

# Van der Waals dispersion energy between atoms and nanoparticles

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**Abstract.** In this work, we focus on the atom-surface interaction where the geometry of the surface is highly symmetric (i.e. sphere, cylinder and plane) and the atom is in ground state. We first present the main features of our model, based on the susceptibility tensors of the two partners in interaction, to determine a general expression of the dispersive energy of van der Waals interaction. Some results are given as applications of this model which addresses recent nanophysical problems, for example, when atoms are in the vicinity of metallic nanoshells, nanospheres or nanowires.

## 1. Introduction

A great deal of effort has been devoted to the problem of microsystems such as an atom or a molecule interacting, at short or large distance, with the surface of a solid. It has been shown, both theoretically and experimentally, that the vicinity of the surface strongly modifies the dynamical properties of the atomic system, giving rise to a wide variety of ‘surface effects’, such as van der Waals (vdW) interaction, desorption energy, alteration of radiative properties, etc. More recently, the interest in this field has been renewed by the realization of micro-, meso- and nanostructures [1]. These are of various kinds but, for our purpose, they can be classified into two classes: (i) those leading to a positive curvature of the surface, such as microspheres [2] or tips of near-field microscopes (STM, AFM, etc.) [3–5]; (ii) those in which the curvature of the surface is negative, such as microcavities and porous materials [6–11], fullerenes [9], carbon nanotubes [12]. The latter class deals with the important general problem of the physics of confined atoms or molecules. Theoretical methods have been developed to calculate dispersive and inductive interactions between a microsystem and a macroscopic one treated as a continuous and homogeneous medium. A very concise and general formalism, using generalized susceptibilities [13], is particularly well-suited to treat the problem of ground state atom or molecule in the vicinity of a sphere. In this formalism, the van der Waals energies are readily calculated once the surface field gradient susceptibility tensor, is determined. The paper is organized as follows: in section 2 the problem of an atom inside a nanoshell of inner radius  $a$  and outer radius  $b$  is considered (see figure 1). The response potentials and the propagators inside the nanoshell are used to evaluate the van der Waals energy. The empty cavity is obtained by making the outer radius infinite and the case of an atom in the vicinity of a filled nanosphere is obtained by taking the limit when the inner radius goes to zero. In section 3 similar quantities as before, i.e., the response potential, the



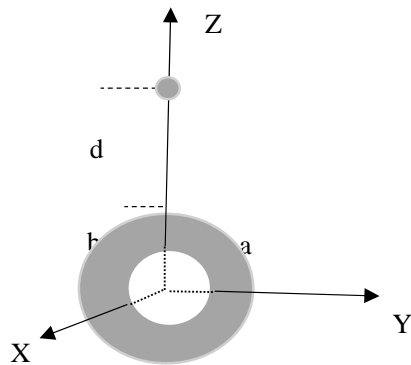
propagators outside the nanowire of radius  $a$  (see figure 2) are introduced to determine the van der Waals for an atom near a metallic nanowire.

## 2. van der Waals energy between atoms and nanoparticles

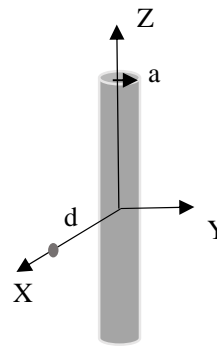
In this work, we only present the essentials which enables us to determine the dispersion van der Waals energy (for more details one can see for example Refs.13, 16).

### 2.1. Atom near a metallic nanoshell

Consider an atom in interaction with a spherical nanoshell of inner radius  $a$  and external radius  $b$  (see figure1). The metallic nanoshell is assumed as a continuum medium with dielectric function taking into account the mobility of the electrons. For more realistic description we use a simplified Lindhard dielectric function, in the hydrodynamic model, involving the spatial dispersion effect in the metal [14].



**Figure 1.** Atom at distance  $d$  from a nanoshell of inner and outer radii  $a$  and  $b$ .



**Figure 2.** Atom on  $x$  axis in the vicinity of a cylindrical nanowire.

At intermediate distances, avoiding both chemisorption and retarded effects, the nanoshell is considered as continuum medium and dispersion van der Waals energy is given by [15]

$$U_d(\vec{R}) = \frac{\hbar}{2\pi} \sum_{m,n=1}^{\infty} \frac{1}{(2m-1)!!(2n-1)!!} \int_0^{\infty} d\xi \quad {}^{(m)}\chi^{(n)}(\omega) [m+n] \quad {}^{(m)}S^{(n)}(\vec{R}, \vec{R}, i\xi) \quad (1)$$

${}^{(m)}S^{(n)}(\vec{R}, \vec{R}, i\xi)$  and  ${}^{(m)}\chi^{(n)}(\omega)$  are respectively the susceptibility tensor of the field gradient of the nanoshell and the multipolar polarizability tensor of the atom at frequency  $\omega = i\xi$ . The tensors are of order  $(n+m)$  and the symbol  $[m+n]$  represents their contraction. When one considers only the dipolar contribution, this expression simplifies to

$$U_d(\vec{R}) = \frac{\hbar}{2\pi} \int_0^{\infty} d\xi \quad \alpha(i\xi) \{S_{xx}(\vec{R}, \vec{R}, i\xi) + S_{yy}(\vec{R}, \vec{R}, i\xi) + S_{zz}(\vec{R}, \vec{R}, i\xi)\} \quad (2)$$

$\alpha(\omega)$  is the dynamic atomic polarizability which could be written, following Drude Model [13], as

$$\alpha(\omega) = \frac{\alpha(0)\omega_0^2}{\omega_0^2 - \omega^2} \quad (3)$$

where  $\alpha(0)$  is the static polarizability,  $\omega_0$  the angular frequency of the vibrating electrons and the susceptibility tensor is defined as [16]

$${}^1S^1(\mathbf{r}, \mathbf{R}, \omega) = -\sum_{\ell, m} T_{\ell m}^1 \frac{a^{2\ell+1}}{r^{\ell+1}} \Delta_{\ell}(a, b, \omega) O^1 Y_{\ell}^m(\Omega) \quad (4)$$

$T_{\ell m}$  involves Clebsch-Gordan coefficients,  $\Delta_{\ell}(a, b, \omega)$  is the reflection factor of the nanoshell and  $O^1$  is a tensor operating on the spherical harmonic  $Y_{\ell}^m$ :

$$O^1 Y_{\ell}^m(\Omega) = -r^{\ell+2} \nabla \left[ \frac{1}{r^{\ell+1}} Y_{\ell}^m(\Omega) \right] \quad (5)$$

The reflection factor of a nanoshell, with radii  $a < b$ , is written then

$$\Delta_{\ell}(a, b, \omega) = \frac{\ell \{a G_{\ell}(b, \omega) + \ell [F_{\ell}(a, \omega) G_{\ell}(b, \omega) - F_{\ell}(b, \omega) G_{\ell}(a, \omega)]\} - b [a + \ell F_{\ell}(a, \omega)]}{(\ell+1) \{a G_{\ell}(b, \omega) + \ell [F_{\ell}(a, \omega) G_{\ell}(b, \omega) - F_{\ell}(b, \omega) G_{\ell}(a, \omega)]\} - b [a + \ell F_{\ell}(a, \omega)]} \quad (6)$$

with  $G_\ell(r, \omega) = b^2 \sum_{k,k'} N_{k\ell} N_{k'\ell} j_\ell(kr) j_\ell(k'r) \Xi_\ell^{-1}(k, k', \omega)$ ,

and  $F_\ell(r, \omega) = a^2 \sum_{k,k'} N_{k\ell} N_{k'\ell} j_\ell(kr) j_\ell(k'a) \Xi_\ell^{-1}(k, k', \omega)$ ,

Following the work done by C. Girard et al [17], we neglect the off-diagonal elements of the matrix  $\Xi_\ell(k, k', \omega)$  which will be simplified and related to Lindhard dielectric function  $\epsilon(k, \omega)$  by

$$\Xi_\ell(k, k', \omega) = k^2 \epsilon(k, \omega) \delta_{k,k'} \quad (7)$$

The reflection coefficient of a nanosphere is easily deducible from eq.(6) when the radius  $a$  goes to zero

$$\Delta_\ell(b, \omega) = \frac{\ell G_\ell(b, \omega) - b}{(\ell+1)G_\ell(b, \omega) + b} \quad (8)$$

By taking into account this, the van der Waals energy reads to

$$U_d(R) = \sum_\ell C_\ell(a, b) \frac{a^{2\ell+1}}{R^{2\ell+1}} \quad (9)$$

where  $C_\ell(a, b)$  are called the dispersion coefficients which carry the nonlocal behavior of the metal

$$C_\ell(a, b) = \frac{\hbar}{2\pi} (\ell+1)(2\ell+1) \int_0^\infty d\xi \Delta_\ell(a, b, i\xi) \alpha(i\xi) \quad (10)$$

## 2.2. Atom near a metallic nanowire

In a similar manner, except that the cylindrical symmetry involve a new set of eigenmodes, we have a relation describing the dispersive interaction between an atom and a metallic nanowire is  $U_d(R) =$

$$\frac{\hbar}{\pi^2} \alpha(0) \omega_0^2 \sum_{n=1}^\infty \int_0^\infty dk_\parallel [k_\parallel^2 K_n'^2(k_\parallel R) + (k_\parallel^2 + \frac{n^2}{R^2}) K_n^2(k_\parallel R)] \int_0^\infty d\xi \frac{\Delta_n(k_\parallel, a, i\xi)}{\omega_0^2 + \xi^2} \quad (11)$$

Where  $k_\parallel$  is the component of the wave vector  $\mathbf{k}$  along the wire z-axis. The reflection factors of the nanowire are given by the following relation [18]

$$\Delta_n(k_\parallel, a, i\xi) = -\frac{I_n(k_\parallel a) - k_\parallel F_n(k_\parallel, a, i\xi) I_n'(k_\parallel a)}{K_n(k_\parallel a) - k_\parallel F_n(k_\parallel, a, i\xi) K_n'(k_\parallel a)} \frac{K_n'(k_\parallel a)}{I_n'(k_\parallel a)} \quad (12)$$

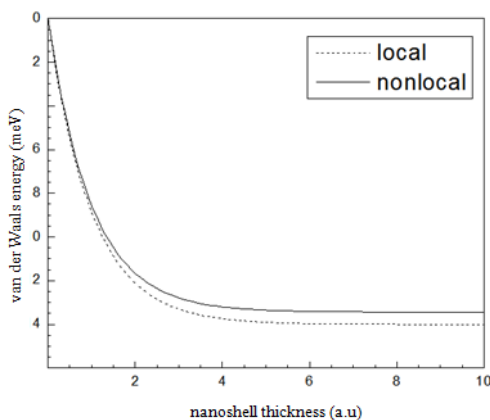
$I_n$ ,  $K_n$ ,  $I_n'$  and  $K_n'$  respectively are the modified Bessel functions and their derivatives. The functions  $F_n$  are given by the following relation [19]

$$F_n(k_\parallel, a, i\xi) = \frac{\xi^2}{\xi^2 + \omega_p^2} \frac{I_n(k_\parallel a)}{k_\parallel I_n'(k_\parallel a)} + \frac{\omega_p^2}{\xi^2 + \omega_p^2} \frac{I_n(\beta a)}{\beta I_n'(\beta a)} \quad (13)$$

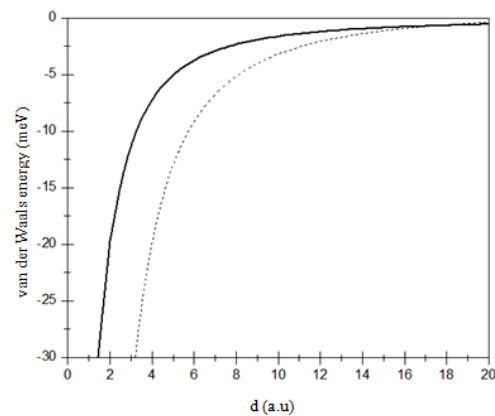
These functions contain all the dynamic information about the nanowire.

## 3. Numerical results and conclusions

Numerical calculations have been made for a Kr atom in the vicinity of a gold nanoshell, a nanosphere and a nanowire. Note that, only in a local treatment, the dispersive energy  $U_d$  depends on



**Figure 3.** Van der Waals energy, in terms of the thickness, for Kr atom-Au Nanoshell (inner radius=5nm and outer radius=5.5nm). Full line, nonlocal treatment; dotted line, local treatment.



**Figure 4.** Van der Waals energy in terms of  $d$  the approach distance Kr atom-Au nanowire (radius 1.5 nm). Full line, nonlocal treatment; dotted line, local treatment.

the distance  $d$  as  $Cd^{-3}$  (where the coefficient  $C$  is geometry dependent). In figure 3, the energy is plotted, when the atom is near a nanoshell as a function of the thickness  $e=b-a$ , the distance  $d$  being fixed at 6 a.u and a difference between local and nonlocal treatments namely for small distances is observed. The asymptotic value of  $U_d$  at large  $e$  coincides with the energy of the atom in front of an infinite metallic medium limited by a plane while case of a nanosphere is simply deduced by cancelling the radius  $a$  from the equations given above. Figure 4 represents the energy values when a Krypton atom is absorbed by a gold nanowire which confirms that the local energy is larger than the nonlocal one.

One can conclude that with this method, using susceptibilities of the two partners in interaction, one gets van der Waals energies (namely the quantum part of energy due to fluctuating charges) between atoms and nanoparticles with spherical or cylindrical symmetry. The method is readily extendable to molecules provided that one adds higher multipolar contributions. Spatial dispersion effect becomes very important when the atom is very close to the particle (few angstroms).

### Acknowledgments

M. Boustimi thanks the King Abdulaziz City for Science and Technology for supporting him within the framework of the project number 11-NAN2198-10.

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