

## SELFORGANIZATION OF FULLERENE CLUSTERS

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The paper introduces a plasmon-Frenkel-exciton model [1] for fullerene solids and explains a possible reason for the formation of van-der-Waals  $C_{60}$  cluster complexes. The interaction of the cluster and an organic (non-polar) liquid solvent will be considered. The motivation of this interest is related also to experiments on the photoclusterization in the water solution [2] and cluster formation in beams [3].

### ENERGY OF VAN-DER-WAALS INTERACTION

Typically van-der-Waals energy is given by shift of plasmon zero-oscillation energy in a solid comparing with a single cluster. This shift is due to Coulomb interaction between clusters. The origin of the van-der-Waals forces is the same as the origin of depolarization shift of dipole frequency in a dielectric medium. One can easily calculate this depolarization shift following the method of the mean field for the case of cubic crystal and for rotationally invariant system (liquid, for example). That is valid for fullerene condensed matter, which forms fortunately face-centered cubic lattice with four clusters in a cell.

Let us calculate the mode frequencies taking into account a dipole-dipole interaction. It was shown that higher multipole interaction terms can be neglected [4,5].

The dipole excitation of a single cluster is a basic unit in our consideration. An electron density of  $C_{60}$  is known to possess a collective mode with the frequency about 25 eV. This is a surface plasmon on the fullerene sphere. It was obtained within phenomenological model [6] as well as within more sophisticated approach (see [7-10]). We will use the dipole plasmon as an elementary excitation of the fullerene "super-atom" unit.

The van-der-Waals interaction force can be written using the fluctuation-dissipation theorem as an integral over the frequency of the combination of dynamic polarizability of the  $C_{60}$  cluster and dielectric function of the medium. Then this integral can be evaluated in the complex plane of the frequency. The collective plasma mode of the cluster, having the maximal frequency between dipole excitations, makes the main contribution as an excitation having the maximal oscillator strength.

Let us remind that the frequency of the dipole collective mode of  $C_{60}$  coincides with the plasmon frequency of a hollow metal sphere [11]:

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

here  $\omega_1$  is the dipole mode frequency,  $\omega_p$  is the plasma frequency, 240 is the number of valence electrons of the cluster,  $m$  and  $e$  are electron mass and charge. The sphere radius  $R$  is taken  $\sim 3.3 \text{ \AA}$  to describe the fullerene plasmon properly. Considering the fullerene solid we use the Lorentz-Lorenz approximation basing on a high polarizability of the single cluster,  $\alpha$ , which reads as:

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

We took  $\alpha(0) \simeq R^3$  which is valid with a high accuracy [12]. A packing factor, coming into the dielectric function along with the dynamic polarizability, is as follows:

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

where  $\nu = 4/d^3$  is the density of the clusters,  $d \simeq 14.2 \text{ \AA}$  is the lattice constant. This results in  $\eta \simeq 0.79$ . The square of dimensionless plasma frequency is conveniently used as a dynamic variable:

$$x = \omega^2/\omega_1^2.$$

Then the Lorentz-Lorenz formula gives the high frequency limit of the dielectric function:

$$\epsilon(\omega) = \frac{1 + 2\eta/3(1-x)}{1 - \eta/3(1-x)} = \frac{1 + 2\eta/3 - x}{1 - \eta/3 - x} = \frac{x_L - x}{x_T - x} \quad (4)$$

which in turn gives us a plasma longitudinal frequency  $\omega = \omega_1 \sqrt{x_L} \simeq 26.2$  eV along with a transverse excitation frequency  $\omega = \omega_1 \sqrt{x_T} \simeq 19.6$  eV as zero and pole of the dielectric function  $\epsilon$ . Then the van-der-Waals energy is simply a difference between the bare plasma frequency of the cluster and the frequency of the modes in the solid. It reads as:

$$W = \hbar\omega_1 (\sqrt{x_L} + 2\sqrt{x_T} - 3) \sim -\hbar\omega_1 \frac{\eta^2}{24} \quad (5)$$

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  $\eta$ . As it is seen from Eq.(5) the first order terms are cancelled out. The interplay between the parameters  $\omega_1$  and  $\eta$  gives us also the plasma frequency on the boundary between some mediums, in the liquid, in the medium with polarizable dopant and so on. We will discuss it at length elsewhere. Substituting the numbers into Eq.(5) one gets the van-der-Waals energy about  $-1.1$  eV per cluster in the solid. The one of the first papers containing similar consideration to be mentioned is [8]. In the next section we will compare the result with the energy in solution.

## FULLERENE IN SOLUTION

The plasma frequency in a solution is lower than in a solid phase owing to the depolarization shift is much weaker in any typical organic solvent than in a fullerene solid. The reason is that the fullerene cluster has the very high frequency of the bare plasmon due to large number of highly polarizable electrons. A standard medium is nearly transparent at this frequency. More precisely the dielectric function of the medium is slightly less than the unity at the frequency of  $C_{60}$  plasmon.

Below we present a correct method of calculation of the frequency of plasma mode of  $C_{60}$  in a liquid insulator. According [6], the surface plasmon in  $C_{60}$  is a spherical oscillation of electron density  $\sigma_{LM}$ . 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 an electric field is given by:

$$\frac{2L+1}{R} \varphi_{LM}^{ind} = 4\pi\sigma_{LM} \quad (6)$$

where  $\varphi^{ind}$  is an induced part of the potential;  $L, M$  are the multipole power indexes. We close the equation system by writing a response function,  $\chi$ , for fullerene cluster as:

$$\frac{4\pi R}{2L+1} \sigma_{LM} = -\frac{4\pi R}{2L+1} \chi_L \varphi_{LM}^{act} \simeq \frac{\omega_L^2}{\omega^2} \varphi_{LM}^{act} \quad (7)$$

where  $\varphi^{act} = \varphi^{ext} + \varphi^{ind} = \varphi_{LM}^{ext} + 4\pi R \sigma_{LM} / (2L+1) + \varphi_{LM}^{sol}$  is an acting potential. The selfconsistency of the calculation is proved by using of this acting potential, including an induced potential of  $C_{60}$  plasmon as well as the potential occurring owing to charge density induced in the solvent. Here  $\chi_L(\omega)$  is the response function of a single sphere. The equation (7) is easily obtained from classic charge liquid equations [6,7]. This consideration is more general than our  $L=1$  case of the dipole plasmon mode. However, for the spherical symmetry Eq.(7) holds for any multipole.

When the potential induced in the solvent is absent,  $\varphi_{LM}^{sol} = 0$ , we return to the bare plasmon frequency. The corresponding bare dispersion equation reads as:

$$-\frac{4\pi R}{3} \chi_1 = \frac{\omega_1^2}{\omega^2} = 1 \quad \text{or} \quad \frac{1}{x} = 1. \quad (8)$$

We will simply change the unity to the dielectric function to take into account the potential induced in the solvent. It follows from the substitution of Eq.(7) into Eq.(6) and taking the standard RPA sum. As a result the plasma frequency in the solution is:

$$\Omega(\epsilon) = \omega_1 \sqrt{\epsilon(\Omega)} \quad (9)$$

The frequency is smaller than the bare  $C_{60}$  frequency. So far we obtain the plasmon in the single cluster, in the fullerene solid and in the solution. We will use for the dielectric function of the liquid solvent the common formula:

$$\epsilon(\Omega) = \frac{\Omega^2 - \omega_L^2}{\Omega^2 - \omega_T^2} \quad (10)$$

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

$$W \simeq -\frac{3}{2}\hbar\omega_1 \frac{\omega_L^2 - \omega_T^2}{\omega_T^2} \frac{\omega_T^2}{\omega_1^2} = -\frac{3}{2}\hbar\omega_1 (\epsilon_0 - 1) \left(\frac{\omega_T}{\omega_1}\right)^2 \quad (11)$$

here  $\epsilon_0$  is the static permittivity of the solvent, which is related to the transverse and longitudinal frequencies. The typical values for  $\epsilon_0$  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 we have to conclude that by this energetic reason the solid fullerene should be more stable than in the solution.

Let us consider a fullerene dimer, the similar problem was solved in Ref.[5,6] for  $C_{119}$  molecule. The plasmon frequency is split in an axial field. Therefore new modes bring the energy of interaction between clusters in the dimer. Then the van-der-Waals energy of the dimer coupling reads as:

$$W \simeq -\frac{3}{2}\hbar\omega_1 \left(\frac{R}{H}\right)^3 \left(1 + \frac{3}{2} \frac{\omega_L^2 - \omega_T^2}{\omega_T^2} \frac{\omega_T^2}{\omega_1^2}\right) \quad (12)$$

where  $H \simeq 8 \text{ \AA}$  is 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 the dimer is about -0.7 eV.

## PLASMON MODES IN ICOSAHEDRAL COMPLEX

Recent experiment shows that in fullerene beams the supercluster is forming [4]. The mass-spectra analysis signs that the cluster of 13  $C_{60}$  is especially stable. The most evident structure of such super-cluster is an icosahedron made by central fullerene and closed packed shell of all other 12 clusters. Our aim is to find a solution for self-consistent high-frequency polarizability of the supercluster and calculate the van-der-Waals forces. The poles of polarizability as before are given by the frequencies of plasmon modes in  $(C_{60})_{13}$ . We will briefly discuss the method of calculation of these frequencies for icosahedral system.

First of all, one has to evaluate a fullerene-fullerene interaction to obtain the shift of plasmon frequency in the supercluster. It was shown for the fullerene dimer [6] that the dipole-dipole interaction is enough to be considered (all higher multipole corrections are negligible). The same dipole approximation will be used below. The shift of plasmon frequency of the central  $C_{60}$  depends on the acting field which is given by the sum of the fields from all other external fullerenes. The same time the field of the central cluster influences on the external ones. Besides that each external  $C_{60}$  has five more nearest neighbors acting on it. To account the mentioned above terms one has to solve the dynamical matrix of dimension  $39 \times 39$ . Each dipole plasmon has 3 components (which are, in general, not only shifted but split).

The full solution of the problem will be given elsewhere. Let us show here the mean-dipole-moment approximation of the problem which possesses the analytical solution and allows to evaluate the van-der-Waals energy. The exact way to perform this approximation comes from the group-theoretical consideration.

The 13 fullerenes of the supercluster form  $\Gamma_0$ , the reducible representation (RR) of the icosahedral group  $Y$ . The dipole problem stated above has the Hamiltonian (dynamical) matrix forming another RR of  $Y$  group which is the direct product of the dipole representation and  $\Gamma_0$ . It can be expanded into the direct sum of irreducible representations (IRs) of  $Y$ :

$$T_1 \times \Gamma_0 = A + 4T_1 + T_2 + 2G + 3H \quad (13)$$

where we use the standard notation  $A, T, G, H$  for IRs of  $Y$  with the dimensionality 1, 3, 4, 5. The triply degenerate IR,  $T$  has an additional label because of there are two distinct IRs of such type in  $Y$ . Simple check of the overall dimensionality judges that the expansion is not false:  $1 + 12 + 3 + 8 + 15 = 39$ . This RR  $T_1 \times \Gamma_0$  contains only 3

dipole active modes. What are them? If one considers the RR of single central cluster, one finds only one icosahedral IR, and it is exactly of such a type. The second IR comes from the spherically averaged 12-cluster shell of external fullerenes. The last mode, having full icosahedral symmetry, has more complicated symmetry and will be discussed elsewhere. Let us write the dynamical matrix in the following form:

$$\begin{vmatrix} x-1 & \mathcal{T}_C \\ \mathcal{T}_C & (x-1)\mathcal{I} + \mathcal{T}_B \end{vmatrix} \quad (14)$$

where the submatrices  $\mathcal{T}_C$  and  $\mathcal{T}_B$  depict the dipole-dipole interaction of central fullerene with the shell and the interaction within the shell correspondingly and  $\mathcal{I}$  is an identity matrix. Each  $C_{60}$  (excepting the central one) interacts with five closest clusters from the shell and the central fullerene. Let describe more precisely the  $6 \times 6$  submatrices of the interaction. The self-energy term  $x-1 \equiv \omega^2/\omega_1^2 - 1$  is as before given in units of the plasmon energy of the single fullerene  $\omega_1^2$ . Without interaction this term gives the bare plasma frequency for each dipole plasmon mode, which will be 6-ly degenerate in this case. The dipole-dipole interaction tensor reads as:  $\tau_{ij}(\mathbf{e}) = \frac{1}{R^3}(\delta_{ij} - 3 e_i e_j)$ , where  $R$  is the distance between dipoles and  $\mathbf{e} = \frac{\mathbf{R}}{|\mathbf{R}|}$ . Then the interaction terms are given by:  $\mathcal{T}_B = \sum_{f \in \text{NN}} \tau(\mathbf{f})$ , where the sum is taken over nearest neighbors (NN), and  $\mathcal{T}_C = \sum_{g \in Y} \tau(\mathbf{g})$  for central cluster. The total matrix Eq.(14) gives us all plasma mode frequency shifts.

The result is:

$$W \simeq -\frac{45}{2} \frac{e^2}{R} \left(\frac{R}{L}\right)^3 \quad (15)$$

here we evaluated the plasmon dipole momentum as  $eR$ .  $L$  is the distance from the center of supercluster to the center of  $C_{60}$  in the shell, it could be about  $10\text{\AA}$ . Van-der-Waals energy of such cluster is about 3.1 eV.

In summary, we used a plasmon mode approximation for calculation of van-der-Waals energies of different cluster systems. The approach is shown to be consistent for the cluster-medium and cluster-cluster interaction. We applied the method for the calculation of the van-der-Waals energy of formation of  $C_{60 \times 13}$  supercluster.

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