An introduction to dispersive interactions

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Abstract
Dispersive forces are a kind of van der Waals intermolecular force which
could only be fully understood with the establishment of quantum mechanics
and, in particular, of quantum electrodynamics. In this pedagogical paper, we
introduce the subject in a more elementary approach, aiming at students with
basic knowledge of quantum mechanics. We perform original calculations
using a semiclassical method by the name of the fluctuating-dipole method,
and focus primarily on the interaction of atoms with macroscopic bodies, in
particular with a spherical, less usual geometry.

1. Introduction

Dispersive forces are the most intriguing kind of van der Waals forces, not subject to purely
classical explanations, and have many different practical and theoretical applications, such as
the adhesion force of a gecko (see [1, 2] and references therein), colloidal chemistry, as well as
their connection to the Casimir effect [3]. We here endeavour to present an original calculation
on the subject based on a simplified semiclassical method, whose results are nonetheless of
relevance. Dispersive interactions are rarely seen on undergraduate or even graduate curricula,
largely due to having electrodynamics and quantum mechanics as prerequisites, and our work
has the benefit of being also accessible, at an introductory level, to such students.

Since our work can also be read as a first contact to the field, we seize the opportunity
to offer a historical background on the subject, which constitutes section 2. To establish
basic concepts and notation, section 3 is dedicated to reobtaining the interaction between a
polarizable atom and a conducting plane wall, presenting the fluctuating-dipole method. We
then proceed to our novel calculation, performed in section 4: the interaction between an atom
and a perfectly conducting sphere, also using the fluctuating-dipole method. In section 4 are
to be found the main original results, which we comment on in section 5. A last section is
dedicated to our final remarks.

2. History

The existence of attractive intermolecular forces between molecules of whatever kind has long been assumed due to the possibility of every gas to liquefy. The first quantitative (although indirect) characterization of these forces was done by van der Waals in his 1873 thesis [4] in the equation of state for real gases, which can be written, for one mol of gas, as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

(1)

in which P, V and T are the pressure, volume and temperature of the gas under consideration, respectively, and R is the universal gas constant. The parameters a and b—the van der Waals constants, which vary from one gas to another—can be evaluated through fitting this equation with experimental data. While the parameter b relates to the finite molecule volume, and to the fact that an individual molecule cannot access the entire volume V of the gas, the term (a/V^2) relates to an attractive intermolecular force. Such forces received the general name of van der Waals forces. It should be stated that when one mentions intermolecular forces as such, one assumes that the separation between the molecules in question (or atoms, in the case of monoatomic gases) is large enough to exclude the overlapping of electronic orbitals. These forces are usually distinguished in three types, to wit: orientation, induction and dispersion van der Waals forces, which we briefly discuss—more detailed discussions can be found in [5, 6, 3].

Orientation forces occur between two polar molecules, i.e. two molecules possessing permanent electric dipoles, e.g. water molecules. These forces were first computed by Keesom [7, 8], considering the thermal average of the interaction energy of two randomly oriented electric dipoles $\mathbf{d}_1$ and $\mathbf{d}_2$. Although the amount of possible attractive orientations equals the amount of repulsive ones, once we take into account that attraction setups correspond to smaller energies and that the Boltzmann weight is $e^{-\mathcal{E}/k_B T}$ (that is, it diminishes with increasing energy $\mathcal{E}$), it can be easily understood why orientation forces are attractive. As shown in [9], for high temperatures, i.e., $k_B T \gg d_1 d_2 / 4\pi\epsilon_0 r^3$ (where k_B is the Boltzmann constant, $\mathbf{r}$ is the vector from one dipole (molecule) to the other and $r = |\mathbf{r}|$) the Boltzmann weight can be approximated to $(1 - \mathcal{E}/k_B T)$ and the interaction energy is

$$\langle\mathcal{E}\rangle = \frac{\int (1 - \mathcal{E}/k_B T)\mathcal{E}\,d\Omega_1 d\Omega_2}{\int (1 - \mathcal{E}/k_B T)\,d\Omega_1 d\Omega_2},$$

(2)

where the sum is over all possible orientations of $\mathbf{d}_1$ and $\mathbf{d}_2$. Since $\mathcal{E}$ is of the form

$$\mathcal{E} = \frac{3(\mathbf{d}_1 \cdot \hat{\mathbf{r}})(\mathbf{d}_2 \cdot \hat{\mathbf{r}}) - \mathbf{d}_1 \cdot \mathbf{d}_2}{4\pi\epsilon_0 r^3},$$

(3)

it is intuitive (and can be easily shown) that $\int \mathcal{E}\,d\Omega_1 d\Omega_2 = 0$ when we sum over all orientations. We then find

$$\langle\mathcal{E}\rangle = -\frac{1}{(4\pi)^2 k_B T}\int \mathcal{E}^2\,d\Omega_1 d\Omega_2.$$

(4)

Performing all angular integrations, we find

$$\langle\mathcal{E}\rangle_{\text{orient}} = -\frac{2d_1^2 d_2^2}{3k_B T (4\pi\epsilon_0)^2 r^6}.$$

(5)

We also note that orientation forces decrease with increasing temperature, which is natural since higher temperatures make repulsive orientations as accessible as attractive ones.

It was recognized by Debye [10, 11] and others that there ought to exist an interaction between a polar molecule and an apolar, albeit polarizable, one, once the polar molecule

induces a dipole in the other one. This gives rise to a dipole–dipole attraction force, responsible for the induction van der Waals forces. (In fact, even a quadrupole or higher permanent multipole can induce such a dipole and gives rise to induction forces.) The attractive character of these forces follows from the fact that an induced dipole is parallel to the inducing field (assuming an isotropical polarization) and that the interaction energy between an electric field and a parallel dipole is always negative. Moreover, further assuming that the molecular polarizability α is linear, i.e., $\mathbf{d}_2 = \alpha \mathbf{E}_1$, where $\mathbf{d}_2$ is the induced dipole and the field $\mathbf{E}_1$ is generated by the permanent dipole $\mathbf{d}_1$, leads to

$$\mathcal{E} = -\frac{\alpha}{2(4\pi\epsilon_0)^2 r^6}\left(3(\mathbf{d}_1 \cdot \hat{\mathbf{r}})^2 + d_1^2\right) \tag{6}$$

and to a nonvanishing $\int \mathcal{E}\,\mathrm{d}\Omega_1$—which can be understood as a result of the correlation of the dipoles. We then consider, in a first approximation, only the first term of the expansion of the weight $\mathrm{e}^{-\mathcal{E}/k_{\mathrm{B}}T}$ in equation (2), and find

$$\langle\mathcal{E}\rangle_{\mathrm{induct}} = -\frac{\alpha d_1^2}{(4\pi\epsilon_0)^2 r^6}, \tag{7}$$

which is nonvanishing at increasing temperatures. Since $U(r)$ is proportional to $(-1/r^6)$, the force has a $(-1/r^7)$ behaviour.

It just so happens that the correction term (a/V^2) can enhance the ideal gas approximation for each and every gas known in nature, including gases constituted of apolar molecules (or atoms), like the noble gases. This leads to the conclusion that there should also exist intermolecular forces between pairs of apolar molecules. Whereas the aforementioned intermolecular forces involving at least one polar molecule are classically conceivable, this third kind of van der Waals forces, the dispersive ones, occurring between two apolar, albeit polarizable, molecules, can only be fully understood within the framework of quantum mechanics. It was only in 1930—after the development of quantum mechanics—that Eisenschitz and London [12] demonstrated for the first time how such a force can appear, by performing a second-order perturbation theory on a quantum system composed of two atoms. Their result can be cast in the form of the following potential:

$$U(r) = -\frac{3\hbar\omega_0\alpha^2}{(4\pi\epsilon_0)^2 4r^6}, \tag{8}$$

where ω_0 is the dominant transition frequency. An important result of their work is that these forces depend on the polarizabilities α of the atoms in question, which are related to the refractive index, and consequently to the electromagnetic dispersion in a medium composed of such atoms. The proportionality constant in this power law could then be evaluated by the two authors from fitted parameters of optical dispersion measurements. This evaluation, further developed in a paper of the same year by London alone [13], motivated London's coining such forces as *dispersive* forces in the latter article. This explanation successfully overturned the attempts to base interatomic forces between apolar molecules on permanent-quadrupole interaction, since it best fits experimental data as the van der Waals constant a itself. In London's words [13] (translated by the authors themselves),

> *Since the van der Waals attraction, according to the previous picture, is proportional to the square quadrupole moment, using the wave-mechanical model one obtains [for H_2], keeping parameters otherwise fixed, only 1/9 (according to Keesom), 1/67 or 1/206 (according to Debye) of the actual value of the constant a of the van der Waals equation.*

Although the important calculation of the $(-1/r^6)$ power law is performed in the first article, being only mentioned in the second one, the latter is far more often cited than the former, and these forces are also called 'London forces'.

Dispersive forces are, then, the electromagnetic forces that occur between atoms or molecules possessing no permanent electric or magnetic multipole whatsoever, and are due to quantum fluctuations on the atomic charge and current distributions. They occur not only between two atoms, but also between atoms and macroscopic bodies, as shown for the first time in 1932 by Lennard-Jones [14], who calculated such interaction between a polarizable atom and a perfectly conducting plane wall. Dispersive forces can be further divided into two kinds: nonretarded and retarded. London's work refers exclusively to nonretarded forces, which result when one considers light speed to be infinite, so the interaction instantaneous. Retarded interactions, first calculated by Casimir and Polder in 1948 [15], take into account the finiteness of interaction propagation speed and require the quantization of the electromagnetic field. In this case, the dipole field of a first molecule will only reach a second one after a time interval of r/c, and the reaction field of the second molecule at the first one will be delayed in $2r/c$. Such delays decrease the correlation between the fluctuating dipoles, which causes the retarded force to drop more rapidly with distance than the nonretarded one. In an atomic system, a characteristic time is given by the inverse of a dominant transition frequency ω_0, and a distance r is said to be long (or, equivalently, retardation effects become relevant) when $r/c \gtrsim 1/\omega_0$. It should be clear that nonretarded forces are a good approximation when the molecule separation is small, which is the regime of validity of the London forces.

Although Eisenschitz's and London's results were obtained by the use of perturbative quantum mechanics, it is possible in the short-distance limit to estimate such forces with a much simpler method, known to have produced good results in calculations of this kind— as the atom–atom and the atom–wall van der Waals interactions—that goes by the name of fluctuating-dipole method. This method can be found, for instance, in [3, 5] and has also been shown to be useful in enabling, with little effort and requiring less background on quantum mechanics, various discussions on dispersive forces, such as nonadditivity [16] or the nonretarded force between an electrically polarizable atom and a magnetically polarizable one [17].

Our interest in this paper lies in nonretarded van der Waals forces, and, more specifically, in the force between an atom and a macroscopic body. We wish to further develop the calculations of such forces by approaching a problem with curved geometry, to wit, the nonretarded ('London') force between an atom and a perfectly conducting sphere. We shall approach this problem making use of the fluctuating-dipole method.

Dispersive forces involving macroscopic bodies are of undeniable importance for direct experimental verification, as seen in [18–20] (check also [21] and references therein). An aspect of van der Waals forces related to the interaction with macroscopic bodies is the nonadditivity, which leads to the fact that one cannot, in principle, obtain the correct van der Waals dispersion force in macroscopic cases by simply performing pairwise integration of the power law found for the atom–atom case. The reader interested in this feature of dispersive forces should consult [3, 5, 6].

The modern quantum field theory explanation for such forces relies on the fact that there is, even in sourceless vacuum, a residual electromagnetic field whose vacuum expectation values $\langle \mathbf{E}(\mathbf{r}, t) \rangle$ and $\langle \mathbf{B}(\mathbf{r}, t) \rangle$ are zero, but whose fluctuations $\langle \mathbf{E}^2 \rangle$, $\langle \mathbf{B}^2 \rangle$ do not amount to zero. This vacuum field can induce an instantaneous dipole in one polarizable atom (or molecule), and the field of this induced dipole, together with the vacuum field, induces an instantaneous dipole in the second atom (molecule). It can thus be said that the vacuum field induces fluctuating dipoles in both atoms and the van der Waals dispersive interaction energy
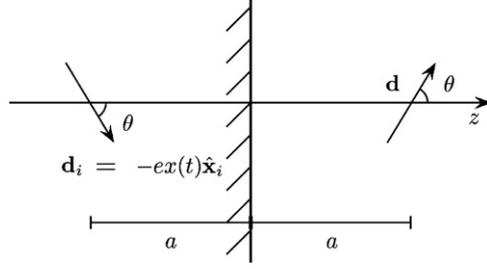
Figure 1. Image configuration for a real dipole **d** in front of a conducting wall. The magnitudes of **d** and $\mathbf{d}_i$ are the same. Both dipoles (and the entire figure above) lie on the same plane.

corresponds to the energy of these two correlated zero-mean dipoles. A more detailed analysis of dispersion forces and quantization of the electromagnetic field can be found in Milonni's book [3]. A further review on dispersive forces is Holstein's paper [22].

3. Calculation of the atom–wall London force

Let us then calculate the dispersive interaction between an atom and a conducting wall. Since we are interested in an intermolecular force, we want to exclude wavefunction overlapping by having an atom–plate distance a larger than the atom radius. This allows us to evaluate the interaction calculating the leading nonvanishing term in an expansion a_0/a, a_0 being the Bohr radius.

It can be shown quantum-mechanically that the multipole of the atom that contributes the most for this kind of interaction is the dipole (see [23] for a demonstration in the atom–atom case), thus motivating our picture of the atom as a dipole. Furthermore, we know that this dipole is not permanent, but fluctuates with a zero-mean value. The fluctuating-dipole method models the atom as constituted by a fixed nucleus and by an electron of charge $(-e)$ and mass m. The binding force between them is taken to be classical harmonic, thus leading to a harmonic-oscillating dipole $\mathbf{d}(t)$ of frequency ω_0 when the atom is left undisturbed:

$$\ddot{\mathbf{d}}(t) + \omega_0^2 \mathbf{d}(t) = 0. \tag{9}$$

We take, for simplicity, the oscillation direction to be fixed, albeit arbitrary, and so we have

$$\mathbf{d}(t) = -e\, x(t)\, \hat{\mathbf{x}}, \tag{10}$$

where $x(t)$ is the position of the electron relative to the nucleus and $\hat{\mathbf{x}}$ is the (fixed) unit vector in the direction of oscillation. It should be clear that in this case $x(t)$, too, obeys equation (9).

Since the atomic polarizability is defined by the expression $\mathbf{d} = \alpha \mathbf{E}$, one can calculate the static atomic polarizability predicted by this model equating the (static) force exerted by an external electric field $\mathbf{E}$ to the harmonic binding force:

$$-eE\hat{\mathbf{x}} = \frac{m\omega_0^2}{-e} \underbrace{(-ex\hat{\mathbf{x}})}_{\mathbf{d}} \Rightarrow \alpha = \frac{e^2}{m\omega_0^2}. \tag{11}$$

To calculate the interaction of a dipole with a perfectly conducting plane wall, we need to make use of the image method. The image produced when a real dipole **d** stands before a conducting plane is a dipole $\mathbf{d}_i$ of the same magnitude of the real one, and whose direction is described in figure 1.

We now proceed to calculate the equations of motion of the electron of the polarizable atom under the influence of the electric field generated by the image dipole. Since the real dipole oscillates, so does the image one, and we need, then, the field created by an oscillating dipole. The expression of this field is rather cumbersome, mainly due to retardation and radiation effects. Fortunately, we are only interested in the small-distance, nonretarded regime, which means that the atom–plate distance is small compared to the atom's dominant transition wavelength. In this case only, we can neglect retardation and work with the quasi-static field created by such a dipole,

$$\mathbf{E}(\mathbf{r}, t) = \frac{3(\mathbf{d}(t) \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{d}(t)}{(4\pi\epsilon_0)r^3}. \tag{12}$$

The equation of motion for the electron of the real atom, once we project the forces acting on it to the direction of allowed motion (that is, the direction $\hat{\mathbf{x}}$ of the dipole), becomes

$$\ddot{x}(t) + \omega_0^2 x(t) = \frac{-e}{m4\pi\epsilon_0}\left[\frac{3(\mathbf{d}_i \cdot \hat{\mathbf{z}})\hat{\mathbf{z}} - \mathbf{d}_i}{(2a)^3}\right] \cdot \hat{\mathbf{x}}, \tag{13}$$

where $\hat{\mathbf{z}}$ and a are defined in figure 1. Using the expression of $\mathbf{d}_i$ from figure 1, and writing the scalar products as a function of the angle θ, we have

$$\ddot{x}(t) + \omega_0^2 x(t) = \frac{e^2 x(t)}{m4\pi\epsilon_0}\frac{1 + \cos^2\theta}{8a^3}. \tag{14}$$

But this is a simple harmonic oscillator equation, whose frequency is

$$\omega = \omega_0\sqrt{1 - \frac{e^2(1 + \cos^2\theta)}{4\pi\epsilon_0 m 8a^3\omega_0^2}} \tag{15}$$

$$= \omega_0\left\{1 - \frac{e^2(1 + \cos^2\theta)}{4\pi\epsilon_0 m 16a^3\omega_0^2} + \mathcal{O}\left(\frac{e^2/m\omega_0^2}{4\pi\epsilon_0 a^3}\right)^2\right\} \tag{16}$$

The term in parentheses in the last equation can be recognized, using equation (11), as $(\alpha/4\pi\epsilon_0 a^3)$. It is a known fact that, in general, the polarizability of an atom relates directly to its volume, i.e., to a_0^3. This can be shown to be valid in the fluctuating-dipole model once we replace $\hbar\omega_0$ for the dominant transition energy. In other words, equation (16) shows the leading term in a a_0^3/a^3 expansion—which suits us, since, as mentioned earlier, we are interested in the case $a_0/a \ll 1$. We now quantize the system merely turning classical harmonic oscillators into quantum ones of same frequency. When the external fields alter the frequency of the oscillator, we can quantum-mechanically say that its energy was altered too. Now, the essence of the method lies in identifying the zero-point energy variation as a potential energy, i.e., $U := \hbar(\omega - \omega_0)/2$. This means to compute the difference in energy between our system as it is and the corresponding existing system if there were no electric field and interpret that difference as an interaction potential. Assuming the atom to be isotropic, we replace $\cos^2\theta$ by its spatial average of $1/3$. We thus find as a leading term

$$U(a) := \frac{\hbar(\omega - \omega_0)}{2} = -\frac{\hbar\omega_0\alpha}{(4\pi\epsilon_0)24a^3}, \tag{17}$$

and this is the atom–wall dispersive potential found by this method. The frequency ω_0 introduced before is identified with a dominant transition frequency of the atom.

In spite of the apparent naivety of this method, quantum-mechanical calculations arrive at the same result except for a different prefactor. This is typical for the fluctuating-dipole method, and all dependences on parameters as a, α, ω_0 are correctly displayed by this semiclassical method.

$$\mathbf{d}_i = \frac{R^3}{z_r^3} \left(2(\mathbf{d}\cdot\hat{\mathbf{z}})\hat{\mathbf{z}} - \mathbf{d} \right)$$
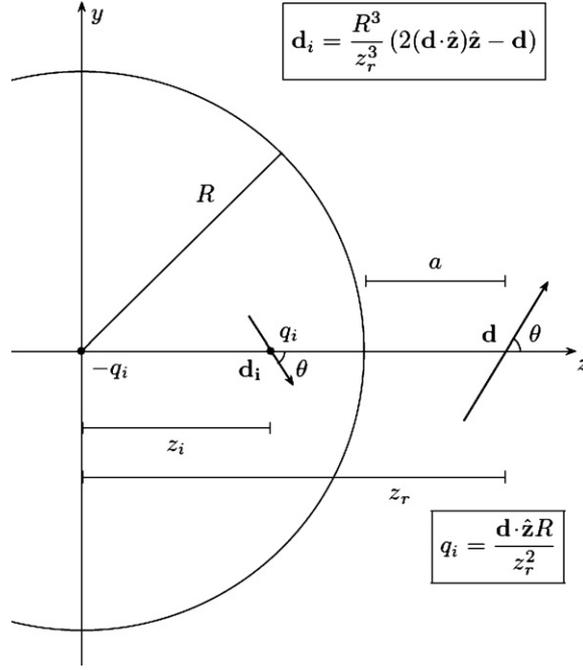
$$q_i = \frac{\mathbf{d}\cdot\hat{\mathbf{z}}R}{z_r^2}$$

Figure 2. Image configuration for a real dipole **d** before a conducting sphere. The values of the image dipole and image charges are indicated. R is the radius of the sphere, a, the sphere–atom separation, $z_r := R + a$ and $z_i := R^2/z_r$.

4. Calculation of the atom–sphere London force

We now calculate the van der Waals dispersive nonretarded interaction between a perfectly conducting sphere and a polarizable atom, now using the fluctuating-dipole method in this more involved geometry.

All previous considerations about the atom made in the last section apply, especially its polarizability and the interpretation of its frequency ω_0 as a dominant transition frequency. We need to study the reaction of the sphere to the presence of a dipole, in other words, the images produced in this situation. This classical problem has a more complex geometry, but has been solved by Santos and Tort in [25], and the solution is described in figure 2. We define $z_r := R + a$, where R is the radius of the sphere and a is the minimum atom–sphere separation. There is one image dipole $\mathbf{d}_i$ at radius $z_i := R^2/z_r$, and a first image point charge q_i at the same position. If the sphere is assumed grounded, these are all the necessary images; a second image point charge $(-q_i)$ at the centre of the sphere is necessary if the sphere is neutral. We shall work with the neutral sphere and recover the other case later on. The magnitude of these images is signalled in figure 2. Keeping in mind that, as before, forces due to the fields of the images must be projected onto the allowed direction, we find the following equations of motion for the electron of the polarizable atom:

$$\ddot{x}(t) + \omega_0^2 x(t) = \frac{-e}{m 4\pi \epsilon_0} \left[q_i \hat{\mathbf{z}} \left(\frac{1}{(z_r - z_i)^2} - \frac{1}{z_r^2} \right) + \frac{3(\mathbf{d}_i \cdot \hat{\mathbf{z}})\hat{\mathbf{z}} - \mathbf{d}_i}{(z_r - z_i)^3} \right] \cdot \hat{\mathbf{x}}. \tag{18}$$

With the values of the images to be seen in figure 2, expressing the scalar products as a function of the angle θ and using equation (10) to extract the factor $x(t)$ out of each term, we get

$$\ddot{x}(t) + \omega_0^2 x(t) = \frac{e^2 x(t)}{m 4\pi\epsilon_0} \left[\frac{R \cos^2\theta}{z_r^2} \left(\frac{1}{(z_r - z_i)^2} - \frac{1}{z_r^2} \right) + \frac{R^3}{z_r^3} \frac{(1 + \cos^2\theta)}{(z_r - z_i)^3} \right]. \tag{19}$$

This is again a simple harmonic oscillator equation, whose original frequency ω_0 was altered to

$$\omega = \omega_0 \left\{ 1 - \frac{e^2/m\omega_0^2}{4\pi\epsilon_0} \left[\frac{R \cos^2\theta}{z_r^2} \left(\frac{1}{(z_r - z_i)^2} - \frac{1}{z_r^2} \right) + \frac{R^3}{z_r^3} \frac{(1 + \cos^2\theta)}{(z_r - z_i)^3} \right] \right\}^{1/2}. \tag{20}$$

Replacing $\alpha = e^2/(m\omega_0^2)$ and expanding in a Taylor series

$$\begin{aligned}
\omega = \omega_0 \Bigg\{ &1 - \frac{\alpha}{2(4\pi\epsilon_0)} \left[\frac{R \cos^2\theta}{z_r^2} \left(\frac{1}{(z_r - z_i)^2} - \frac{1}{z_r^2} \right) \right. \\
&+ \left. \frac{R^3}{z_r^3} \frac{(1 + \cos^2\theta)}{(z_r - z_i)^3} \right] + \mathcal{O} \left(\frac{\alpha}{4\pi\epsilon_0} \xi \right)^2 \Bigg\},
\end{aligned} \tag{21}$$

ξ being a generic form depending on the parameters a and R, proportional either to a^{-3} (when $a \ll R$) or to $\left(R/z_r^4 \right)$. Either way, the last term on the r.h.s. of equation (21) may be neglected, since we assume the atom–sphere distance to be much greater than the Bohr radius.

Once again we turn classical harmonic oscillators into quantum ones, replace $\cos^2\theta$ by $1/3$ and take the zero-point energy difference $\hbar(\omega - \omega_0)/2$ as a potential. The leading term amounts to

$$U = -\frac{\hbar\omega_0\alpha}{(4\pi\epsilon_0)12} \left\{ \frac{4R^3}{z_r^3(z_r - z_i)^3} + \frac{R}{z_r^2} \left(\frac{1}{(z_r - z_i)^2} - \frac{1}{z_r^2} \right) \right\} \tag{22}$$

and setting the expression in terms of the parameters R and a:

$$U_R(a) = -\frac{\hbar\omega_0\alpha}{(4\pi\epsilon_0)24a^3} \left\{ \frac{8}{(2 + a/R)^3} + \frac{2a/R}{(2 + a/R)^2} - \frac{2a^3/R^3}{(1 + a/R)^4} \right\}. \tag{23}$$

The first term is due to the image dipole, the second one to the charge q_i and the third to the charge $-q_i$, located at the centre of the sphere. If the sphere is supposed *grounded* instead of *neutral*, the last term must be suppressed. Quantum calculations also agree with both results, except for a different prefactor.

5. Discussion of the results

Consistency requires that the result of equation (23) for the atom–sphere case recover the atom–wall case in the limit $R \to \infty$ keeping a constant, in which the conducting sphere would turn into a conducting plane wall. Doing this directly from the general expression of equation (23), we find for both a neutral and a grounded sphere

$$U_\infty(a) = -\frac{\hbar\omega_0\alpha}{4\pi\epsilon_0 24a^3}, \tag{24}$$

which coincides with the result given by equation (17). In fact, equation (23) has been conveniently written in terms of the atom–wall interaction times a function depending only on the ratio a/R.
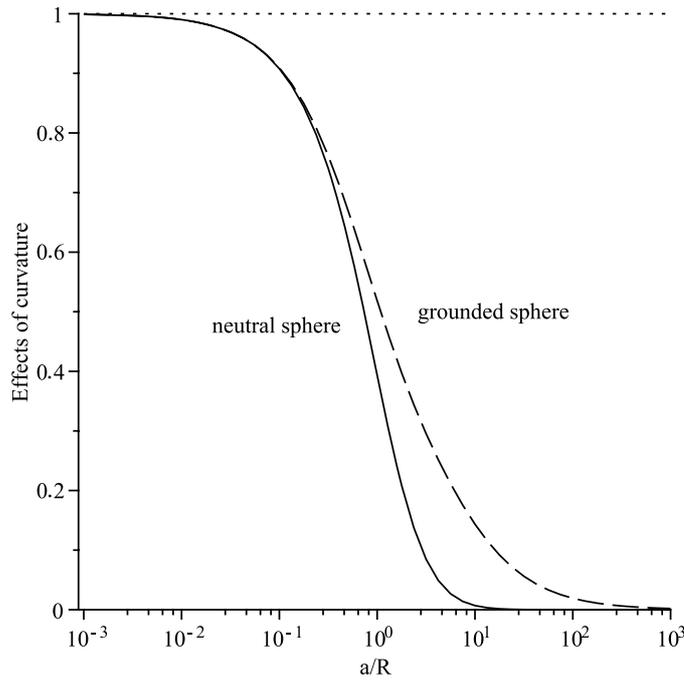
Figure 3. Graph of the curvature effects on the potential between atom and sphere, the terms in curly brackets in equation (23), as a function of a/R.

Another interesting limit we can take is the limit $R \ll a$, in which the neutral sphere would turn into a so-called conducting point:

$$U_{0^+}(a) = -\frac{3\hbar\omega_0\alpha R^3}{4\pi\epsilon_0 2a^6}. \tag{25}$$

This is formally equivalent to the asymptotic behaviour as $R \to 0$, a constant. Besides serving as a very useful approximation for situations in which the conducting sphere is much smaller than other distances in question, equation (25) can be directly related to the London interaction between two (neutral) atoms, as follows: $\alpha/4\pi\epsilon_0$ has the dimensions of a volume and is straightforwardly related to the volume of the atom. In the case of a sphere, it can be shown that its polarizability $\alpha_{\text{sphere}} = 4\pi\epsilon_0 R^3$. We thus reobtain from equation (25) the atom–atom case, equation (8) (apart from a prefactor $\frac{1}{2}$, see section 6).

A comparison between equations (17) and (23) allows us to interpret the terms in curly brackets in the latter as the effect of sphere curvature on the potential. We then present a graph of the curvature effects as a function of the ratio a/R for both the neutral and grounded sphere, figure 3.

6. Final remarks

After providing a historical background to dispersive interactions, we have performed calculations of the van der Waals nonretarded dispersive forces. We emphasized the pedagogical character of this paper by choosing the fluctuating-dipole method, accessible to undergraduate students with basic knowledge of quantum mechanics, starting with the

well-known interaction between a polarizable atom and a perfectly conducting plane wall. We then proceeded to the case of a sphere, which constitutes an interesting, new application of the fluctuating-dipole method in situations with curved objects. This specific atom–sphere geometry has been dealt with before in the literature [27–30] for different sphere attributes and/or regimes other than the nonretarded.

It is worth emphasizing that our results are valid for any ratio a/R, as long as the conditions for the nonretarded regime are obeyed. We performed an important consistency check on the expression for our potential, which is the limit $R \to \infty$, in which the sphere turns into a plane. Our results agree in that limit. A remarkable feature is the calculation of the force when the sphere turns into a conducting point. Besides its possible approximative value, it was able to recover the atom–atom interaction when substituting the sphere volume for its polarizability.

The fluctuating-dipole method has its limitations, and cannot account for all prefactors when compared to more complete methods. Generalizations of the results in hand require a quantum treatment of the atoms and, to take into account the electromagnetic retardation, the quantization of the field itself. Another interesting additional correction is a prefactor 1/2, which can be explained solely on the grounds of classical electromagnetism, and is described in [31].

Acknowledgments

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