Van der Waals versus optical interaction between metal nanoparticles

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We derive closed expressions for the Casimir–Polder potential between metal nanoparticles as well as for the light-induced interaction owing to the gradient force. Within the validity of the dipole approximation, the maximum interaction energy turns out to be proportional to the plasma frequency, and it is comparable to the thermal energy at $T = 300$ K. On the other hand, the light-induced interaction depends linearly on the light intensity, and only for strongly focused laser beams ($10 – 100$ mW/μm^2) does it become comparable in strength to the Casimir–Polder interaction. © 2008 Optical Society of America

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Laser-irradiated metal nanostructures give rise to locally enhanced fields. Because of their strong spatial confinement, these fields are associated with high field gradients and hence exert forces on polarizable objects [1]. In recent years, several proposals have been put forth to turn these gradient forces into practical use for nanoscale manipulation [2–8]. Because of the short interaction range the optical gradient force needs to be balanced against other forces, notably electrostatic forces and dispersion (van der Waals–Casimir–Polder) forces. The relative strength of these forces has been the subject of several recent studies [9–12].

Both the Casimir–Polder potential and the light-induced potential hold great promise for nanoscale manipulation and activation. Of particular interest is the interplay between the two potentials because it allows the interaction forces to be balanced between attractive and repulsive. For any practical proposal it is necessary to have simple expressions at hand, which allow one to estimate the order of magnitude of the forces and to assess important size and material parameters. Here, we derive simple analytical expressions for both the Casimir–Polder potential and the light-induced potential for a particle pair separated by a distance d. Within the limits of the dipole approximation, we find that the maximum interaction energy for a pair of metal particles is proportional to $\hbar\omega_p$, with ω_p being the plasma frequency. Light intensities of $\approx 10 – 100$ mW/μm^2 are required to generate gradient forces comparable in strength to the Casimir–Polder interaction.

The van der Waals interaction and its macroscopic counterpart, the Casimir interaction, are paradigmatic examples for mechanical forces induced by electromagnetic fluctuations [13–15]. Following the steps outlined in [1,16], the fluctuation-averaged force $\langle \mathbf{F} \rangle$ acting on a nanoparticle with polarizability α_1 located at $\mathbf{r}_1$ can be written as

$$\langle \mathbf{F}(\mathbf{r}_1) \rangle = \sum_j \int_{-\infty}^{\infty} \frac{\omega}{\pi c^2 \varepsilon_0} \left[\frac{\hbar\omega}{1 - e^{-\hbar\omega/k_B T}} \right] \times \mathrm{Im}\{\alpha_1(\omega)\nabla_1 G_{jj}(\mathbf{r}_1,\mathbf{r}_1;\omega)\}d\omega, \qquad (1)$$

where G_{jj} are the diagonal elements of the Green's tensor of the reference system (in absence of the particle) and ∇_1 denotes the gradient with respect to the first variable. This expression is consistent with the formula obtained by Mahanty and Ninham for the interaction energy between atoms modeled as harmonic oscillators [17]. Note that the force is determined by the properties of the environment that are encoded in the Green's function $\overleftrightarrow{\mathbf{G}}$. In this Letter we consider the force acting on the particle at $\mathbf{r}_1$ due to another particle at $\mathbf{r}_2$ with polarizability α_2. To first order, the Green's function $\overleftrightarrow{\mathbf{G}}$ is

$$\overleftrightarrow{\mathbf{G}}(\mathbf{r},\mathbf{r}_1) = \overleftrightarrow{\mathbf{G}}^o(\mathbf{r},\mathbf{r}_1) + \frac{\omega^2}{c^2 \varepsilon_0} \overleftrightarrow{\mathbf{G}}^o(\mathbf{r},\mathbf{r}_2)\alpha_2(\omega)\overleftrightarrow{\mathbf{G}}^o(\mathbf{r}_2,\mathbf{r}_1),$$

$$(2)$$

where $\overleftrightarrow{\mathbf{G}}^o$ is the free-space Green's function. Because finite temperatures affect the force only at large distances, where it is already fairly small [15,16], we restrict ourselves to the case of $T = 0$ K. It is straightforward to show that $\nabla \cdot \langle \mathbf{F} \rangle = 0$, and hence the force can be derived from a potential U given by

$$U = -\frac{\hbar c}{16\pi^3 \varepsilon_0^2 R^6} \int_0^{\infty} \alpha_1(ic\eta)\alpha_2(ic\eta)e^{-2\eta R}$$

$$\times [3 + 6\eta R + 5(\eta R)^2 + 2(\eta R)^3 + (\eta R)^4]d\eta. \quad (3)$$

We have made use of the fact that the integrand is analytical and that $\alpha_i(\Omega)$ is purely real on the imaginary axis $\Omega = ic\eta$. Equation (3) is the celebrated

Casimir–Polder potential valid for any interparticle separations $R = |\mathbf{r}_1 - \mathbf{r}_2|$. It is a well-known exercise to evaluate the potential for the limiting cases of large and small interparticle distances, see, e.g., [1,13,15]. For short distances the potential is referred to as the van der Waals potential and depends on the dispersive properties of the particle polarizabilities. In this regime it scales with the inverse sixth power of the particle separation R. In the large distance limit one obtains an inverse seventh power distance dependence [14]. In this limit, the potential depends only on the static ($\omega = 0$) polarizabilities of the particles, and hence it does not matter what their spectral properties are.

We now consider the Casimir–Polder potential between two identical nanoparticles with radii a. As long as the particles are larger than the electron mean-free path their linear response can be represented by a local, but dispersive, dielectric constant $\varepsilon(\omega)$. We first assume that ε is given by a general single Lorentzian function as

$$\varepsilon(\omega) = 1 + \omega_p^2 / [\omega_0^2 - \omega^2 - i\gamma\omega], \qquad (4)$$

where ω_p is the plasma frequency, ω_0 is a resonance (transition) frequency, and γ is a damping constant (decay rate). The polarizability can be represented in the quasi-static limit as

$$\alpha(\omega) = 4\pi\varepsilon_0 a^3 [(\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 2)], \qquad (5)$$

where we assumed that the particle is surrounded by vacuum ($\varepsilon = 1$). To evaluate the Casimir–Polder potential according to Eq. (3) we need to express α in terms of the imaginary frequency $ic\eta$. Combining the expressions for ε and α, and defining $\tilde{\alpha} = \alpha(4\pi\varepsilon_0 a^3)^{-1}$ we obtain

$$\tilde{\alpha}(ic\eta) = \frac{\omega_p^2}{\omega_p^2 + [3\omega_0^2 + 3c\eta(c\eta + \gamma)]}. \qquad (6)$$

Obviously, for any value of η in the range $[0\ldots\infty]$ this expression is smaller than one. For $\eta \to 0$, the maximum value is obtained for $\omega_0 = 0$, i.e., a Drude metal. Hence we can expect that the Casimir–Polder potential is stronger for metal particles than for dielectric particles.

We now set $d = R - 2a$, with d being the interparticle distance, expand a^6/R^6 for small d, and get the following asymptotic value:

$$\max[U] = -\frac{3\hbar c}{64\pi} \int_0^\infty \tilde{\alpha}_1(ic\eta)\tilde{\alpha}_2(ic\eta)d\eta \approx -\frac{\sqrt{3}}{256}\hbar\omega_p, \qquad (7)$$

where, in the last step, we assumed that $\gamma \ll \omega_p$.

Equation (7) is a very interesting result as it predicts that the order of magnitude of the interaction potential between two nanoparticles at short distance is solely defined by the plasma frequency. The latter is a function of electron density n and effective electron mass m_e according to $\omega_p = \sqrt{ne^2/(m_e\varepsilon_0)}$. For semiconductors, ω_p is typically in the infrared

whereas for noble metals it is in the visible spectrum and in the UV. For gold $\hbar\omega_p \approx 9.1$ eV and for aluminum $\hbar\omega_p \approx 15.2$ eV. With these values the maximum interaction potential for metal nanoparticles is in the range of $\max[U] = -[1\ldots4]k_BT$ ($T = 300$ K). This is comparable to the energy associated with hydrogen bonds, slightly stronger than molecular van der Waals bonds ($\approx 0.5k_BT$), and much weaker than typical covalent bonds ($\approx 20k_BT$). As an example, Fig. 1 shows the interaction potential between two gold particles with radii $a = 10$ nm. The curves are normalized with the thermal energy k_BT.

In contrast to the Casimir–Polder potential, the light-induced potential can be significantly enhanced by plasmon resonances [5,7,8,12]. Let us consider a particle pair with polarizabilities α_1 and α_2 located at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. The light-induced potential experienced by the particle at $\mathbf{r}_1$ is [1]

$$U_g(\mathbf{r}_1, \mathbf{r}_2; \omega) = -(1/4)\mathrm{Re}\{\alpha_1(\omega)\}|\mathbf{E}(\mathbf{r}_1; \omega)|^2, \qquad (8)$$

where $\mathbf{E}$ is the complex amplitude of the local electric field. The latter is excited by an incident radiation field $\mathbf{E}_0$ oscillating at frequency ω. The local field can be expressed in terms of a series of interactions of different orders, i.e.,

$$\mathbf{E}(\mathbf{r}_1) = \mathbf{E}_0(\mathbf{r}_1) + \frac{\omega^2}{c^2\varepsilon_0}\overleftrightarrow{\mathbf{G}}^o(\mathbf{r}_1, \mathbf{r}_2)\alpha_2(\omega)\mathbf{E}_0(\mathbf{r}_2)$$

$$+ \frac{\omega^4}{c^4\varepsilon_0^2}\overleftrightarrow{\mathbf{G}}^o(\mathbf{r}_1, \mathbf{r}_2)\alpha_2(\omega)\overleftrightarrow{\mathbf{G}}^o(\mathbf{r}_2, \mathbf{r}_1)\alpha_1(\omega)\mathbf{E}_0(\mathbf{r}_1)$$

$$+ \cdots. \qquad (9)$$

The first term (zero order) ignores the presence of the second particle at $\mathbf{r}_2$ and accounts only for the radiation field. The second term (first order) denotes the field scattered from the second particle. The third term (second order) would be the scattered field from the first particle that is then rescattered by the second particle. The interaction order increases by one for every subsequent term. For simplicity, we con-
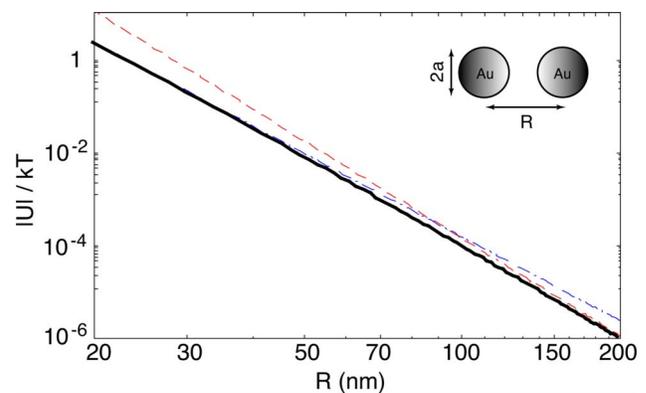

Fig. 1. (Color online) Casimir–Polder potential $U(R)$ between two gold nanoparticles with radii $a = 10$ nm. The potential is normalized with the thermal energy k_BT ($T = 300$ K). The dashed curves indicate the van der Waals potential ($\propto R^{-6}$) and the Casimir potential ($\propto R^{-7}$), respectively. The two lines intersect at $R \approx 90$ nm.

sider an incident field polarized along the particle–particle axis. Choosing $\alpha_1 = \alpha_2 = \alpha$, the series [Eq. (9)] for the local field can be resummed to give

$$E(R) = E_0 \sum_{n=0}^{\infty} (2\tilde{\alpha})^n e^{nikR} (a/R)^{3n} (1 - ikR)^n$$

$$= \frac{E_0}{1 - 2\tilde{\alpha} e^{ikR} (a/R)^3 (1 - ikR)}, \qquad (10)$$

where $\tilde{\alpha} = \alpha (4\pi\varepsilon_0 a^3)^{-1}$. This result is correct as long as the series converges. For very short distances $kR \ll 1$ this requires that $|2\tilde{\alpha}(a/R)^3| < 1$. The shortest distance is $R = 2a$, and hence $|\tilde{\alpha}| < 4$. For a gold particle, the maximum value of $|\tilde{\alpha}|$ is 1.74 and occurs at a wavelength of $\lambda = 526$ nm. Thus Eq. (10) is an accurate expression for the local field for all distances R.

Inserting the expression for $E(R)$ into Eq. (8), subtracting the potential at infinity $U_g(R \to \infty)$, and considering $kR \ll 1$ yields

$$U_g(R) = - |E_0|^2 \operatorname{Re}\{\alpha\}$$

$$\times \left[\frac{\operatorname{Re}\{\tilde{\alpha}\}(a/R)^3 - |\tilde{\alpha}|^2 (a/R)^6}{1 - 4 \operatorname{Re}\{\tilde{\alpha}\}(a/R)^3 + 4|\tilde{\alpha}|^2 (a/R)^6} \right] \quad |\tilde{\alpha}| < 4.$$

$$(11)$$

Because the result is proportional to $\operatorname{Re}\{\alpha\}$ the light-induced potential scales with a^3. Figure 2 shows $U_g(R)$ for a pair of $a = 10$ nm gold nanoparticles ($\lambda = 535$ nm). It is evident that the light-induced potential decays much slower compared to the Casimir–Polder potential. U_g scales roughly with R^{-3}. This slower decay makes the light-induced force important at larger particle separations. At contact ($R = 2a$), a light intensity of $I_0 = 80$ mW/μm^2 is needed for the potential between two gold particles ($a = 10$ nm) to be equal to $k_B T$. Such intensities are
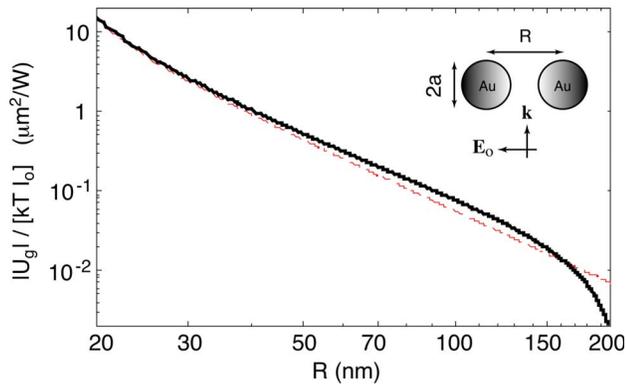

Fig. 2. (Color online) Light-induced potential $U_g(R)$ between two gold nanoparticles with radii $a = 10$ nm irradiated with $\lambda = 535$ nm. The potential is normalized with the thermal energy $k_B T$ ($T = 300$ K) and with the incident intensity $I_0 = (1/2)\varepsilon_0 c |E_0|^2$. The dashed curve follows from the approximation $kR \ll 1$ [Eq. (11)].

much stronger than typical background radiation. It is interesting to note that to the blue side of the particle plasmon resonance, the real part of the polarizability can become negative. For example, for silver $\operatorname{Re}\{\alpha(\lambda = 350 \text{ nm})\} = -3.9$. The balance between the attractive Casimir–Polder force and the repulsive light-induced force could be employed to generate a stable trap.

In conclusion, we have evaluated the van der Waals and light-induced potential between two metal nanoparticles and found an interaction energy proportional to the plasma frequency (with a small prefactor) that is comparable to the thermal energy at $T = 300$ K. Both potentials can be represented by simple analytical expressions, which provide an efficient means to estimate critical parameters in new schemes of optical manipulation and activation. In principle, our model allows us to incorporate higher-order corrections by adding additional interaction orders to the Green's function in Eq. (2) and including higher multipoles in Eq. (9). Higher multipoles, not included here, are expected to become important near the contact point.

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