)$ has only poles at $\omega \approx \pm\Omega - i\Gamma/2$ but $\vec{\alpha}(\omega)$ has two branch lines located below the real ω -axis. These branch lines (which can be considered as an infinite sequence of closely-spaced poles) is a mathematical manifestation of disorder induced broadening. I note also that even if the original particles have isotropic polarizability $\vec{\alpha}_A(\omega) = \mathbf{1}\alpha_A(\omega)$, the "average" particles have only one axis of symmetry (namely the z-axis). Thus, disorder affects the $\parallel$ - and $\perp$ -modes differently.

Let me now present some numerical results to illustrate the consequence of disorder⁸. Figure 7 shows the absorbance (decomposed into $A_{\parallel}$ and $A_{\perp}$, the absorbance by the $\parallel$ - and $\perp$ - modes, respectively) for a system of Drude particles with $\hbar\Omega = 4\text{eV}$, $R = 50\text{\AA}$, $\hbar\Gamma = 0.158\text{eV}$ and occupying a fraction $c=0.3$ of the lattice sites.

Fig. 7

The dashed line in Fig. 7 shows the imaginary part of the absorbance of the particle system when the dipole-dipole coupling between the particles has artificially been put equal to zero. This curve is, of course, a Lorentzian centered at $\hbar\Omega = 4\text{eV}$ and with a full width at half maximum $\text{FWHM} = \Gamma$. As a result of the interaction between the particles, the $\parallel$ -mode is red-shifted while the $\perp$ -mode is blue-shifted, just as for the ordered particle system studied above. The shape and width of $A_{\parallel}$ and $A_{\perp}$ are, however, strongly influenced by disorder. For the ordered structure these functions are both Lorentzian with the same $\text{FWHM} = \Gamma$. As Fig. 7 shows, disorder gives rise to asymmetrical peaks, $A_{\perp}$ having a tail towards lower frequencies and $A_{\parallel}$ towards higher frequencies. Moreover, both peaks are broadened, the $\parallel$ -peak being much broader than the $\perp$ -peak. This remarkable result will be discussed further below.

Fig. 8

Figure 8 shows the variation of the width with concentration c . The broadening is seen to be largest for relatively small values of c . The average distance between neighboring particles in this range is typically three to six times larger than the particle radius. Thus, multipole interactions which are not included in the present calculations and which are known to be important at small inter-particle spacing have negligible effect on the spectra shown in Fig. 7.

Fig. 9

Figure 9 shows an experimental absorption spectrum obtained by Yamaguchi et al. for small silver particles located on the surface of a film of polyvinyl alcohol⁹. The theoretical results presented above are obtained for a two-dimensional system of Drude particles located in vacuum and therefore cannot be quantitatively compared with these experimental data. For example, the "image" dipoles induced in the substance will affect the dipole interaction between the silver particles and the "self-image interaction" will cause a red-shift of both the $\parallel$ - and $\perp$ -absorption peaks⁹. Interband transitions will also modify the absorption profile at frequencies $\hbar\omega \gtrsim 3.5\text{eV}$. Nevertheless, the basic disorder-induced

structure predicted by the theoretical calculations is clearly visible in the experimental spectra:

- (i) The $\perp$ -peak has a tail towards lower ω and the $\parallel$ -peak towards higher ω
- (ii) The $\parallel$ -peak is much broader than the $\perp$ -peak.

We close this section with a simple discussion of why the $\parallel$ -peak is much broader than the $\perp$ -peak. In a random distribution of particles there will be particle clusters of various sizes and shapes. Each cluster will have different resonance frequency owing to the dipole-dipole coupling between the particles. Thus there will be a distribution of absorption peaks which for an infinite system merge into a continuous absorption band. Consider now the simplest possible clusters consisting of two particles separated by a fixed distance ℓ . For the $\perp$ mode all such clusters will have exactly the same resonance frequency. This is not the case for the $\parallel$ -mode. Consider for example the two clusters pictured in Fig. 10.

Fig. 10

The contribution to the local electric field at particle a from particle b is $2\vec{p}/\ell^3$ for cluster (a) but $-\vec{p}/\ell^3$ for cluster (b). Thus these clusters will have rather different resonance frequencies $\Omega(1 - 2(R/\ell)^3)^{-1/2}$ and $\Omega(1 + (R/\ell)^3)^{-1/2}$ respectively). Similar differences exist in larger clusters so that, as a result, the distribution of resonance frequencies will be much broader for all $\parallel$ -mode than for the $\perp$ -mode.

C Three – Dimensional Systems

Almost all interpretations of the optical properties of three-dimensional systems of small particles is based on a model proposed by Maxwell-Garnett (MG) in 1904. However, the MG-model is strictly valid only for particles forming a cubic lattice. The reason is that the MG-model is based on the Clausius-Mosotti relation which only holds for cubic lattices, see Fig. 11.

Fig. 11. - (a) In deriving the Clausius-Mosotti formula one utilizes that the sum of the dipole fields from all the particles within a spherical region centered at one of the particles adds up to zero at the origin; (b) In a random distribution of particles the sum of dipole fields from the particles within a sphere is in general nonzero. It is true that on the average it will vanish but one must calculate the dielectric function before performing the ensemble average. It is only in this way one will account for fluctuations in the local electric field owing to the different local particle arrangements occurring in a random particle distribution.

The optical properties of a three-dimensional system of randomly distributed particles¹⁰ can be accurately treated using a three-dimensional version of the lattice gas model described in Sec. IIB. That is, assume that spherical particles with radius R are distributed among the lattice sites of a simple cubic lattice (lattice constant $a=2R$) until a fraction c of the lattice sites are occupied. This generates an almost random distribution of particles with the constrain that the particles do not penetrate into each other. As in the two-dimensional case, one can apply the CPA to obtain an accurate solution of the disorder problem. Here I will only present the result of a few numerical calculations¹⁰ and compare them with the predictions of the MG-model as well as with experiments.

Fig. 12

Fig. 13

The solid curves in figure 12 show the imaginary part of the (long wavelength, i.e., $q=0$) dielectric function $\epsilon(\omega)$ for a system of Drude particles ($\hbar\omega_p = 9.2\text{eV}$, $\Gamma = 0.2\text{eV}$) in a continuous dielectric host (water). Results are presented for three different filling factors, namely, $f=0.1, 0.2$ and 0.3 (the filling factor is the ratio between the particle volume to the total volume). The calculation is based on particles randomly distributed on a face-centered cubic (fcc) lattice. The dotted curve in Fig. 12 is the prediction by the MG-model, i.e., $(\text{Im}\epsilon)_{\text{MG}}$ is a Lorentzian with full width at half maximum Γ . Compared with the MG-result, the Lattice gas model predicts a strongly broadened, red-shifted and assymmetric peak. The variation of the broadening and red-shift with the filling factor is shown in greater detail in Fig. 13 where results are presented for a fcc-lattice as well as for a sc-lattice. Calculations have also been performed for a bcc-lattice which gives results similar to a fcc-lattice.¹⁴

Fig. 14

Figure 14 compares the theory with experimental data obtained by Kreibig¹¹ for small silver particles in gelatin. Note that the lattice gas model gives much better agreement between theory and experiment than the oversimplified MG-model. In particular the width as a function of the filling factor is well described by the lattice gas model - see the inset.

III CONCLUSION

The formalism presented in this paper can be applied to gain insight into the optical properties of many interesting and important small particle systems, including

- Spectroscopy of atoms and molecules adsorbed on surfaces²;
- Photosynthesis: The energy transport from the antenna chlorophyls to the active centers^{2,12};
- Optical properties of rough metal surfaces: Many rough metal surfaces can be considered as consisting of a flat surface covered with randomly distributed small bumps of various sizes and shapes¹³. The formalism in Sec. 3 is well suited to treat the optical properties of such surfaces.
- Optical properties of inhomogeneous materials¹⁰;
- Surface-enhanced Raman scattering (SERS)^{7,8}.

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