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Increase of van der Waals Attractive Force under Electromagnetic Field

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A formula for the photoincreased van der Waals attractive force is derived, which includes the effects of the frequency of illuminated electromagnetic waves and of the size of particles. The interparticle interaction energy as a function of the frequency of the electromagnetic wave shows a sharp maximum at the resonance frequency. In the small limit of the size, the van der Waals force under on-resonance irradiation conditions approaches that of molecules and in the large limit the force is drastically reduced. The largest interparticle interaction is found at the size of a few tens of nm. This novel effect is found to be typical of nano-systems.

In a previous report,[1)] we showed how the van der Waals attractive force of metallic ultrafine particles (UFPs) is increased under an illumination of the Mie resonance frequency. The basic idea is that a gigantic dipole oscillation is induced by the external field, which couples with the collective mode of a surface plasmon of the conduction electrons in a small particle. This photo-induced dipole affects the electronic states of surrounding metallic UFPs resulting in an in-phase dipole-induced dipole oscillation. Hence this novel photo-induced dipole–dipole interaction contributes to the interparticle interaction in addition to the normal van der Waals attractive forces.

The additional interparticle contribution is a function of the size of the particles, the power of light, and the frequency of the electromagnetic wave. The peak value of this dipole–dipole interaction at the on-resonance position for particles of 10 nm in radius is 10—100 times larger than a normal dispersion force for conventional light sources and 1000 or more for a laser. However these values of course change with the size of a particle and may approach the value for molecules at the small size limit and should disappear at the large size limit.

In this paper, we extend the previous treatment so as to include the effects of the size and the wavelength of an external irradiation field as variable parameters. Within the framework of the static-field approximation, the effect arising from the inhomogeneity of the electric field at the volume of particles is taken into account as a correction term as well as the size effect (these two effects were neglected in our previous report), both of them broaden the width of the plasma resonance absorption band. We derive the analytical expression of interparticle interaction under irradiation in the framework of the local-density-functional method and examine its asymptotic behavior in several limiting cases. We have found that the photo-induced van der Waals force is indeed a real physical process in systems of nanometer scale.

Interaction Energy in the Excited State

First, we calculate the photoinduced electric dipole in an irradiated metallic particle and then the induced dipole on surrounding particles. That is, we are engaged solely in the case of one-particle excitation. The electric dipole located at origin $\boldsymbol{P}_{\text{irr}}$ induced by the external field, $\boldsymbol{E}(\omega)=\boldsymbol{E}_0 \exp(-i\omega t)$, is given by

$$\boldsymbol{P}_{\text{irr}} = \alpha(R,\omega)\boldsymbol{E}(\omega), \tag{1}$$

in which $\alpha(R,\omega)$ is the particle polarizability at frequency ω for a particle of radius R. In order to pose explicitly a quantum size effect on the polarizability, we will introduce a real space complex-valued effective polarizability of the particle, as shown later. The induced electric dipole moment on surrounding particles with the static polarizability α_0 caused by $\boldsymbol{P}_{\text{irr}}$ is given by

$$\boldsymbol{P}_{\text{ind}} = -\alpha_0 \,\text{grad}\,(\boldsymbol{P}_{\text{irr}}\cdot\boldsymbol{d})/d^3, \tag{2}$$

where $\boldsymbol{d}$ is the position vector relative to a counter-particle. This induced dipole moment causes an electric field $\boldsymbol{E}_{\text{i}}$ at the origin. Then $\boldsymbol{P}_{\text{irr}}$ can interact with this field. Hence the interaction between the externally excited dipole and the induced dipole leads to the relationship

$$\begin{aligned} U &= -\boldsymbol{P}_{\text{irr}}\cdot\boldsymbol{E}_{\text{i}}/2 \\ &= -\frac{\alpha^2(R,\omega)}{d^6}\alpha_0 E_0{}^2\{1+3\cos^2\theta\}/2, \end{aligned} \tag{3}$$

in which $\alpha_0 E_0{}^2$ is a power of radiation received by a particle and θ is an angle between $\boldsymbol{P}_{\text{irr}}$ and $\boldsymbol{d}$. Finally after averaging $\cos^2\theta$, we get the interaction energy U_{int} being

$$U_{\text{int}} = -\frac{\alpha^2(R,\omega)}{d^6}\alpha_0 E_0{}^2. \tag{4}$$

To get a concrete expression of U_{int}, we have to derive an analytical expression of the polarizability of small metallic particles. Phenomenologically, the polarizability of small metallic particles is given as follows in the static field approximation.[2,3]

$$\alpha(R,\omega)=\frac{R^3\omega_M^2}{\omega_M^2-\omega^2-i\Gamma\omega}. \tag{5}$$

The imaginary part in the denominator of Eq. 5 stands for the damping of plasmon oscillation and ω_M is the Mie resonance frequency ($=\omega_p/\sqrt{3}$; ω_p is the bulk plasma frequency). A model of a small particle is depicted in Fig. 1 where the surface of the particle is indicated by a broken line that stands for the background positive charges of metals. The density of free electrons in a particle shows a slowly damping tail extending outside the surface. The induced electron density at the surface is associated with the surface plasmon oscillation. The peak position (D_M) of this induced density is around the centroid of a charge distortion and its absolute value is about 1 Å.[2] By comparing the complex dipole polarizability Eq. 5 phonomenologically introduced with that by the time-dependent local-density-functional approximation, we get the following relationship[2]

$$\Gamma\omega = Im\sum(R,\omega), \tag{6}$$

where $\sum(R,\omega)$ is the quantity related to the complex self-energy pertaining to quantum-mechanical scattering processes at the surface region. The shift and broadening of the surface plasmon resonance are directly related to the real and imaginary part of this self-energy. The self-energy term is approximated as[2]

$$\sum(R,\omega)=D(\omega)\omega_s^2/R, \tag{7}$$

in which ω_s is the surface plasmon frequency ($=\omega_p/\sqrt{2}$) and $D(\omega)$ is the complex valued centroid of the surface screening charge. The real part of $D(\omega)$ stands for the characteristic length of the spilling-out electron charge and the imaginary part is related to energy dissipation at surface. Since the imaginary part of the centroid $D(\omega)$ is nearly constant around ω_M and is given by D_M/k (k is a numerical factor), Eq. 6 can be rewritten as[2]

$$\Gamma\omega_M = 3D_M\omega_M{}^2/2Rk, \tag{8}$$

for frequencies close to ω_M. Therefore the phenomenological parameter in Eq. 5 is related to the geometrical parameters (R and D_M) of a particle through

$$\omega_M/\Gamma=\frac{2k}{3}(R/D_M). \tag{9}$$

Substituting Eq. 5 into Eq. 4 and seting $\omega=\omega_M$, we obtained $U_{\rm int}$ at the resonance position as

$$U_{\rm int}=-\frac{R^6\alpha_0E_0^2}{d^6}\frac{4k^2}{9}\left(\frac{R}{D_M}\right)^2. \tag{10}$$

In the quantum limit, i.e. when R approaches zero, the value in the parenthesis is on the order of unity because a minimum value of R is on the order of 1 Å and D_M is also of the same order. Hence we define U_m as the interaction in the quantum limit

$$U_m=-\frac{R^6\alpha_0E_0^2}{d^6}. \tag{11}$$

and this is considered to be a typical value for the *intermolecular* interaction induced by external fields. If we replace $\alpha_0E_0{}^2$ in the numerator to $\hbar\omega_M$, the interaction energy is identical to the normal van der Waals energy (a typical value is 10^{-19} J) in the dark except for a numerical factor.[4]

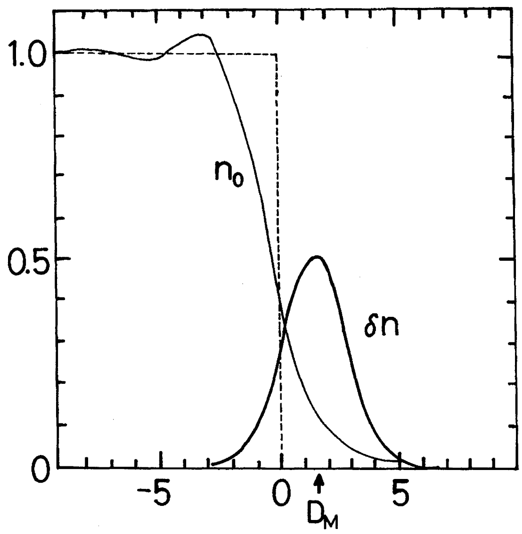

Fig. 1. Model potential of metals. Broken line: background positive charge. Thin solid curve: ground-state density profile (n_0) of free-electrons. Bold curve: induced electron density (δn) associated with surface plasmon. D_M stands for Re$D(\omega)$ at $\omega=\omega_M$ and roughly coincides with the maximum position of the induced electron density δn. The imaginary part of $D(\omega)$ is related to the energy dissipation of absorbed photon. The abscissa stands for the normal distance from the surface in atomic units. The ordinate is the real part of the normalized charge density.

Effects of Size and Irradiation Frequency

To extend this treatment to larger particles, the dephasing effect must be taken into account. The dephasing of plasmon oscillation to the external field and the retarded dipole–dipole interaction are predominant in the size region larger than 20 nm and these contributions can be taken into account by expanding the imaginary part as a series of (R/λ) in the former case and (d/c) in the latter case.[5] For much larger particles, the size of which is comparable to or larger than the wavelength of a radiation field, the skin effect is predominant. That is, the electric vector of alternating fields is no longer constant over the particle size and is a function of the position in the particle. Therefore Mie resonance oscillation is completely averaged out over a particle region giving an extremely broadened lineshape. However we leave this extreme case and confine ourselves within the static field approximation where R is less than λ. Moreover, we neglect the so-called retardation effect in this paper because of the complexity of the expression for the interaction energy in this case. The dephasing effect and size effect can be incorporated into the imaginary term in Eq. 5 through Γ. Hence the damping of plasmon oscillation due to the dephasing effect can be expressed as follows.

$$\begin{aligned}\Gamma &= \Gamma_0(D_M/kR)+\Gamma_1(R/\lambda)+\Gamma_2(R/\lambda)^2+\text{higher terms}\\ &\approx \Gamma_0(D_M/kR)+\Gamma_1(R/\lambda)\exp\left[(\Gamma_2/\Gamma_1)(R/\lambda)\right].\end{aligned} \quad (12)$$

Here the first term on the right side of the first equation stands for the plasmon damping in the quantum region and Γ_0 is the limiting linewidth at $R\approx D_M$ in this region, the second term stands for the dephasing effect, and higher terms stand for the dynamical depolarization. Therefore, the term with the coefficient Γ_1 or Γ_2 can be regarded as a classical effect. Further, in Eq. 12, we introduce an approximation given by the second equation. This approximation is correct up to the second order in (R/λ). Substituting Eq. 12 into Eq. 5 and then Eq. 4, we obtain the frequency and the size dependence of the interaction energy, assuming that the damping term does not largely depend on ω, as

$$U_{\text{int}} = U_m \frac{\omega_M^2\Gamma_0^2}{(\omega_M^2-\omega^2)^2+\omega_M^2[\Gamma_0(D_M/kR)+\Gamma_1(R/\lambda)\exp((\Gamma_2/\Gamma_1)(R/\lambda))]^2}. \quad (13)$$

Limiting Cases

A. Irradiation Frequency Dependence for Small Particles. Now we will simplify the frequency dependence of Eq. 13 assuming the size of particles to be much smaller than the irradiation wavelength ($R\ll\lambda$). Under these conditions, the terms in Eq. 12 displaying classical size effects disappear. Hence the interaction energy leads to

$$U_{\text{int}}/U_m = \frac{(\Gamma_0/\omega_M)^2}{[1-(\omega/\omega_M)^2]^2+(\Gamma_0/\omega_M)^2(D_M/kR)^2}. \quad (14)$$

Equation 14 approaches $(\Gamma_0/\omega_M)^2$, i.e., nearly zero for $\omega\rightarrow 0$ because the value of $(\Gamma_0/\omega_M)^2$ is usually very small, $(kR/D_M)^2$ for $\omega\rightarrow\omega_M$, and zero again for $\omega\rightarrow$infinity. That is, a maximum interaction is realized at the Mie resonance frequency and it is proportional to R^2 as precisely shown in our previous paper.[1] In Fig. 2, we calculate the interaction energy Eq. 13 normalized to U_m as a function of radiation frequency ω in the case of $R=10$ nm, $\lambda_M=500$ nm, $k=1$ and $\Gamma_2/\Gamma_1=10$.

B. Size Dependence at On-Resonance Position. The size dependence of the interaction energy at $\omega=\omega_M$ is expressed as

$$U_{\text{int}}/U_m = \frac{\Gamma_0^2}{[\Gamma_0(D_M/kR)+\Gamma_1(R/\lambda)\exp((\Gamma_2/\Gamma_1)(R/\lambda))]^2}. \quad (15)$$

In the quantum limit where $R\rightarrow 0$, Eq. 15 becomes

$$U_{\text{int}}/U_m = (kR/D_M)^2. \quad (16)$$

Thus the interaction energy is proportional to the square of the size of a particle in the small size region. At the smallest limit, U_{int}/U_m becomes unity, corresponding to the case for a hypothetical molecule (no increase is observed). For large R, the linewidth of the surface plasmon resonance becomes very broad, as indicated in Eq. 12. That is, the interaction energy grows initially as R^2 from the molecular value U_m with increasing size and then gradually decreases to zero after passing through a maximum value. The interaction energy is depicted in Fig. 3 as a function of size using the same parameters as those in Fig. 2. The peak position is around 20 nm for the given parameters. The peak value 9000 does not agree with that of Fig. 2 because we assumed $R=10$ nm in Fig. 2.

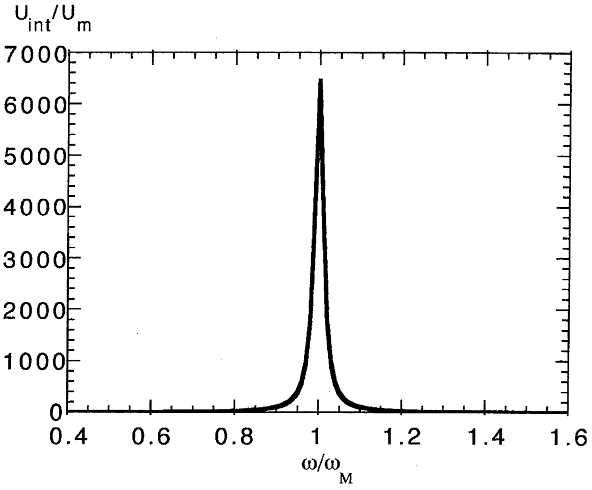

Fig. 2. Frequency dependence of the interaction energy Eq. 13. Parameters used are $R=10$ nm; $\lambda_M=500$ nm; $D_M=0.1$ nm; $k=1$; $\Gamma_0/\omega_M=1$; $\omega_M/\Gamma_1=\Gamma_2/\Gamma_1=10$.

Discussion

As has already been pointed out, a gigantic interparticle attraction force coupled with the Mie resonance absorption stems from a factor (R/D_M) in Eq. 14, where R is assumed to be around a few tens of nm. It is well-known that a normal van der Waals force originates from the second order perturbation

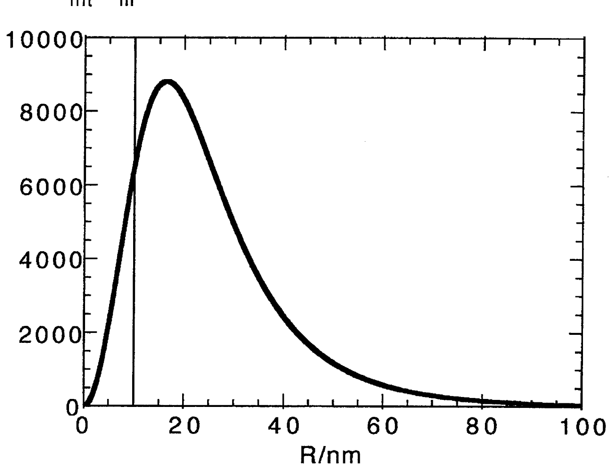

Fig. 3. Size dependence of the interaction energy Eq. 14. Parameters used are the same as those in Fig. 2 except the irradiation frequency being set at $\omega=\omega_M$ and R being a variable.

of a target molecule caused by other molecules. Through this perturbation, the wave function of the molecule fluctuates with high frequencies. In this case the range of fluctuation is confined to the coherent region of the wave functions, i.e. the molecular size, which implicates $(R/D_M)\approx 1$ for small molecules. In such a case, the interaction energy is equivalent to those derived from a normal molecular polarizability. Hence the system has to be a mesoscopic scale for a large increase to be observed as is the case in Fig. 3. The crossover from the mesoscopic to the classical case where the retardation effect is large may lie in the region of several tens of nm. In this size range, we expect more drastic reduction in interaction energy than shown in the figure resulting in the shift of the peak position toward smaller sizes.

The key issue of this enhancement is the existence of the real in-phase coherent oscillation of electrons in a surface plasmon excitation. If a system is made of an assembly of independent non-interacting molecules, no increase will be expected because of the out-of-phase electron oscillations. It should be noted that whether $\alpha_0 E_0^2$ can be replaced by $\hbar\omega_M$ in Eq. 11 depends on the experimental conditions. For $\lambda=500$ nm, the value of $\hbar\omega_M$ is 2.48 eV (4×10^{-19} J). If the value of $\alpha_0 E_0^2$ is lower than this energy, the interparticle interaction induced by an external field is weaker than the normal van der Waals force. For a conventional high pressure mercury lamp, the value of $\alpha_0 E_0^2$ for a 10 nm particle is around 10^{-21} J or less, much smaller than $\hbar\omega_M$. We need a high power density of 10 W cm^{-2} and a duty time of ns for the Hg lamp to get comparable energy with $\hbar\omega_M$. However, this difficulty is overcome with the use of a laser. Of course, no enhancement is expected for $E_0=0$, i.e., under no irradiation.

As for the ω dependence, we notice that the peak is very sharp in contrast to that in the size dependence. Only 10% deviation of ω from ω_M results in the drastic reduction of the interaction energy to as low as 1.5% of the maximum value. This in turn justifies the approximations adopted in this paper, where we mainly take care of the vicinity of ω_M. Through this paper, we have not taken into account the damping effect on the interaction lifetime. This contribution cannot be neglected in real metallic particles apart from molecules. The damping of the plasma oscillation reduces the interaction time between two particles which may also reduce the interaction energy.

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