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## Photoenhanced van der Waals Attractive Force of Small Metallic Particles

Keisaku Kimura

Department of Material Science, Himeji Institute of Technology, Science Garden City,  
Kanigohri, Hyogo 678-12, Japan

Received: March 9, 1994; In Final Form: May 26, 1994<sup>®</sup>

The phenomenon of photoinduced coagulation of Au nanocolloids is theoretically studied as due to the photoenhanced van der Waals attractive force. The dielectric function of metals as a function of size of a particle, external field frequency, and the momentum of wavevector derived from a local density functional approach is used to give the polarizability of metal small particles. It is found that a giant electric dipole moment, the magnitude of which directly reflects the size of a particle, is induced by an illumination of the photon with a Mie resonance frequency. From the polarizability of particles and the induced electric dipole thus derived, the interparticle interaction energy is given as a function of the size of a particle. Thus, the effective Hamaker constant (macroscopic interparticle attraction energy) of small particles under illumination is several orders of magnitude higher than in dark conditions, giving rise to instantaneous coagulation of nanometer-sized particles in solution. This phenomenon is suggested to be a characteristic of the mesoscopic scale.

### Introduction

Recently, we have reported that the coagulation of nanometer-sized gold colloids in organic media is drastically promoted by the irradiation of an electromagnetic wave at a Mie resonance frequency.<sup>1</sup> The gold ultrafine particles (average diameter ~10 nm) in 2-propanol, being stable over several years in dark conditions, coagulated to sediment within 30 h upon irradiation by a high-pressure mercury lamp, showing that the acceleration of the rate of aggregation was at least 1000 times higher than that in the dark. The same effect was also observed for gold particles in chloroform,<sup>1</sup> ethanol,<sup>1</sup> and water.<sup>2</sup> It was also shown that the coagulation was characteristic of an irradiation frequency of the Mie resonance as proved by the wavelength dependence of the illuminating light.<sup>3</sup> No theory interpreting this phenomenon has been presented so far to my knowledge. It is well-known that the coagulation of colloidal particles is accelerated by the addition of electrolyte to colloidal solutions through the reduction of electrostatic repulsive force. This effect, analogous to the salting-out effect, was also found in the present system using sodium chloride as reported in the previous paper.<sup>3</sup> Nanometer-sized gold dispersions in 2-propanol completely coagulated to sediment at the instance of the addition of  $8.6 \times 10^{-4}$  M NaCl. Following a generally accepted colloid theory, DLVO (Deryagin-Landau-Verwey-Overbeek), particles in a liquid are stabilized by the surface electric charges of the same sign which prohibit the mutual access of particles due to the van der Waals attraction force. More accurately, the repulsive force caused by an electrical double layer around particles prevents further approach of other particles. The balancing between an electrostatic repulsion force of charged particles and a van der Waals attraction force determines the stability and instability of colloidal systems. When one adds salt to colloid dispersion, particles spontaneously aggregate as a result of the reduction of the thickness of the electrical double layer (corresponding to the increment of electrostatic screening effect by ions). In this case, one can control the electrostatic potential by the concentration and by the valence of electrolytes (Schulz-Hardy rule).<sup>4</sup> Our findings therefore bear resemblance to the

result of electrolyte addition. However, in the photoinduced coagulation, the concentration and the type of electrolyte species, if they exist, of the colloid solution remain unchanged before and after the irradiation of light. There is another possibility following DLVO theory. If the van der Waals force is enhanced by the irradiation at the Mie resonance frequency, the interparticle potential energy drastically decreases, causing spontaneous coagulation among particles in close proximity. That is to say, the slow coagulation phase with a potential barrier in the dark is switched to the fast coagulation phase without a barrier by the irradiation. Hence, the whole rate process should be governed by the enhancement of the van der Waals force induced by the irradiation.

In this paper, we propose a simplified model which enables a van der Waals force to be enhanced, owing to a giant electric dipole oscillation of small metallic particles induced by the Mie resonance absorption. We derive a model formulation of a van der Waals force with and without the electromagnetic radiation at the Mie resonance frequency. On application of a microscopic dielectric function to the polarizability of metals, the macroscopic attraction energy, i.e., a Hamaker constant, is shown to be enhanced between 100 and 5000 times that in dark circumstances depending on illumination conditions. We apply the Hamaker constant thus obtained to the DLVO theory to calculate the potential barrier for particle coagulation. We show by numerical calculation how this potential barrier reduces upon irradiation of the Mie resonance frequency.

### Theoretical Treatment

**Interaction between Small Particles in the Ground State.** Let us confine ourselves to a phenomenon occurring within the distance of several tens of nanometers from a particle surface. Hence, we can neglect the retardation effect. Following a generalized microscopic dispersion theory—the susceptibility theory propounded by McLachlan<sup>5</sup>—the interaction energy of two neutral particles 1 and 2 in the ground electronic state embedded in medium 3 at a center distance  $d$  apart is given by the following equation for the nonretarded case.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1994.

$$U = -\frac{3\hbar}{\pi d^6} \int_0^\infty \frac{\alpha_1(i\xi) \alpha_2(i\xi)}{\epsilon_3^2(i\xi)} d\xi$$

$$= -\frac{3\hbar}{\pi d^6} I \quad (1)$$

Here  $\epsilon_3(i\xi)$  is the dielectric function of medium 3, and  $\alpha_1(i\xi)$  and  $\alpha_2(i\xi)$  are the polarizabilities of particles 1 and 2 as a function of imaginary frequency  $i\xi$ . First, we restrict ourselves to the case of two identical particles ( $\alpha_1 = \alpha_2$ ) in a vacuum where  $\epsilon_3$  can be given as  $\epsilon_0$ , the dielectric constant of vacuum. Furthermore, we adopt a static field approximation. In the next step, we derive the analytical expression for the interaction potential  $U$  in dark conditions using eq 1. We note in eq 1 that the interaction potential contains all frequencies through the integration of  $\alpha$ . Finally, we compare the interaction energy in dark conditions ( $U_d$ ) with that under irradiation ( $U_{irr}$ ) at the Mie plasmon frequency. In the following, we will engage in a rather simple model in order to overview the physical process of this phenomenon.

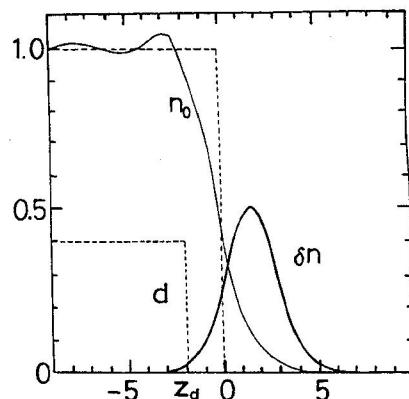
**Dielectric Function and Polarizability of Small Metallic Particles.** Recently, Liebsch<sup>6</sup> has derived polarizabilities of simple metal and noble metal particles based on a jellium model for conduction electrons by using the time-dependent local-density-functional approximation which includes the overall contribution of the ordinary monopole surface plasmon and of the so-called multipole surface plasmon. The resultant dielectric function thus derived was applied to estimate the size dependence of the Mie resonance position and the frequency dependence of the polarizability of small Ag particles, giving good agreement with the published experimental data. We now use his expression for the particle polarizability in the limit of the small wavevector approximation (this is held for optical absorption spectra) and neglect the shift term  $\Delta$  in the formalism in order to derive analytical relations between the incident irradiation and the resultant interparticle interaction. This simplification may be justified by the observation that the excitation at the interband transition has little effect on the observed coagulation. The model used is shown in Figure 1. The surface of a particle is defined by the background positive charge which is neutralized by the inner d-electron medium and by conduction electrons with a slowly damping density tail toward the surface. The induced electron density associated with surface plasmon has its maximum in the surface region. This peak profile is due to the tail of wave functions spilling out into a vacuum. The complex dipole polarizability of small jellium-like metal particles can be expressed by

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

where  $R$  is the radius of a particle,  $\omega$  is the frequency of an external field, and  $\epsilon$  is an effective local dielectric function. This complex polarizability is in accord with the excess polarizability of small particles given by Stratton.<sup>7</sup> The dielectric constant in eq 2 is given by<sup>6</sup>

$$\epsilon(R,\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Sigma(R,\omega)} \quad (3)$$

where  $\omega_p$  is the bulk plasma frequency and  $\Sigma(R,\omega)$  is 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 parts of this energy, respectively. Phenomeno-



**Figure 1.** Schematic illustration of electron densities at metal surface taken from ref 6. Broken line: background positive charge; the polarizable medium representing the 5d states extends up to  $z < z_d$ . Thin solid curve: ground-state density profile of the free electron ( $n_0$ ). Bold curve: induced electron density ( $\delta n$ ) associated with surface plasmon. The abscissa is in atomic units. The data are taken for silver.

logically,  $\Sigma(R,\omega)$  is often expressed as  $-i\Gamma(R)\omega$  in which  $\Gamma(R)$  is the damping of the plasma oscillation due to the classical surface scattering process characterizing the width of the resonance absorption band. The effect of a medium suspending a particle was also neglected. Qualitatively, this assumption can be justified for the case of the photoenhanced coagulation phenomenon which was observed in both aqueous and non-aqueous solutions having a large difference in dielectric constant. That is, it is not largely sensitive to the species of media. Hence, the dielectric function of metals is usually expressed simply as

$$\epsilon(R,\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\Gamma(R)\omega} \quad (4)$$

In general, the particle polarizability is given from eqs 2 and 3 as follows

$$\alpha(R,\omega) = R^3 \frac{\omega_M^2}{\omega_M^2 - \omega^2 - \Sigma(R,\omega)} \quad (5)$$

where  $\omega_M = \omega_p/\sqrt{3}$  (Mie resonance frequency). The polarizability has the maximum value around  $\omega = \omega_M$ . Now we can derive the interaction energy  $U$  in two cases: in dark conditions (normal van der Waals energy) and in illumination conditions at the Mie resonance frequency.

**A. Dark Condition.** After London, the dispersion energy is recognized as instantaneous high-frequency fluctuations of the ground state wave function of small particles associated with the mixing of the excited state wave function under the influence of counterparticles. Therefore, we must know an analytical form of the  $\omega$  dependence of  $\Sigma(R,\omega)$  in whole region from static to infinite frequency in pursuing the integral in eq 1, which is unfortunately unknown for real metals. Consequently, instead of directly treating the  $\omega$  dependence of  $\Sigma(R,\omega)$ , we use the phenomenological relation (4) for dielectric constant of metals where  $\Gamma$  is assumed to be independent of  $\omega$ . Substituting eq 4 into eq 2, we obtain the integrant  $I$  in eq 1 as

$$I = \omega_M R^6 \int_0^\infty \left( \frac{1}{t^2 + bt + 1} \right)^2 dt \quad (6)$$

where  $t = \xi/\omega_M$  and  $b = -\Gamma(R)/\omega_M$ . The integrant in eq 6 gives  $\pi/4 + (\Gamma(R)/\omega_M)/4$  after a definite integral in which the second term contributes less than 5% to the leading term. Hence

it is dropped. Finally, we obtain the interaction energy in the dark case,  $U_d$ , as

$$U_d = -\frac{3R^6}{4d^6}\hbar\omega_M \quad (7)$$

which is identical to the normal dispersion energy (known as London equation<sup>8</sup>) where  $U_d$  is given by  $(-3\alpha^2/4d^6)\hbar\omega_M$ . This expression can be derived from eq 7 simply by taking a limit of  $\epsilon \rightarrow \infty$  in eq 2, that is, if we use a static electronic polarizability of metals. In deriving eq 7, we neglect the  $\Gamma(R)/\omega_M$  term which contributes several percent to the main term. In other words, the magnitude of true interaction energy is larger by as much as several percent than that given by the London equation. Furthermore, the resultant interaction energy (eq 7) is independent of  $\Gamma$  as a result of dropping the  $\Gamma(R)/\omega_M$  term. Regardless of the simplification of  $\epsilon(R,\omega)$ , the resultant  $U_d$  thus derived coincides with the experimental value within errors of several tens percent.<sup>9</sup>

**B. Illuminated Condition.** First, we calculate the electric dipole moment induced in the irradiated particle at a given frequency and then the induced dipole of surrounding particles. In order to evaluate the dielectric function at the external electromagnetic radiation with the resonant frequency, we need a precise knowledge of the complex self-energy. The self-energy for noble metals is approximated as<sup>6</sup>

$$\Sigma(R,\omega) = D(\omega)\omega_s^{*2}/R \quad (8)$$

in which  $\omega_s^*$  is the effective surface plasmon frequency incorporating the effect of s-d interaction and  $D(\omega)$  is the centroid of the surface screening charge. The real part of  $D(\omega)$  stands for the typical length of the spilling-out electron charge. In order to get the functional relation of  $\Sigma(R,\omega)$  in eq 3 regarding  $\omega$ , we approximate further  $\omega_s^*$  to be  $\omega_s$  ( $=\omega_p/\sqrt{2}$ ). This corresponds to neglect of s-d interaction in  $\omega_s^*$  giving a constant shift in resonance frequency, which is not serious in the current treatment because we do not care about the size dependence of the Mie resonance position. Furthermore, it is known that the s-d contribution is not so large for noble metals.

When a particle is illuminated by the Mie resonance frequency  $\omega_M$ , eq 8 becomes

$$\Sigma(R,\omega_M) = 3D_M\omega_M^2/2R \quad (9)$$

where  $D_M$  stands for  $\text{Re } D(\omega)$  at  $\omega = \omega_M$  and roughly coincides with the position of the maximum induced electron density shown in Figure 1. Since the plasmon excitation is a real process, we substitute eq 9 into eq 5 giving eq 10,

$$\alpha(R,\omega_M) = \frac{2}{3}R^3\left(-\frac{R}{D_M}\right) \quad (10)$$

Here  $D_M$  is shown to be about  $-0.85 \text{ \AA}$  for silver.<sup>6</sup> Therefore, the photoinduced electric dipole is given by

$$\mu_{\text{irr}} = \alpha(R,\omega_M) E(\omega_M) \quad (11)$$

in which  $E(\omega_M)$  stands for the external electric field at the Mie resonance frequency. For weak-intensity light sources, the number of particles absorbing Mie resonance energy is very small, leading to only one exciting particle being surrounded by other ground state particles which are perturbed by the photoinduced electric dipole given by eq 11. The induced electric dipole moment on the surrounding particles is approximately given by

$$\mu_{\text{ind}} = \mu_{\text{irr}}\alpha_0/d^3 \quad (12)$$

where  $\alpha_0$  is the static polarizability of a particle. Hence, the dipole-induced dipole interaction leads to

$$\begin{aligned} U_{\text{irr}} &= -\frac{\mu_{\text{irr}}\mu_{\text{ind}}}{d^3} \\ &= -\frac{\alpha(R,\omega_M)^2\alpha_0 E^2(\omega_M)}{d^6} \end{aligned} \quad (13)$$

Using eq 10, eq 13 under irradiation of Mie resonance now reads as

$$U_{\text{irr}} = -\frac{4}{9}\frac{R^6}{d^6}\left(-\frac{R}{D_M}\right)^2 E^2 \alpha_0 \quad (14)$$

where  $E^2\alpha_0$  is the energy of the electromagnetic wave received by a particle. Comparing eq 14 with eq 7 in the dark case, we note that a factor  $(R/D_M)^2 E^2 \alpha_0$  is introduced in eq 14 and that this factor depends on both the size of a particle and the power of the external field. If two particles under consideration are simultaneously excited under a strong radiation field such as by laser irradiation, the interaction energy becomes

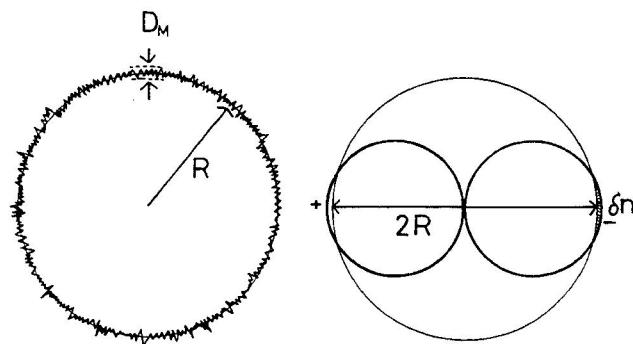
$$\begin{aligned} U_{\text{two}} &= -\frac{4}{9}\frac{R^6}{d^3}\left(-\frac{R}{D_M}\right)^2 E^2 \\ &= -U_{\text{irr}}\left(\frac{d^3}{R}\right) \end{aligned} \quad (15)$$

This interaction may contribute mainly in the region of longer distance ( $d > R$ ) than the events given by eq 14. Noting the fact that normal dispersion force is always acting on the particles irrespective of the irradiation, the total interaction energy may be a sum of  $U_d$  and  $U_{\text{irr}}$  under irradiation.

**Effect of Irradiation on the Interaction Potential.** Now we shall compare the interaction energy under illumination of the Mie resonance frequency with that under dark conditions. At low radiation power, we use eqs 7 and 13, leading to the energy ratio

$$\frac{U_{\text{irr}}}{U_d} = \frac{16\alpha_0 E^2}{27\hbar\omega_M}\left(-\frac{R}{D_M}\right)^2 \quad (16)$$

Under the experimental conditions of the previous report,<sup>3</sup> the value  $R$  is on the order of 10 nm and that of  $D_M$  is 0.1 nm utmost leading to  $R/D_M \sim 100$ . The average energy ratio  $\langle\alpha_0 E^2\rangle/\hbar\omega_M$  is  $10^{-3}-10^{-2}$  for a conventional light source and 1 for a laser. Hence, the ratio of interactions becomes 10–100 for conventional light and 10 000 for a laser. That is, the interaction potential is enhanced by at least about 1 order in magnitude when particles are illuminated by the Mie resonance frequency. The larger the particles, the larger ratio  $R/D_M$  becomes, giving much stronger interaction among particles. Hence, this ratio is a very important parameter in this process. In Figure 2 is shown the schematic model of a p-type (Froelich mode) plasmon mode and that of the inhomogeneous electron fluctuation in the normal dispersion. Recall that the electric dipole moment is given by the charge  $\delta n$  multiplied by the distance  $2R$  between the two charges with opposite sign in an excited particle. To the contrary in a dark condition, the electric dipole moment is given by  $\delta n$  multiplied by  $D_M$ . Then the magnitude ratio is  $R/D_M$  except for a numerical factor.



**Figure 2.** (left) Schematic model of the out-of-phase oscillation of a dark particle. An electric dipole moment is given by  $\delta n D_M$  and independent of  $R$ . (right) Schematic model of the in-phase oscillation of a surface plasmon excitation of a spherical particle. A p-type surface plasmon mode ( $l = 1$ : Froelich mode) is taken as an example. The electric dipole moment is given by  $\sim \delta n 2R$ , which is much larger than the normal dispersion.

The interaction potential of macrobodies is often expressed by using a Hamaker constant  $A$ , which is connected with the interparticle potential  $U$  in the dark (eq 7) or illuminated (eq 14) conditions given in this paper.<sup>10</sup>

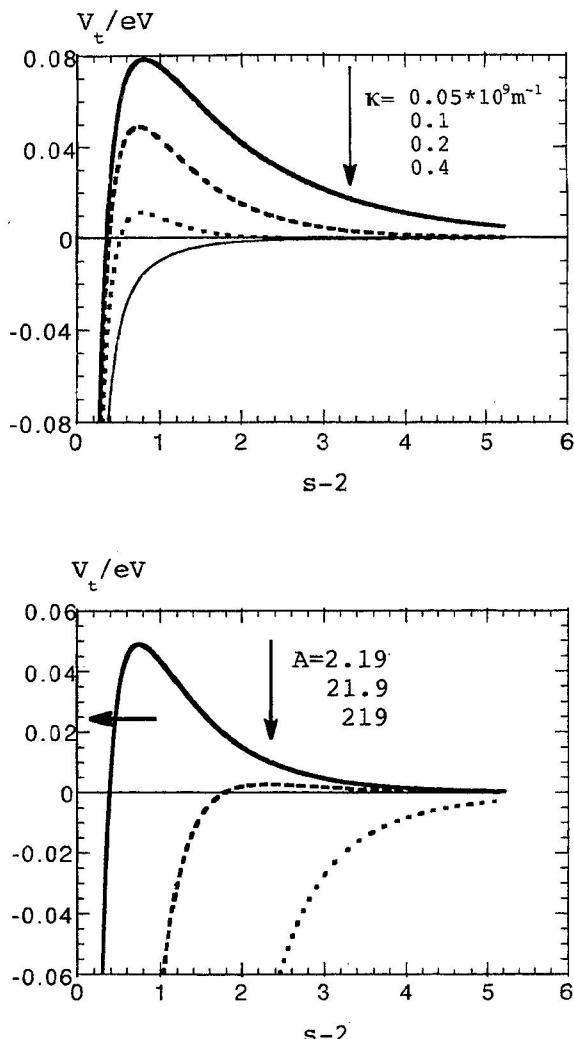
$$A = U d^6 \pi^2 \rho^2 \quad (17)$$

where  $\rho$  is the atomic number density of a particle. Since  $U$  is proportional to  $d^{-6}$ ,  $A$  is independent of the distance of particles. Moreover, we can easily find accurate experimental values of  $A$  in the literature. Therefore, we will use  $A$  in the following section. Since the Hamaker constant is directly related to the van der Waals force as stated above and since this force includes not only the well-known London dispersion force but also dipole-dipole, dipole-induced dipole, and other multipole interactions, we might name the newly found photoinduced dipole interaction to be a kind of van der Waals force. So the Hamaker constant including this effect can be called the effective Hamaker constant.

**Interparticle Potentials in Colloid Dispersion.** Since the aggregation process of ultrafine particles is governed both by the interparticle attraction force and the electrostatic repulsive force, let us now derive the interparticle potential of charged particles taking account of these two factors in dark and in illuminated conditions. Following the DLVO theory, the overall interaction potential  $V_t$  of charged spherical particles of the same radius  $R$  and center distance  $d$  is given by<sup>11</sup>

$$V_t = \frac{4\pi\epsilon R(s-1)\psi_0^2}{s} \ln \left[ 1 + \frac{1}{s-1} e^{-\kappa R(s-2)} \right] - \frac{A}{6} \left[ \frac{2}{s^2-4} + \frac{2}{s^2} + \ln \frac{s^2-4}{s^2} \right] \quad (18)$$

where the dimensionless parameter  $s$  is  $d/R$ ,  $\psi_0$  a surface potential of a particle,  $\kappa$  the inverse of the electric double-layer thickness which is functions of formal charge of ions, ionic concentration, dielectric constant of solvent, and temperature, and  $A$  the effective Hamaker constant which has been considered to be a material constant so far. In order to incorporate the medium effect whose contribution to the interaction potential has been neglected in the present treatment, we can use the reduced Hamaker constant,  $A_{red}$ , in such a way as  $A_{red} = (\sqrt{A} - \sqrt{A_m})^2$  in which  $A_m$  is the Hamaker constant of the medium. However, we will follow the simplest case as in eq 18. The first term in eq 18 represents the electrostatic repulsive interaction between charged particles based on the overlapping



**Figure 3.** (a, top) Total interaction potentials  $V_t$  with several ionic concentrations as a function of surface distance  $s - 2$  where  $s = d/R$ .  $A = 2.19$  eV (experimental value: gold in organic liquids),<sup>14</sup>  $R = 10$  nm,  $\epsilon_r = 19.9$  (2-propanol),  $V_0 = 60$  mV; the varied parameter is the inverse of the electrical double-layer thickness  $\kappa$  in the range from  $0.05 \times 10^9$  to  $0.4 \times 10^9 \text{ m}^{-1}$ , which corresponds to the thickness (Debye length) from 2.5 to 20 nm. (b, bottom) Total interaction potential  $V_t$  with several Hamaker constants.  $R = 10$  nm,  $\epsilon_r = 19.9$ ,  $V_0 = 60$  mV, and  $1/\kappa = 10$  nm; the varied parameter is the Hamaker constant  $A$  from 2.19 eV (experimental value in dark) to 219 eV (estimated value for the irradiation at the Mie resonance). An arrow on the ordinate stands for the level of kinetic energy  $kT$  at room temperature.

of the electric double layer,<sup>12</sup> and the second is the van der Waals attraction force between particles.<sup>13</sup> The former is independent of irradiation, and the latter depends on the Mie resonance irradiation. The change of the ionic concentration of electrolytes affects the magnitude of parameter  $\kappa$ , and numerous studies on this subject have been completed. As has already been pointed out in the previous section, the electromagnetic wave irradiation at the Mie resonance contributes to the value  $A$ . This contribution can be accounted for by increasing the value  $A$  in eq 18. The effect of the variation of these parameters on the interaction potential  $V_t$  is examined by model calculations, and the result is shown in Figure 3. The value  $\kappa$  ranges from very low ionic concentration corresponding to our current condition to the concentration under a normal experimental condition. The value  $A$  is taken for gold<sup>14</sup> ranging from dark conditions (2.19 eV) to low-power irradiation (219 eV). We should note that the peak of a barrier in the figure does not almost shift for the change in the electric double-layer

thickness, while in the change of the Hamaker constant, the energy barrier shifts apparently toward longer distance causing a long-range attractive force, and finally the barrier disappears. In fact, as stated in the previous report,<sup>3</sup> the interaction potential seemed to have a long-range attractive force via the irradiation.

## Discussion

As has already been discussed, the gigantic interparticle attraction force coupled with the Mie resonance stems from the factor  $R/D_M$  in eq 10. The physical meaning of the ratio  $R/D_M$  can be interpreted as follows. The inhomogeneous fluctuation of electron clouds mixing in the ground state is the cause of the so-called dispersion force. Among these zero-point oscillations, the oscillation of the electron cloud at surface region is most effective. Hence, the maximum wavenumber is given by  $1/D_M$  in magnitude. This contrasts to the in-phase oscillation of the electron density in the plasmon oscillation where the electric dipole is due to the surface spill-out electron density (see Figure 1) multiplied by the size of particles ( $\sim 2R$ ). Therefore, the range of the dipole oscillation spans over the size of particles, giving a definite wavenumber of  $1/R$  in contrast to the fluctuation of the electron clouds confined at surface region in the normal van der Waals force. Following this discussion, we have the ratio  $R/D_M$ . The key issue is the real coherent oscillation of electrons for plasmon excitation of a particle.

In dark conditions, the static electronic polarizability becomes  $R^3$  resulting from eq 2 which coincides with the expression derived from London's treatment for hydrogen atoms regardless of the difference in size. Therefore, we can consider eq 10 as being an insertion formula down to the atomic scale, although eq 8 itself cannot be applied to atoms. Mathematically, eq 10 equals that in a dark case when  $R$  is of the order of 0.1 nm, i.e., of the atomic scale. This situation is fulfilled in two cases. First is the case for a particle that is indeed a molecule or of a molecular size. Then the factor  $R/D_M$  equals  $\sim 1$ . The second is the case where a particle is large, but there is no coherent motion. This situation is realized in case of an off-resonance or a dark condition. The quantity  $R$  comes from eq 8 where  $R$  is introduced to give the minimum wavevector  $q$  in a particle. Here, a collective mode of the conduction electrons is simply expressed by the minimum wavevector. In other words,  $q$  is assumed to be a good quantum number. In a normal dispersion force, the electronic fluctuation of a ground state molecule of course cannot be described by a quantum number. It is well-known that this process stems from the second-order perturbation caused by other molecules. In this case the range of fluctuation is confined to the spillover region of wave functions, i.e.,  $D_M$  instead of  $R$ . Therefore,  $R/D_M$  equals 1. In such a case, eq 10 is reduced to that of the normal molecular polarizability. As a conclusion, this enhancement effect can be observed only in the system of a mesoscopic scale.

Concerning Figure 3, we note that the parameter  $\kappa$  contributes  $V_t$  in such a way to depend on the function  $e^{-\kappa R(s-2)}$ , in contrast to the Hamaker constant  $A$  as  $A/s^2$ ; i.e.,  $\kappa$  has a prominent effect in short range, whereas  $A$  affects over a long distance. This is easily seen in the Figure 3a for a parameter  $\kappa$  and Figure 3b for  $A$ . We can switch on or off the parameter  $A$  for attractive force by a factor from 10 to 10 000 by the irradiation. This enhancement in  $A$  results in a drastic change on the barrier height as shown in Figure 3b where we use  $A$  as a variable parameter because it is very difficult to estimate from eqs 14 and 18. However, the suppression of potential arising from switch on must continue as long as a particle being across the peak position in the potential of a dark case in order to promote particle

aggregation. Otherwise, a particle may feel a large potential barrier before it collides with its counterpart. Hence, one may question whether or not there is enough time for particles diffusing a distance of nanometers.

The radiation from a conventional light source is emitted in a wavetrain, lasting roughly on the order of picoseconds, in contrast to that of mercury lamp,  $\sim 10^{-9}$  s. That is, a mercury lamp can be regarded as a quasimonochromatic light source among other conventional sources.<sup>15</sup> Therefore, the conduction electrons of a particle bear a forced plasmon oscillation during the lifetime of the radiation, on the order of  $10^{-9}$  s. During this period, a particle can travel only 1 nm or less by the diffusive motion as a simple calculation shows. Hence, the excitation of particles is not always effective for coagulation for a nanosecond short coherent excitation. This is the reason why the aggregation process is not so fast (it took about 30 h as stated in the previous report) considering the rate of the fast coagulation, typically on the order of several tens of seconds. Using a laser may cause dramatic enhancement in the aggregation, and this effect was observed in the gold/water system where aggregation began after 10 min irradiation though the exact Mie resonance condition was not fulfilled.<sup>2</sup> The appearance and disappearance of potential barrier switched by photoirradiation within very short time intervals causes drastic effect near the surface of metal small particles, and the physics of this short time in solution is not yet well recognized.

In this paper, we restrict ourselves to the photoenhanced van der Waals attraction force for metallic ultrafine particles. Of course, this mechanism can be applied to other large molecules and particles which undergo the *coherent electric oscillation* induced by the photoirradiation, i.e., electric dipole oscillation in the excited states. Hence, we expect a large enhancement of van der Waals potential when large molecules and polymers are illuminated by the resonant radiation. The coherent charge density wave of solids is the other candidate when it is excited similar to the plasmon oscillation. This may have the same effect to induce a large attraction force. The lower limitation of the size of a particle for this phenomenon has been already discussed, and the effect is described by  $R/D_M$ . On the other hand, the upper limitation of the size of a particle is restricted by the condition of the coherence of a plasma oscillation. For example, the assumption of  $R \ll \lambda$  does not hold for large particles. Damping of plasmon due to resistance of metals and the skin effect are other factors affecting the coherence of plasmon. In such a system, the retardation and the alternating field effects play essential roles.<sup>16</sup> The crossing from mesoscopic to classical behavior may lie in the region of several tens of nanometers. Our finding shows the existence of a new type of van der Waals force which can be artificially controlled. In this paper, we treat only the on-resonant irradiation. Off-resonant irradiation leads a peculiar effect that is disregarded in this paper. A quantitative treatment taking both the size of a particle and the irradiation frequency into account is now in progress.

**Acknowledgment.** The author express his gratitude to Mr. N. Satoh and Prof. K. Kawamura for the stimulating and constructive discussions. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (Ultrafine Particles, 1993) from the Ministry of Education, Science and Culture, Japan.

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