

COMPARING OF THE VAN-DER-WAALS ENERGY OF THE FULLERENE IN SOLIDS AND IN SOLUTIONS: DIELECTRIC FUNCTION FORMALISM

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The dielectric function approach was used to evaluate the van-der-Waals energy of C_{60} cluster interaction in different systems through the calculation of the change of the collective mode energy. Within the same approach the analytic expression for the attraction in the fullerene solid, in the fullerene dimer, in a solution, in a compound material is obtained. The correct mean field result for the plasmon frequency of C_{60} cluster in the insulating uniform medium is presented.

After last six year efforts which are manifested by hundreds of papers on the physics, chemistry of the fullerenes and the fullerene based materials it is known a lot about the electronic structure of the single macromolecule which is the base of the different materials like the doped solids and the chemical adducts. A variety of the computational methods, from *ab initio* calculation to an empirical approach, was used to compute the energy of the inter-cluster interaction in the fullerene solid. The review of the calculation and experiment will be presented elsewhere¹ (some references are in²).

The dielectric function formalism is a simple theoretical approach allowing to evaluate the energy of the van-der-Waals interaction in the fullerene condensed phase. The same approach was used for the evaluation of the interaction of the single cluster with the surface of different solids in³. The method allows us to calculate van-der-Waals energy of the fullerene cluster dissolved in the organic (non-polar) dielectric liquid⁴. It is worth to note that the result used before for the cluster in the medium⁵ does not work for the fullerene. Within the dielectric function approximation (DFA) the correct analytical expression of the van-der-Waals energy in the liquid insulator is dealt with below. This consideration is very similar in the spirit to the fullerene dimer plasmon energy calculation⁶. The energy of the dimer-fullerene-cluster formation due to the dipole-dipole van-der-Waals interaction is given.

It is known that fullerene forms solid solutions (or the clathrate crystals) with some solvents. We showed that the analytic expression can be obtained for the case of the "guest-host" lattice in frame of the same DFA.

We described the solid fullerene within the DFA in the simplest one-pole-approximation which is correct in the high frequency region^{7b}.

The van-der-Waals energy is given by the shift of the zero-oscillation energy of the

collective mode in the solid comparing with the single cluster. The main part of this interaction is determined by the plasma modes of the solid. We found⁷ that the quantum-mechanical model as well as the classical hydrodynamic approach gives the C_{60} collective mode frequency. The plasmon contribution into the dielectric function of the fullerene solid is the strong and wide dipole collective peak which was observed experimentally in electron energy losses. Thus, we will consider the fullerene solid as the lattice of the dipoles oscillating at the plasma frequency.

1. THE ENERGY OF THE VAN-DER-WAALS INTERACTION

As usual the van-der-Waals energy is the difference between the zero-oscillation energy of the plasmon in the solid and the same one in the single cluster. This shift is due to the Coulomb interaction between clusters. The origin of the van-der-Waals forces is the same as the depolarization shift of the plasma mode frequency in the dielectric medium.

In the case of the cubic crystal and for the rotationally invariant system (liquid, for example) one can easily calculate this depolarization shift following the method of the mean field. The Lorentz-Lorenz approximation gives the dielectric function including the local field effects. The collective mode frequencies results from this function. The approach is valid for the solid fullerene, which fortunately forms face-centred cubic lattice.

We calculated the mode frequencies for the face centred cubic cell with C_{60} four clusters in the approximation of the dipole-dipole interaction. It was shown that the higher multipolar interaction terms can be neglected⁶. However, it is not the restriction because of the DFA allows to include any multipole correction if one needs more accuracy.

It was shown that C_{60} electron system has the collective mode with the frequency about 25 eV. This is the surface plasmon on the fullerene sphere. It can be described phenomenologically as well as within more sophisticated quantum-mechanical approach (see⁷ and references [10-14] in Ref.^{7b}). So far, it is the dipole plasmon which we will use as the elementary excitation of the fullerene "super-atom" unit.

In other terms, the van-der-Waals interaction can be written using the fluctuation-dissipation theorem as the integral over the frequency of the combination of the C_{60} cluster dynamic polarizability and the dielectric function of the medium. Of course, in the case of the pure C_{60} crystal it is the same function as the polarizability. Then this integral can be evaluated in the complex plane of the frequency. The main contribution comes from the excitation having the maximal oscillator strength. It is the dipole collective plasma mode of the cluster.

Let us remind that the frequency of the dipole plasmon can be found as the hollow metal sphere plasmon frequency:

$$\omega_1 = \omega_p \sqrt{\frac{2}{3}} \simeq 22 \text{ eV}; \quad \omega_p = \sqrt{\frac{240 e^2}{mR^3}} \simeq 26.9 \text{ eV}, \quad (1)$$

here ω_1 is the bare plasma frequency, 240 is the number of valence electrons with the electron mass m and the charge e . The sphere radius R is taken $\simeq 3.3 \text{ \AA}$ to describe the fullerene plasmon properly. The details of the calculation can be found in⁷. The dynamic polarizability of the single cluster, α is given by expression:

$$\alpha(\omega) = R^3 \frac{1}{1 - \omega^2/\omega_1^2}, \quad (2)$$

A packing factor coming into the dielectric function along with the dynamic polarizability reads as:

$$\eta = 4\pi\nu\alpha(0) = 4\pi \frac{4}{d^3} R^3 \quad (3)$$

where $\nu = 4/d^3$ is the density of the clusters, $d \simeq 14.2 \text{ \AA}$ is the lattice constant. The multiplier R^3 gives the characteristic volume scale of the problem. It coincides with the static polarizability $\alpha(0) = R^3$. The parameter η is approximately taken as 0.79. It will be very convenient to use the square of dimensionless plasma frequency as the frequency variable below:

$$x = \omega^2/\omega_1^2. \quad (4)$$

Then the dielectric function in the Lorentz-Lorenz approximation (the mean field) and in neglecting of all terms besides the plasmon pole at ω_1 reads as:

$$\epsilon(\omega) = 1 + \frac{4\pi\nu\alpha(\omega)}{1 - 1/3} = 1 + \frac{\eta/(1-x)}{1 - 1/3} = \frac{1 + 2/3 \eta - x}{1 - 1/3 \eta - x}. \quad (5)$$

Let use the notation:

$$x_L = 1 + \frac{2}{3}\eta, \quad x_T = 1 - \frac{1}{3}\eta \quad (6)$$

for the zero and the pole of the dielectric function $\epsilon(\omega)$. Thus, the Lorentz-Lorenz formula gives the plasma longitudinal frequency $\omega_L = \omega_1\sqrt{x_L} \simeq 26.2 \text{ eV}$ along with the transverse excitation frequency $\omega_T = \omega_1\sqrt{x_T} \simeq 19.6 \text{ eV}$. Then the van-der-Waals energy is the simple difference between the plasma frequency of the cluster and the modes in the solid. It reads as:

$$W = \frac{1}{2}\hbar\omega_1 (\sqrt{x_L} + 2\sqrt{x_T} - 3) \simeq -\hbar\omega_1 \frac{\eta^2}{24} \quad (7)$$

We stress that the only two parameters, determining the van-der-Waals energy, are the plasmon energy and the packing factor. In the expression above we used the expansion on the small parameter η in order to emphasise that the van-der-Waals interaction is the second order process, hence, it includes η^2 and has the negative sign. The interplay between the parameters ω_1, η gives us, for example, the plasma frequency on the boundary between some mediums⁸, in the liquid [6], in the medium

with polarizable dopant and so on. We will discuss it at length elsewhere. Substituting the numbers into Eq.(7) one gets the van-der-Waals energy about -0.36 eV per cluster in the solid. The one of the first papers containing similar consideration to be mentioned is⁹. In the next section we will compare the result with the energy in the uniform insulating medium.

2. FULLERENE IN LIQUID MEDIUM

The C_{60} plasma frequency in the solution is different from the solid phase. It is because of the depolarization shift is much weaker in a typical organic solvent than in the solid. What is the reason? The fullerene cluster has the very high frequency of the bare plasmon (collective mode of the single cluster) due to the large number of the highly polarizable electrons. The standard medium is nearly transparent at this frequency. More precisely the dielectric function of the medium is only slightly less than the unity at the frequency of C_{60} plasmon. It means in turn that the depolarization resulting from the medium is negative. Such a value of the dielectric function is not very common. In earlier papers the depolarization shift of the plasmon of the C_{60} cluster in the dielectric liquid has been calculated improperly.

In⁵ the dielectric function has not been considered, in contrary, the static permittivity has been used for the liquid surrounding the cluster. Then the boundary conditions change so that the plasma frequency linearly depends on the permittivity of the solvent. Then the difference in the plasma frequency according to the model of Barton and Eberlein reads as follows:

$$\delta\omega_1 \simeq \frac{1}{3}(1 - \epsilon), \quad (8)$$

here we expanded the expression Eq.(8) on the small positive parameter $0 < 1 - \epsilon \ll 1$. Usually, the static permittivity is larger than unity, thus the plasma frequency gets the negative gain and the van-der-Waals energy in the solutions is negative. Unfortunately it is not the case if one considers the fullerene. The dielectric function in Eq.(8) has to be taken at the plasma frequency of C_{60} . It is seen from Eq.(8) that then the plasmon frequency shifts upward, that does not consist with the solubility of the fullerene. The energy gain seems to be naturally negative. In order to save the situation we note that $\epsilon = \epsilon(x)$ is the function of the frequency by itself that was omitted in⁵.

Let us calculate the motion of the collective mode driven by the acting electrical potential: $\varphi^{\text{act}} = \varphi^{\text{ext}} + \varphi^{\text{ind}} = \varphi_{LM}^{\text{ext}} + 4\pi R\sigma_{LM}/(2L + 1) + \varphi_{LM}^{\text{sol}}$, consisting from 3 parts – the external potential, the potential induced on the considered C_{60} cluster and the potential induced in the medium (*e.g.* in solvent). According⁷, the surface plasmon in C_{60} is the spherical oscillation of electron density σ_{LM} . For central symmetry of the cluster we use expansion of all quantities in complete spherical harmonics $P_L(r)Y_{L,M}(\Omega)$ those form a complete set on a sphere. In spherical geometry a radial jump in electric field on the surface of the fullerene sphere is given by:

$$\frac{2L+1}{R} \varphi_{LM}^{\text{ind}} = 4\pi\sigma_{LM} \quad (9)$$

where L, M are multipole power indexes (or angular momentum and its projection onto z-axis). The selfconsistency of the calculation is proved by this acting potential including the induced potential of the C_{60} plasmon as well as the potential due to charge density induced in the solvent. We close the equation system by writing the motion equation for the fullerene plasmon as:

$$\frac{4\pi R}{2L+1} \sigma_{LM} = -\frac{4\pi R}{2L+1} \chi_L(\omega) \varphi_{LM}^{\text{act}} \simeq -\frac{\omega^2}{\omega^2}, \quad (10)$$

where χ is a response function of single sphere. This expression is easily obtained from classic charge liquid equations⁷. The mentioned above one-pole-approximation follows from the last approximate equality for $\chi(\omega)$. The consideration is more general than the below considered case of the dipole plasmon mode $L = 1$. However, for the spherical symmetry the expression Eq.(10) holds for any multipole.

When the potential induced in the solvent is absent in Eq.(10), $\varphi_{LM}^{\text{sol}} = 0$, we return to the bare plasmon frequency – the plasmon of the single fullerene cluster. The corresponding bare dispersion equation reads as:

$$-\frac{4\pi R}{3} \chi_1 = \frac{\omega_1^2}{\omega^2} = \frac{1}{x} = 1, \quad (11)$$

It is easy to convince yourself that in the medium one simply changes the unity in the right part of expression to the dielectric function which is including the solvent potential. It is seen from the substituting of the Eq.(10) into Eq.(9) and the taking the standard RPA sum. As a result the plasma frequency in the solution is:

$$\Omega(\varepsilon) = \omega_1 \sqrt{\varepsilon(\Omega)} \quad (12)$$

The frequency is smaller than for the bare C_{60} that corrects the result from⁵ Eq.(8). We will use for the dielectric function of the liquid solvent the common formula:

$$\varepsilon(\Omega) = \frac{\Omega^2 - \omega_L^2}{\Omega^2 - \omega_T^2} \quad (13)$$

where ω_L is the typical longitudinal frequency of $\varepsilon(\Omega)$, and ω_T is the transverse frequency. With this definition the van-der-Waals energy can be written as:

$$W \simeq -3/2\hbar\omega_1 \frac{\omega_L^2 - \omega_T^2}{\omega_T^2} \frac{\omega_T^2}{\omega_1^2} = -3/2\hbar\omega_1 (\varepsilon_0 - 1) \left(\frac{\omega_T}{\omega_1}\right)^2 \quad (14)$$

here ε_0 is the static permittivity which is related to the transverse and longitudinal frequencies. The typical values for ε_0 is 2.3 for the benzene, 2.4 for the toluene. The van-der-Waals energy is about -0.2 eV for these solvents. So far we compared the plasmon energy of C_{60} in the fullerene solid and in the solution and have to

conclude that by this energetic reason the solid fullerene should be more stable. This discussion is intriguing because the naive thermodynamic evaluation of the entropy of the fullerene solvating does not provide the needed gain in the free energy.

We suppose that solvent softens the van-der-Waals forces between C_{60} clusters near the surface. Certainly, the process has to be recalculated more accurately, including the conditions on the boundary between the fullerene solid and the solvent. That is the simplest speculation about the solvating process. Then the fullerenes may form dimers near the surface. We believe that these selforganized structures, probably, can be found in the solution.

Let us consider the fullerene dimer, the similar problem was done in⁶ for the C_{119} molecule. The plasmon frequency is splitted in the axial field. Therefore, the new modes bring the energy of the interaction between clusters in the dimer as the difference between the frequency of the bare plasmon and new one. The van-der-Waals energy of the dimer coupling reads as:

$$W \simeq -3/2\hbar\omega_1 \left(\frac{R}{H}\right)^3 \left(1 + \frac{3}{2} \frac{\omega_L^2 - \omega_T^2}{\omega_T^2} \frac{\omega_T^2}{\omega_1^2} + \dots\right) \quad (15)$$

where $R \simeq 3.3 \text{ \AA}$ and $H \simeq 8 \text{ \AA}$ are the cluster radius and the inter-cluster distance; here the last term comes from the solvent depolarization, it is a small correction (about a percent) which will be neglected. The typical value of the van-der-Waals energy of such a dimer is about -0.7 eV. It supports the hint about the possibility of the dimer formation.

3. GUEST-HOST MEDIUM

In this section we will give a short introduction into the dielectric function approach applied to the problem of the plasma modes in two-component solid. The same consideration can be carried out in the case of the solid and "hard"-liquid solution which preserves the internal structure of the mixture.

The theory of the plasmon in the clustered material, such as the fullerene solid, the cluster containing matrix and so on, is very similar to the well known theory of the molecular insulator (see for example textbooks^{10,11}). The similarity the more pronounced the more fullerene cluster behaving like the "super-atom". It has the definite dipole transitions into the plasmon states. The dipole excitation is transmitted over the whole crystal because of the localized state (the single cluster plasmon) is not the eigen-state of the Hamiltonian. The resulting plasmon-Frenkel-exciton¹² spreads. Neglecting the spatial dispersion effect we return to the Lorentz-Lorenz modes.

For the solid solution of the fullerene clusters in some matrix we will use the dielectric function in the following form:

$$\epsilon = 1 + \frac{4\pi\nu\sum_i\alpha_i}{1 - \frac{4\pi}{3}\nu\sum_i\alpha_i} \quad (16)$$

where the sum runs over all components of the solution and the density ν is not supposed to vary in the space (that is the "hard" solution condition). Thus, for example, for binary compound, if the density will be chosen as the inverse volume of the elementary cell then the sum can be taken over all molecules within the cell. Let consider the imaginary compound C_{60}/D , which we suppose to have one molecule of the substance D per fullerene cluster. In order to evaluate the substance D molecule polarizability let consider the dielectric function of this substance in solid. Suppose, for definiteness sake, the substance has cubic lattice, therefore its dielectric function reads as:

$$\epsilon_D = \frac{x - x_{LD}}{x - x_{TD}} \quad (17)$$

where the dimensionless longitudinal and transverse frequencies of the pure D material in the high frequency region, which are given in units of the fullerene plasma frequency according to the definition Eq.(4), are supposed to be known. The Mossotti formula, which is nothing more the Lorentz-Lorenz expression rewritten, gives the dynamic polarizability of D as follows:

$$\alpha_D = \frac{3}{4\pi\nu_D} \frac{\epsilon_D - 1}{\epsilon_D + 2} = \frac{1}{4\pi\nu} \frac{\eta_D}{x_D - x} \quad (18)$$

here ν_D is the density of the pure substance D . Here we rewrite the polarizability in the form similar to Eq.(2) and use the constants $\eta_D = (x_{LD} - x_{TD})\nu/\nu_D \ll 1$ and $x_D = \frac{1}{3}x_{LD} + \frac{2}{3}x_{TD} < x_{LD} < 1$. The first parameter, η_D , is small because of the density of the fullerene has to be smaller (due to the larger lattice constant); and the longitudinal-transverse splitting $x_{LD} - x_{TD} = x_{TD}(\epsilon_D(0) - 1)$ is smaller than the longitudinal frequency along, which in turn has to be smaller than unity, $x_{LD} < 1$ (due to the very high plasma frequency of the fullerene cluster). The second parameter, x_D , is the characteristic frequency of the dipole transition in single D molecule. Usually, the dielectric function is constructed on the base of the quantum-chemical calculation of this frequency.

Substituting Eq.(2) and Eq.(18) into Eq.(16) we get the dielectric function of the compound solid solution. Its zeros and poles gives the frequencies of the eigen modes in this solid. The van-der-Waals energy is one half of the difference between these new mode frequencies and the plasma frequencies in the bare molecules. Using the small parameter defined above we found the following expression:

$$W \simeq -W_D - \frac{\eta}{2(1 - \eta/3)(1 + 2\eta/3)} \frac{\nu}{\nu_D} \frac{x_{LD} - x_{TD}}{\sqrt{3(x_{LD} + 2x_{TD})}} \quad (19)$$

here we neglected the terms of order x_D comparing with unity supposing that the plasma mode frequency in the fullerene cluster is much larger than the frequency of the molecule D . The van-der-Waals energy of the pure D substance is extracted from Eq.(19) : $W_D = \frac{1}{2}\hbar\omega_D (\sqrt{x_{LD}D} + 2\sqrt{x_{TD}D} - 3)$.

The last fraction in Eq.(19) is small because of the longitudinal-transverse splitting of D is to be much less than ω_1 . The cohesion energy of the material increases with the decrease of ν_D , the substance D density. The C_{60} is not too dense, therefore, the corresponding fraction in the expression has to be about 0.1. The first fraction is about unity.

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