Van der Waals interaction between surface and particle with giant polarizability

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Abstract. We show that a nanoparticle with a “giant” polarizability $\alpha$ (i.e., with the polarizability volume $\alpha' = \alpha/4\varepsilon_0$ significantly exceeding the particle volume) placed in the vicinity of a surface experiences a strongly increased van der Waals force at distances comparable or smaller than the characteristic scale $R_0 \propto (\alpha')^{1/3}$. At distances close to $R_0$, the oscillation mode of the particle dipole moment softens, so nonlinear polarizability must be taken into account to describe the particle-surface interaction. It is shown that a proper treatment of nonlinear effects results in the van der Waals force that is free of divergences and repulsive contributions.

Keywords: van der Waals interaction, nonlinear polarizability, giant polarizability, hard mode, soft mode.

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1. Introduction

Although van der Waals forces are usually too small to play significant role in interactions between macroscopically large objects, they can become dominant at nanoscale. For example, van der Waals forces are responsible for self-assembly of molecules and nanoparticle arrays, which have been actively studied in recent years [1-4]. In this work, we revisit the well-known problem of the van der Waals interaction between surface and nanoparticle, focusing on the previously unexplored case of a particle with giant polarizability. Here, the term “giant” means that the polarizability volume is significantly larger than the effective volume of the nanoparticle. Lately, giant polarizability has been observed in Na$_14$F$_{13}$ molecular clusters and in a number of other alkali-halide clusters with M$_n$X$_{n-1}$ composition [5, 6]. The polarizability volume of these clusters may be up to 30 times larger than the effective volume of the cluster. Another example could be nanoparticles made of ferroelectric materials, under the conditions close to the ferroelectric transition. We will show that the van der Waals force between a surface and a nanoparticle with a giant polarizability $\alpha$ increases significantly comparing to the standard result when the distance between the particle and surface becomes smaller than the certain characteristic scale $R_0 \propto (\alpha/\varepsilon_0)^{1/3}$, where $\varepsilon_0$ is the vacuum permittivity. The reason for this behavior is softening one of the dipole oscillation modes, which occurs at distances close to $R_0$. Within the description including only the linear part of the polarizability, this softening signals an instability (and would lead to a divergence in the van der Waals force). This implies the necessity to take into account the nonlinear polarizability, which would lead to stabilization of the system.

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A similar setup, considering interaction of a nonlinearly polarizable ellipsoidal nanoparticle with a surface or with another nanoparticle has been recently studied in several articles [7-9]. According to the results of Refs. [7, 8], nonlinearity generates repulsive contributions to the van der Waals force that become dominant at small distances and lead to the emergence of a minimum in the total van der Waals potential at distances about $R_0$. However, nonlinear contributions in Refs. [7, 8] have been taken into account only perturbatively. In our previous paper [9], we have considered interaction between two point-like nanoparticles with giant polarizability, and have concluded that a careful treatment of nonlinearity does not lead to repulsive forces: on the contrary, the van der Waals force is strongly enhanced at distances less or about $R_0$, remaining purely attractive at the same time. In this paper, we show that essentially the same conclusion remains valid in the case of a particle interacting with a surface. We argue that the appearance of the repulsive component in the van der Waals force, reported in Refs. [7, 8] is an artifact of the weak coupling perturbation theory.

2. Model and its analysis in harmonic approximation

We consider an isotropic point-like particle placed in a medium with the relative permittivity $\varepsilon_m$ at distance $R$ from the surface of a substrate (infinitely thick) with the relative permittivity $\varepsilon_s$ (see Fig. 1). The case of a metallic substrate can be obtained by formally setting $\varepsilon_s = -\infty$. We assume that the particle has a linear polarizability $\alpha$ and third-order nonlinear polarizability $-\beta$. We further assume that the particle has an inversion center, so the second-order nonlinear polarizability vanishes, and we set $\beta > 0$ to ensure stability, so the response of the dipole moment $\vec{d}$ of the particle to the local field $\vec{E}$ is described by the expression $\vec{d} = \alpha \vec{E} - \beta \vec{E}^2 \vec{E}$.

![Fig. 1. Schematic view of the system considered: a point-like polarizable particle at the distance $R$ from the interface between two media with different relative permittivities.](image)

We are primarily interested in the case of small distances $R << c/\omega_{s,m}$, where $\omega_s(\omega_m)$ are the characteristic frequencies of the polarization oscillations in the substrate (medium), and the characteristic frequency of the dipole oscillations $\omega_0$ of the particle is supposed to be much smaller than $\omega_{s,m}$. Thus, the retardation effects can be safely neglected. We further assume that nonlinear polarizabilities of both media are small as compared to the nonlinear polarizability of the particle and can be neglected.

In absence of retardation, interaction between the particle and surface can be conveniently described by the method of image charges [10]. If the dipole moment of particle is $\vec{d}(d_x, d_y, d_z)$, with $z$ axis perpendicular to the surface, then the image dipole situated at a distance $R$ below the surface can be written as $\vec{d}_{im}(-kd_x, -kd_y, kd_z)$, where $k = \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s}$. Then, the energy of the system can be written as:

$$E(\vec{d}, R) = \frac{\vec{d}^2}{2\alpha} + \frac{\beta \vec{d}^4}{4\alpha^4} + \frac{\vec{d}^2}{2\omega_0^2} + \frac{1}{32\pi\varepsilon_0\varepsilon_m R^3}\left(\vec{d} \cdot \vec{d}_{im} - 3(\vec{n} \cdot \vec{d})(\vec{n} \cdot \vec{d}_{im})\right),$$

(1)

where $\vec{n} = \vec{R}/R$ is the unit vector along $z$ axis. The minimum of the energy determined by Eq. (1) is reached for $\vec{d} = \pm p_0 \vec{n}$, where, as we shall see below, the “equilibrium” value $p_0$ depends on the distance $R$. Considering small harmonic fluctuations, we write $\vec{d} = \pm p_0 \vec{n} + \hat{p}$, where $\hat{p}(p_x, p_y, p_z)$ describes the fluctuations around $p_0$. A standard quantization procedure yields the following Hamiltonian of the system described by Eq. (1):

$$\hat{H} = E(p_0) + \sum_{i=x,y,z} \left(\frac{\pi_i^2}{2m} + \frac{m \omega_i^2 p_i^2}{2}\right) + \frac{\beta p_0}{\alpha^4} \hat{p}_z^2 + \frac{\beta}{4\alpha^7} (\hat{p}^2)^2,$$

(2)

where $\hat{p}_i$ are the momenta, canonically conjugate to the fluctuations $\hat{p}_i$, $E(p_0)$ is the “static” part of the energy (see below), and for convenience we have introduced the “effective mass” $m = \left(\alpha \omega_0^2\right)^{-1}$. Further, $\omega_i$ are the harmonic normal mode frequencies of the dipole fluctuations.
The equilibrium dipole value $p_0$ and the corresponding static energy can be obtained by the minimization of $E(p_0)$, which yields the following expressions:

$$p_0 = \begin{cases} \frac{\alpha^2}{3\beta R_0} (s-1), & R > R_0(s < 1), \\ 0, & R < R_0(s < 1). \end{cases}$$

$$E(p_0) = \begin{cases} 0, & R > R_0(s < 1), \\ \frac{\alpha^2}{4\beta}(s-1)^2, & R < R_0(s > 1). \end{cases}$$

(5)

that are valid only when $p_0$ is small as compared to $p_m$ (i.e., when $(s-1) << 1$). Far from the softening point, anharmonic terms can be neglected, and one can obtain the Hamiltonian in the second quantization terms in the harmonic approximation:
z-mode), which leads to a divergence in the van der Waals force $F = -\partial E_{\text{harm}}/\partial R$ at $R \to R_0$, due to z-mode softening. However, fluctuations of the dipole moment become large close to the softening point, so one can expect that nonlinear terms will play an increasingly important role in proximity to this point. Further, for $R < R_0$ there are two energetically equivalent states $d = \pm \rho_0$, which are separated by a barrier that vanishes at $R \to R_0$. Therefore, when $R$ is just slightly smaller than $R_0$, tunneling processes between these states become dominant (and also determined by the nonlinear terms). It means that the naive harmonic approximation is not applicable in the close vicinity of the softening point.

3. Effect of nonlinear polarizability

3.1. Weak coupling regime: perturbation theory

Consider first the corrections coming from the last two terms in the Hamiltonian described by Eq. (2). It makes sense, if the system is far from the softening point. In this regime, all modes are “hard”, so one can simply calculate the leading corrections using the first-order perturbation theory in $\lambda$ (for this calculation, we assume that $\lambda << 1$, otherwise the perturbative approach is completely inapplicable). The corrections can be easily obtained using the following averages:

$$\langle p_i^4 \rangle = 3 \langle p_i^2 \rangle^2 = 3 \left( \frac{\hbar}{2 \omega_0} \right)^2,$$

We shall see below, the proper description in the vicinity of the softening point does not exhibit any repulsive contributions, so this minimum should be regarded as an artifact of the perturbation theory. Moreover, including the perturbative corrections in $\lambda$ would add increasingly more and more singular contributions (diverging at $R = R_0$), with alternating signs.

3.2. Weakly nonlinear double-well regime occurs when $(s - 1)^{1/2} >> \lambda$. Similarly to the previous case, this condition ensures that z-mode remains “hard” and can be treated perturbatively. In this case, the potential for the dipole moment is of a double-well type (see Fig. 3, large dashes) and the ground state energy, with the account taken of corrections from nonlinear terms, has the form

$$E_{\text{wav}} = \frac{1}{2} \hbar \omega_0 \left( \sqrt{1 - s} + \sqrt{1 - s + \lambda (f_1(s) + f_2(s))} \right),$$

where we have introduced the following notation:

$$f_1(s) = \frac{3}{8} \frac{\omega_0}{\omega_s} \frac{\partial^2}{\partial s^2},$$

$$f_2(s) = \frac{\omega_0}{\omega_s}^2.$$
Here the frequencies for correction functions $f_1(s)$ should be taken from Eq. (3) for the case when $R < R_0$ ($s > 1$). Since $p_0$ should be small comparing to the $p_{fi}$, one has to require that $(s - 1) << 1$, so the theory is applicable only to a small range of $R$ values.

### 3.2. Strong coupling expansion

When $|1 - s|^{1/2} < \lambda$, one may speak of the strongly nonlinear regime, corresponding to a proximity to the softening point $R = R_0$, where the potential is almost flat (dominated by nonlinear terms) for a range of dipole moments (Fig. 2, dot-dashed and solid lines). In this case, harmonic approximation is not a good starting point, and perturbation theory in $\lambda$ is no longer applicable. The dipole moment fluctuations are large (comparable to $p_0$), so it does not make sense to consider oscillations around a single-well minimum. Without expanding the dipole moment $\hat{d}$ around $p_0$, the Hamiltonian corresponding to Eq. (1) has the following form:

$$\hat{H} = \sum_{i=x,y,z} \left( \frac{\hat{d}_i^2}{2m} + \frac{m\omega_i^2\hat{d}_i^2}{2} \right) + \frac{\beta}{4\alpha^2} \left( \hat{d}_x^2 + \hat{d}_y^2 + \hat{d}_z^2 \right)^2,$$  \hspace{.5cm} (16)

$$\omega_x^2 = \omega_y^2 = \omega_0^2 \left( 1 - \frac{s}{2} \right), \hspace{1cm} \omega_z^2 = \omega_0^2 (1 - s). \hspace{1cm} (17)$$

In this regime, $x$- and $y$-modes remain “hard” and can still be treated perturbatively, but $z$-mode is “soft”. To make use of the known results for quartic oscillator, it is convenient to rewrite the Hamiltonian in dimensionless variables $\tilde{d}_i = \hat{d}_i (m\omega_0 / \hbar)^{1/2}$ and their conjugate momenta $\tilde{\pi}_i$. The Hamiltonian can be represented as a sum of “soft” and “hard” mode parts plus interaction terms, as follows:

$$\frac{\hat{H}}{\hbar\omega_0} = \tilde{\hat{H}}_0 + \tilde{\hat{H}}_0 + \tilde{\hat{H}} + \tilde{\hat{H}}^{(1)}_{int} + \tilde{\hat{H}}^{(2)}_{int},$$

$$\tilde{\hat{H}}_0 = \frac{\tilde{\pi}_i^2}{2} + \frac{g_0 \tilde{d}_z^2}{2} + \frac{g \tilde{d}_z^4}{4}, \hspace{1cm} \tilde{\hat{H}}_0 = \frac{\tilde{d}_i^2}{2m}, \hspace{1cm} i = x,y$$

$$\tilde{\hat{H}}^{(1)}_{int} = \frac{\lambda}{2} \left( \tilde{d}_x^2 + \tilde{d}_y^2 \right)^2, \hspace{1cm} \tilde{\hat{H}}^{(2)}_{int} = \frac{\lambda}{4} \left( \tilde{d}_x^2 + \tilde{d}_y^2 \right)^2.$$  \hspace{.5cm} (18)

where $g_0 = 1 - s$ and $\lambda$ are the quadratic and quartic dimensionless coupling constants.

The “soft” mode is “slow” comparing to “hard” ($d_{xy}$) modes, so we can perform averaging over the “hard” $d_{xy}$ modes, regarding the dipole moment $d_z$ corresponding to the “soft” mode as a constant. Averages of the “hard” modes can be calculated to the first order in $\lambda$ (we, as before, assume that $\lambda << 1$), in the harmonic approximation according to the formulas of the same type as Eq. (12). Such a procedure, applied to the term $\tilde{\hat{H}}^{(1)}_{int}$ describing interaction between “soft” and “hard” modes, leads to a renormalization of the quadratic coupling $g_0$:

$$g_0 \mapsto g = 1 - s + \lambda \frac{1}{\sqrt{1 - s/2}}. \hspace{1cm} (19)$$

The soft $z$-mode can be now treated using the strong-coupling expansion for quartic anharmonic oscillator [14] that is a power series in the parameter $g(4/\lambda)^{1/2}$. Then the ground state energy can be obtained as follows:

$$E_s = \frac{1}{2} \hbar\omega_0 \left( 2 + \frac{1 - s}{2} + \lambda f_2(s) \right) +$$

$$+ \hbar\omega_0 \left( \frac{\lambda}{4} \right)^{1/2} \sum_{n=0}^{\infty} c_n \left( \frac{4}{\lambda} \right)^{2/3} g^n, \hspace{1cm} (20)$$

where $c_n$ are the coefficients of the strong coupling expansion (listed in Ref. [14] up to $n = 22$), the correction involving $f_2(s)$ stems from the interaction $\tilde{\hat{H}}^{(2)}_{int}$ in Eq. (18), and the function $f_2(s)$ is given by Eq. (14) with the frequencies defined by Eq. (17). From the above results, we can see that there is actually no singularity at $s \rightarrow 1$ (at the softening point).

### 4. Discussion and summary

It is instructive to compare the above results obtained within different approximations. Fig. 3 shows the van der Waals potential calculated for a particle in vacuum ($\epsilon_r = 1$) near a metallic surface ($\epsilon_r = -\infty$), with the nonlinear coupling constant set to $\lambda = 0.005$, and Fig. 4 shows the corresponding force. One can see that harmonic approximation (Eq. (9) and Eq. (11), shown in Figs. 3 and 4 as a dotted line) works well far from the mode softening point $R = R_0$, but obviously fails in the proximity of $R_0$ (note the singularity in force), because anharmonic terms play crucial role near the softening point. Weak-coupling first-order perturbation result (Eq. (13) and Eq. (15), shown with a dash-dotted line in Figs. 3 and 4) leads to a small correction to the harmonic approximation far from the softening point, but shows unphysical divergence in the vicinity of $R_0$ (in the first order by $\lambda$, this diverging contribution happens to correspond to a repulsive force, but the sign of the divergence alternates when higher-order corrections are included). The reason for this behavior is the divergence of fluctuations at $R \rightarrow R_0$ due to the vanishing harmonic frequency of the $z$-mode (see Eq. (12)). At a formal mathematical level, one can say that the actual small parameter for the weak-coupling perturbation theory is not $\lambda$ but rather $\lambda/(1 - s)^{1/2}$, and it is not small for distances close to $R_0$ even when $\lambda << 1$. We remark that the spurious short-distance repulsion that appears in our first-order perturbation theory, strongly resembles the nonlinearity-induced repulsion obtained in Refs. [7, 8] on the basis of a quite different phenomenological

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electrodynamics approach (the essential point, though, is that the contribution of nonlinear terms to the energy has been computed to the first order in the nonlinear polarizability constant).

The results of the “hybrid” approach of Eq. (20) combining the strong-coupling expansion for the soft mode and first-order weak-coupling corrections from hard modes, including the renormalization of the quadratic coupling of the soft mode, are shown in Figs. 3 and 4 with a dashed line. One can see that this approximation complements the weak-coupling results: it fails to describe the situation far from the softening point, but gives correct results close to \( R = R_0 \). It is easy to see that if one takes the weak-coupling result far from the softening point and joins it with the strong-coupling result near \( R_0 \), one ends up with a smooth monotonic curve which is free from any singularities and describes the van der Waals interaction that remains attractive at all distances.

Comparing the standard \( 1/R^3 \) expression for the van der Waals interaction (Eq. (10), shown with solid line in Figs. 3 and 4) to the results obtained in other approaches, one can see that the standard result works well at large distances \( R >> R_0 \), but strongly underestimates the van der Waals force at distances comparable to \( R_0 \) and smaller. One can define the enhancement factor \( \eta \) as the ratio of the force calculated using appropriate formulas for each region (Eq. (13), (15), (16)) to the force calculated from the standard result (Eq. (10)):

\[
\eta = \left( \frac{\partial E/\partial R}{\partial E_{st}/\partial R} \right).
\]

This enhancement factor behaves as \( \eta \propto \lambda^{-1/3} \) in the vicinity of the softening point.

To summarize, we have shown that the van der Waals force between a particle with a giant linear polarizability \( \alpha \) and a surface is significantly enhanced at short distances of the order of \( R \propto (\alpha/\varepsilon_0)^{1/3} \). This result is derived in a simplified microscopic model assuming single-oscillator approximation for the particle and including a stabilizing third-order nonlinear polarizability. We also show that a careful treatment of nonlinearity does not lead to any repulsive forces, contrary to some recent theoretical claims [8]. This result may be important for theoretical understanding the van der Waals interactions in systems of alkali-halide molecular clusters with giant linear polarizability [5, 6].

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References


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