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# VAN DER WAALS INTERACTION BETWEEN SPHERICAL METALLIC NANOPARTICLES WITH MUTUALLY INDUCED POLARIZATION

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*An influence of multipole plasmonic resonances, excited on the surface of the spherical metallic nanoparticles, on van der Waals interaction between nanoparticles is investigated in this work. The relations for the size dependences of the interaction free energy, Hamaker parameter and van der Waals force are obtained. It is shown that the improper integral, included in the obtained expressions, is convergent, and the sum is easily calculated due to the fast convergence of the series at increasing multipolarity. The calculations were performed for the case of interaction between spherical nanoparticles of the different radii and different metals in air, on the surface of which the localized plasmonic resonances are excited. It is found that the increase in the distance between the nanoparticles results in the decrease in free energy and van der Waals force and in the increase in Hamaker parameter. In turn, the free energy practically does not change with the change of nanoparticle material and increases sharply with the increase in radius of nanoparticles. In contrast to the free energy, the increase in the nanoparticle radius results in the decrease in Hamaker parameter. The decrease in Hamaker parameter at the same distance between particles takes place when changing their composition (using metals with decreasing plasma frequency). The distance between nanoparticles, at which the sharp decrease in van der Waals force changes to the smooth one, has been determined. The comparison of the calculation results with the case of van der Waals interaction between spherical nanoparticles, caused by electromagnetic fluctuations with the continuous spectrum, is carried out. It is shown that the qualitative character of the size dependences of the free energy and Hamaker parameter remains the same: the free energy decreases and Hamaker parameter increases with increasing distance between interacting nanoparticles. At the same time in the case of the particles with the localized plasmons, excited on their surfaces, the free energy is greater and Hamaker parameter is less than in the case of electromagnetic fluctuations with the continuous spectrum.*

***Keywords****: van der Waals interaction, surface plasmonic resonance, free energy, Hamaker parameter, spherical metallic nanoparticles*

## INTRODUCTION

An interest in the study of the interaction between metallic nanoparticles has increased significantly in the recent decades. This is due to the fact that the enhanced and locally confined optical fields, associated with nanoparticles, nanostructures and their aggregates, enable nanoscale manipulation of the active devices [1, 2], antennas [3, 4], surface-enhanced Raman spectroscopy [5], light trapping [6] *etc*. This phenomenon is obviously associated with multipole fields, resonances and their hybridization [7, 8], charge accumulation in the narrow nanogaps and quantum tunnelling inside nanodimers [9–14]. All these processes are controlled by the localized plasmons.

The nanoparticles of plasmonic metals (Ag, Au, Cu and the others), are widely used due to the excitation of the surface plasmonic resonances (SPR) on their surfaces [15], which are determined by the chemical composition, size, shape of the particles and by the surrounding dielectrics [16]. When plasmonic nanoparticles self-organise in the close proximity to each other, surface plasmons interact, resulting in the shift of the initial plasmonic bandwidth [17]. The plasmonic coupling can be tuned to cover the wide range of spectra depending on morphology and size of the assembled structures. Such spectral

tuning has significant potential for many light-related applications [15, 18], including colourimetric sensing [19], spectroscopic detection [20], photocatalysis [21, 22], plasmonic rulers [23, 24], optical devices [25], nanomedicine [26] and biosensorics [27].

It is known that the interaction between the nanoparticles during their self-assembly is largely determined by van der Waals force, which depends on the polarizability of nanoparticles. In turn, the character of the frequency dependence of the polarizability of nanoparticles is determined by the localized plasmonic resonances, excited on their surface.

In connection with the above, the tasks connected with the study of the influence of multipole SPR on van der Waals interaction between the spherical nanoparticles, as well as the comparison of the obtained results with the case of the continuous spectrum of electromagnetic fluctuations, considered earlier [28], are actual.

## BASIC RELATIONS

Let us consider van der Waals interaction between two spherical metallic nanoparticles, which are located at the distance $d$ with the multipole plasmonic modes excited on their surface. Let us assume that the nanoparticles are of same metal and have the same radius $R$ (Fig. 1).

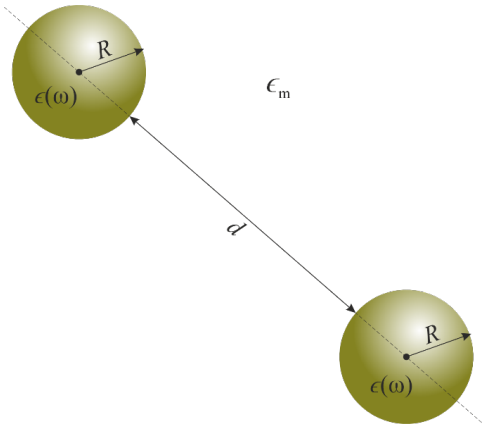


**Fig. 1.** Geometry of the problem

The starting point for the analysis is the following formula for the free energy of van der Waals interaction between spherical nanoparticles [28]

$$F(d)=-\frac{\hbar\omega_p V R^6}{9\pi^4}\sum_{l=1}^{\infty}\left(\epsilon(\mathrm{i}\omega_l)-\right.$$

$$\left.-\epsilon_{\mathrm{m}}\right)^2\int_0^{\infty}\frac{k^8K_1^2(kd)\,dk}{\left[\frac{(kR)^2}{6}\epsilon(\mathrm{i}\omega_l)+(2+kR)\epsilon_{\mathrm{m}}\right]^2}, \qquad (1)$$

where $\omega_p$ is the plasma frequency; $V$ is the volume of the system; $k$ is the wave number; $K_1(x)$ is the first-order McDonald function; $\epsilon_{\mathrm{m}}$ is the dielectric permittivity of medium, in which the nanoparticles are located; $\epsilon(\mathrm{i}\omega_l)$ is the law of dispersion of eigen (multipole) modes of the system.

It should be pointed out that formula (1) follows from the more general relation for work [28]

$$F(d)=k_{\mathrm{B}}TV\sum_{n=0}^{\infty}{}'\int_{-\infty}^{+\infty}\frac{d\mathbf{k}}{(2\pi)^3}\ln\det\left(\hat{\mathbf{I}}-\hat{\mathbf{L}}(\mathrm{i}\omega_n,k)\right), \qquad (2)$$

where the integration is carried out over the whole spherical $\mathbf{k}$-space; $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the temperature, $\hat{\mathbf{I}}$ is the unit operator, and operator matrix $\hat{\mathbf{L}}$ has the form

$$L_{lm}=\sum_{p=-\infty}^{+\infty}\Delta_{lm}(k,\mathrm{i}\omega_n)\Delta_{2p}(k,\mathrm{i}\omega_n)K_{m+p+1}(kd)K_{l+p+1}(kd), \qquad (3)$$

if two conditions are fulfilled:

1) the distance between nanoparticles is significantly greater than their radius $R/d << 1$;

2) the wave parameter is small ($kR << 1$ that corresponds to the quasi-static character of the considered processes.

Taking into account the condition of multipole surface plasmonic resonance for the spherical particle

$$\epsilon\left(\omega_{sp}^{l}\right) = -\frac{l+1}{l}\epsilon_{\mathrm{m}}, \tag{4}$$

and introducing the dimensionless integration variable $x = kd$, we obtain

$$F(d) = -\frac{\hbar\omega_p V R^6}{9\pi^4 d^9}\int_0^\infty dx \sum_{l=1}^{\infty}\left(\frac{2l+1}{l}\frac{x^4 K_1(x)}{\frac{1}{6}\frac{R^2}{d^2}x^2\frac{l+1}{l}-\frac{R}{d}x-2}\right)^2. \tag{5}$$

The expression (5) can be written down in more compact form, which is convenient for the numerical calculations of the size dependence for the free energy

$$F(d) = -\frac{16\hbar\omega_p}{3\pi^4}\frac{R^5}{d^5}\sum_{l=1}^{\infty}\left(\frac{2l+1}{l+1}\right)^2 \mathcal{I}_l\left(\frac{d}{R}\right), \tag{6}$$

where

$$\mathcal{I}_l\left(\frac{d}{R}\right) = \int_0^\infty \frac{x^8 K_1^2(x)\,dx}{\left(x-x_1^l\right)^2\left(x-x_2^l\right)^2}, \tag{7}$$

and

$$x_{1,2}^{l} = \frac{\sqrt{3l}}{l+1}\left(\sqrt{3l} \pm \sqrt{7l+4}\right)\frac{d}{R}. \tag{8}$$

An important characteristic of the energy of van der Waals interaction between nanoparticles is Hamaker parameter, which is related to the free energy as follows

$$F(d) = -\frac{16}{9}\mathcal{A}_{\mathrm{H}}\frac{R^6}{d^9}V. \tag{9}$$

Substituting the relation (6) into (9), we obtain the final expression for the size dependence of Hamaker parameter

$$\mathcal{A}_{\mathrm{H}}(d) = \frac{9\hbar\omega_p}{8\pi^4}\frac{d^4}{R^4}\sum_{l=1}^{\infty}\left(\frac{2l+1}{l+1}\right)^2 \mathcal{I}_l\left(\frac{d}{R}\right). \tag{10}$$

The size dependence of van der Waals force can be determined knowing Hamaker parameter and using the relation

$$\mathscr{F}(d) = -\frac{\mathcal{A}_{\mathrm{H}} R}{12 d^2}. \tag{11}$$

Substituting (10) into (11), we finally obtain

$$\mathscr{F}(d) = -\frac{3\hbar\omega_p}{16\pi^4}\frac{d^2}{R^3}\sum_{l=1}^{\infty}\left(\frac{2l+1}{l+1}\right)^2 \mathcal{I}_l\left(\frac{d}{R}\right). \tag{12}$$

The relations (6), (10) and (12), taking into account formulas (7) and (8), are used to obtain the numerical results.

## CALCULATION RESULTS AND THEIR DISCUSSION

The calculations have been performed for the case of van der Waals interaction between spherical nanoparticles of different metals in air ($\epsilon_{\mathrm{m}} = 1$). The parameters of materials, required for the calculations, are given in Table 1.

**Table 1.** Parameters of metals (see, for example, [29, 30] and references therein)

| Parameters \ Metals | Au | Ag | Cu | Pd | Pt | Al |
|---|---|---|---|---|---|---|
| $n_e$, $10^{22}$ cm$^{-3}$ | 5.91 | 5.85 | 17.2 | 2.53 | 9.1 | 18.2 |
| $\epsilon^{\infty}$ | 9.84 | 3.70 | 12.03 | 2.52 | 4.42 | 0.7 |
| $\hbar\omega_p$, eV | 9.07 | 9.17 | 12.6 | 9.7 | 15.2 | 15.4 |
| $\hbar\gamma_{\mathrm{bulk}}$, eV | 0.023 | 0.016 | 0.024 | 0.091 | 0.069 | 0.082 |
| $v_{\mathrm{F}}$, $10^6$ m/s | 1.41 | 1.49 | 1.34 | 2.84 | 2.98 | 1.91 |

Before we start to discuss the numerical results, let us make a remark concerning the calculation of the improper integral and the sum in the expressions (6), (10) and (12). Since $I_l(x)\to 0$ under $x\to 0$ and $K_1(x)\to 0$ under $x\to\infty$ (and, respectively, $I_l(x)\to 0$), then the improper

integral is convergent and has the finite value for the arbitrary multipolarity $l$. In turn, the sum will have the finite number of addends, which are significantly different from zero, and therefore its calculation will not be difficult. This fact can be explained by the significant decrease in the contribution with increasing multipolarity.

The dependences of the free energy of van der Waals interaction on the distance between nanoparticles Au of the different radius and nanoparticles of different metals and the same radius are given in Fig. 2. The calculation results indicate the significant decrease in the free energy under the increase in the distance between nanoparticles in all considered cases. Moreover, all calculated curves are qualitatively similar, differing strongly (by 2–3 orders of magnitude) quantitatively for van der Waals interaction between nanoparticles of different radii and practically not differing for nanoparticles of the same radius and different metals.

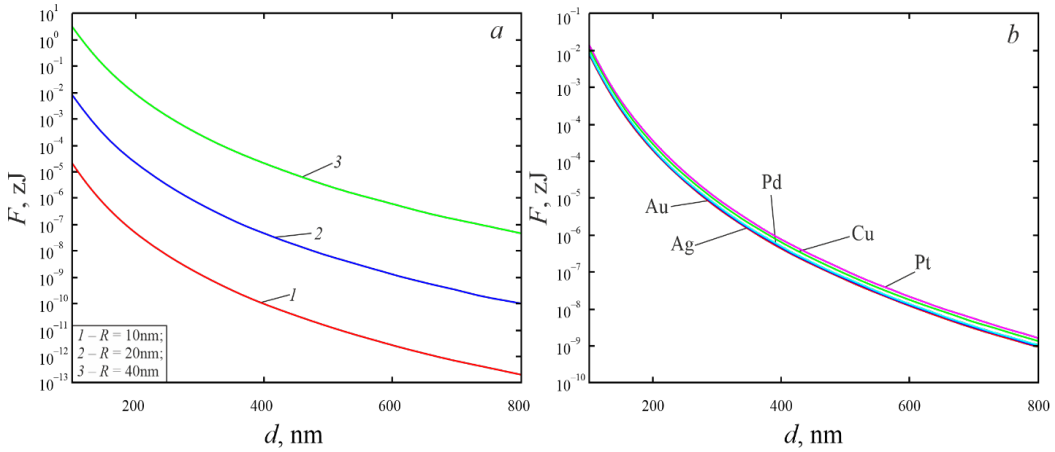


**Fig. 2.** The dependences of the free energy of van der Waals interaction between two spherical nanoparticles Au of the different size (*a*) and nanoparticles of different metals with $R$ = 20 nm (*b*) on the distance between them

The curves for the size dependences of Hamaker parameter are given in Fig. 3. These curves are also qualitatively similar, and Hamaker parameter increases under the increase in the distance between the particles. Let us point out that for the interacting particles, at the same distance from each other, Hamaker parameter is greater for the particles with the smaller radius, and in the case of the nanoparticles of the different composition Hamaker parameter increases in the sequence of metals Au→Ag→Pd→Cu→Pt.

As for the size dependence of van der Waals force (Fig. 4), we note the following: this force in all considered cases decreases with increasing distance between nanoparticles, and this decrease is very sharp under $d \leq 200$ nm in contrast to the smooth decrease under $d \geq 200$ nm.

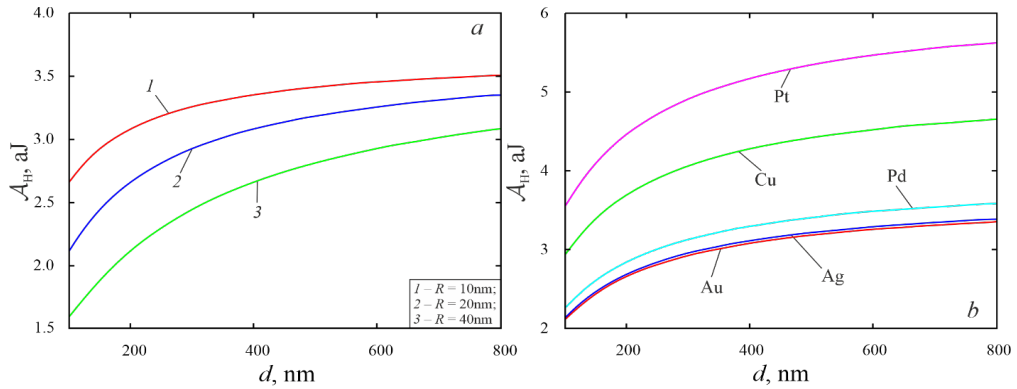


**Fig. 3.** The dependences of Hamaker parameter for two spherical nanoparticle Au of the different size (*a*) and nanoparticles of different metals with $R$ = 20 nm (*b*) on the distance between them

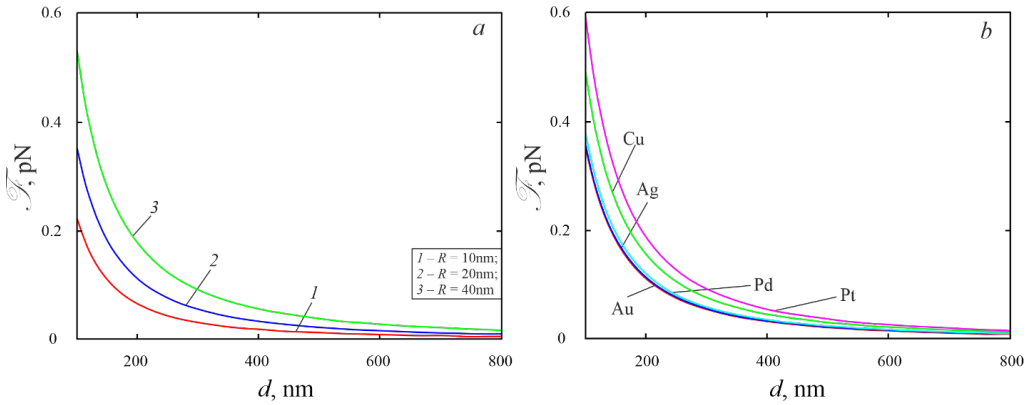


**Fig. 4.** The dependences of van der Waals force of the interaction between two spherical nanoparticles Au of the different size (*a*) and nanoparticles of different metals with $R = 20$ nm (*b*) on the distance between them

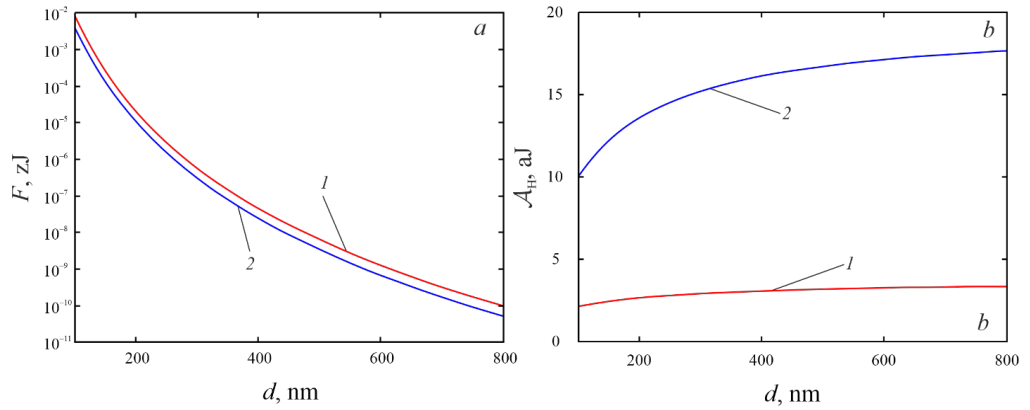


**Fig. 5.** The dependences of the free energy (*a*) and Hamaker parameter (*b*) on the distance between nanoparticles Au with $R = 20$ nm: *1* – discrete spectrum; *2* – continuous spectrum

The comparison of the obtained results with the case of electromagnetic fluctuations with the continuous spectrum, considered in [28], is of interest. The comparison has been performed for the case of van der Waals interaction between nanoparticles Au. The calculation results (Fig. 5) demonstrate that the character of the size dependences of the free energy and Hamaker parameter does not change qualitatively, but the free energy is greater for any distance between nanoparticles under the excitation of multipole surface plasmonic resonances. In turn, Hamaker parameter is greater when plasmonic resonances are not excited.

## CONCLUSIONS

The size dependences for the free energy, Hamaker parameter and van der Waals force have been obtained for the case of the interaction between spherical metallic nanoparticles with the localized multipole plasmonic resonances, excited on their surface.

The calculation results indicate the decrease in the free energy of van der Waals interaction under the increase in the distance between the nanoparticles. At the same time, the value of the free energy for nanoparticles of different radii differs by 2–3 orders of magnitude, while the change in the material of nanoparticles practically does not affect the change in the free energy.

It has been shown that, in contrast to the free energy, Hamaker parameter increases with increasing distance between the interacting nanoparticles, and Hamaker parameter increases with decreasing radius at the same distance between particles.

It is demonstrated that van der Waals force decreases sharply until the distance between nanoparticles is reached $d \approx 200$ nm, and decreases more slowly under the larger distances.

The results for the continuous spectrum of electromagnetic fluctuations, obtained earlier, and the results for the particles with the excited

multipole plasmonic modes (discrete spectrum) have been compared. It has been found that the character of the curves for the size dependences of the free energy and Hamaker parameter does not change, but for interacting Au nanoparticles with the plasmonic resonances, excited on their surface, at arbitrary distance between the particles the free energy is greater and Hamaker parameter is less than for the case of electromagnetic fluctuations with the continuous spectrum.

## Ван-дер-Ваальсівська взаємодія сферичних металевих наночастинок із взаємно індукованою поляризацією

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*В роботі досліджено вплив збуджених на поверхні сферичних металевих наночастинок мультипольних плазмонних резонансів на Ван-дер-Ваальсівську взаємодію між наночастинками. Отримано співвідношення для розмірних залежностей вільної енергії взаємодії, параметра Гамакера та сили Ван-дер-Ваальса. Показано, що невласний інтеграл, що входить в отримані вирази, є схожим, а сума легко обчислюється внаслідок швидкої збіжності ряду зі збільшенням мультипольності. Розрахунки проводилися для випадку взаємодії сферичних наночастинок різного радіуса та різних металів, що знаходяться у повітрі, на поверхні яких збуджено локалізовані плазмонні резонанси. Встановлено, що вільна енергія та сила Ван-дер-Ваальса зменшуються, а параметр Гамакера збільшується зі збільшенням відстані між наночастинками. У свою чергу, вільна енергія практично не змінюється при зміні матеріалу наночастинок і різко зростає зі збільшенням їхнього радіуса. На відміну від вільної енергії, параметр Гамакера зменшується зі збільшенням радіуса наночастинок. Зменшення параметра Гамакера за однакової відстані між частинками має місце при зміні їхнього складу (використання металів із плазмовою частотою, що зменшується). Визначено відстань між наночастинками, за якої різке зменшення сили Ван-дер-Ваальса змінюється на плавне. Проведено порівняння результатів розрахунків із випадком Ван-дер-Ваальсівської взаємодії сферичних наночастинок, викликаної електромагнітними флуктуаціями з неперервним спектром. Показано, що якісний характер розмірних залежностей вільної енергії та параметра Гамакера зберігається: вільна енергія зменшується, а параметр Гамакера збільшується зі зростанням відстані між наночастинками, що взаємодіють. При цьому у випадку частинок із збудженими на їхніх поверхнях локалізованими плазмонами вільна енергія більша, а параметр Гамакера менший, ніж у випадку електромагнітних флуктуацій із неперервним спектром.*

***Ключові слова**: взаємодія Ван-дер-Ваальса, поверхневий плазмонний резонанс, вільна енергія, параметр Гамакера, сферичні металеві наночастинки*

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