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LETTER TO THE EDITOR

The London–van der Waals interaction energy between objects of various geometries

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Abstract

Mathematical expressions for the London–van der Waals (vdW) interaction energies between macroscopic objects of a few common geometrical shapes are derived. The derivation is subjected to the assumption of additivity. The expressions are approximated for some limiting cases. These expressions may find uses for example in complex fluids in calculations of vdW interactions between vesicular (single wall liposomes) and liposomal (onion structures) particles or in colloidal suspensions for the calculation of vdW interaction between colloids that are coated with a stabilizing layer such as adsorbed polymers, polymer brushes or surfactants.

1. Introduction

Expressions for London–van der Waals (vdW) interaction energies between macroscopic objects were first derived about 70 years ago, with a few simple geometries (see for example [1–4]). Expressions for the vdW interaction energies between objects of a few geometries are now available [5–8], yet there are still some important geometries for which an analytic expression for the two-body vdW interaction energy is not available.

In this letter, expressions for the two-body vdW interaction are derived for a few geometrical cases of scientific and practical importance. The following geometries are included:

(i) Two shells: In many colloidal systems, colloids are usually coated with different polymers or surfactants in order to stabilize suspensions (see for example [9–12]) . These coatings form shells around the colloids and the vdW interaction from the coating shells is in many cases a substantial or even major part of the total interaction energy in these systems. Thus, an expression for the interaction between two shells has a practical as well as a scientific purpose.

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(ii) Two parallel walls (of different thicknesses): Many surfaces are coated with a thin layer that changes their wetting properties. Such layers are either made on purpose (as Langmuir–Blodgett or self assembled monolayers [13]) or are naturally occurring surface layers (as is the oxide layer on silicon surfaces). Such surfaces may be coated with a liquid layer which may be either very thin (as in a dewetted surface [6]) or very thick (as in a wetted surface). In order to quantitatively describe the interactions in such systems, a quantitative description of the interactions between any two walls is required.

(iii) A shell and a sphere, a shell and a flat: This case may be viewed as a subdivision of (i), and we have put it in a separate case because of its different physical interpretation. This expression may have importance for coated colloids (as described in (i)), but here it quantitatively describes the contributions of the core of the colloid (of one material) and the shell of a neighbouring colloid (of another material). Additionally, it may be important in the practical case of determining the interactions of the colloids with the wall of the vessel which contains the dispersion.

We should note that we assume smooth surfaces, whereas surfaces (as colloidal particles or solid substrates) are usually not smooth. Thus, as opposing rough surfaces become very close (of order of asperities protrusions), the contribution of small asperities to the interaction energy may become dominant and alter the force law in a way which corresponds to the geometrical structures of the asperities. As the separation further diminishes to an atomic scale, then the molecular conformation in the asperity should also be considered. These phenomena are beyond the scope of this study.

2. London–van der Waals energy between two opposing shells

Two solid spherical particle of radii R_1 and R_2 and at a distance d apart (d is the shortest distance between the surfaces of the particles), have a London–van der Waals attraction energy $E_{\text{sphere}}(R_1, R_2, d)$ which is given by [4]:

$$E_{\text{sphere}}(R_1, R_2, d) = -\frac{A}{6}\left\{\frac{2R_1R_2}{2(R_1+R_2)d+d^2} + \frac{2R_1R_2}{4R_1R_2+2(R_1+R_2)d+d^2} + \ln\left[\frac{2(R_1+R_2)d+d^2}{4R_1R_2+2(R_1+R_2)d+d^2}\right]\right\} \tag{1}$$

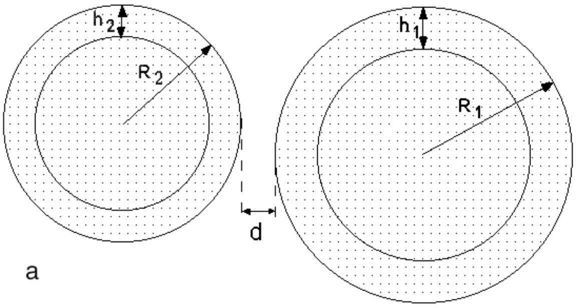
where A is the Hamaker constant. Note that an attractive energy in this study corresponds to a positive Hamaker constant.

Consider now two non-identical solid spheres of radii R_1 and R_2. Let us imagine that each sphere is composed of two parts: one part is the spherical core of radius $R_j - h_j$ where the index j stands for the name of the sphere: 1 or 2 (see figure1(a)), and the other part is a spherical shell of thickness h_j with R_j and $R_j - h_j$ as outer and inner radii respectively.

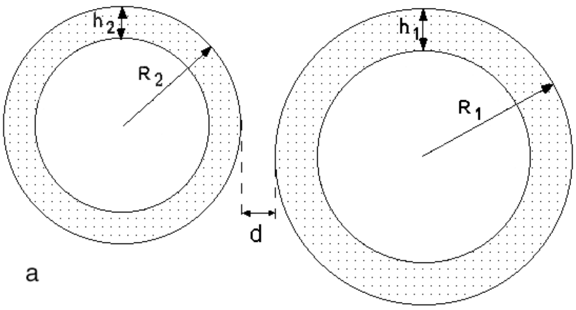
Let: $E_{\text{shell}}(R_1, R_1 - h_1, R_2, R_2 - h_2, d) \equiv E_G(\text{shell}_1, \text{shell}_2)$ be the interaction energy between the two shells. This is a function of the outer radii R_j of the shells, the inner radii $R_j - h_j$ of the shells, and the closest distance d between the shells. We write the total interaction between the two solid spheres of the radii R_1 and R_2 as:

$$E_G(\text{sphere}_1, \text{sphere}_2) = E_G(\text{shell}_1, \text{shell}_2) + E_G(\text{core}_1, \text{core}_2) + E_G(\text{core}_1, \text{shell}_2) + E_G(\text{core}_2, \text{shell}_1) \tag{2}$$

where $E_G(x, y)$ is the interaction energy between a geometrical object x and a geometrical object y, subjected to the geometrical conditions of figure 1. For instance: $E_G(\text{core}_1, \text{shell}_2)$ is a function which describes the vdW interaction energy between the spherical core of sphere



(*a*)



(*b*)

Figure 1. (*a*) A cross-section of two solid spheres. The inner circle represents an imaginary separation of the solid sphere into an outer shell and an inner core. (*b*) A cross-section of two spherical shells.

1 (radius $R_1 - h_1$) and the spherical shell (R_2, $R_2 - h_2$ for outer and inner radii) of sphere 2 when separated by the closest distance $d + h_1$ apart. Similarly we can write:

$$E_G(\text{core}_1, \text{shell}_2) = E_G(\text{core}_1, \text{sphere}_2) - E_G(\text{core}_1, \text{core}_2) \tag{3}$$

and obviously the same is true if the indexes 1 and 2 are reversed.

Substituting equation (3) into equation (2) and by rearranging it we get:

$$\begin{aligned} E_G(\text{shell}_1, \text{shell}_2) = E_G(\text{sphere}_1, \text{sphere}_2) - E_G(\text{sphere}_1, \text{core}_2) \\ - E_G(\text{sphere}_2, \text{core}_1) + E_G(\text{core}_1, \text{core}_2). \end{aligned} \tag{4}$$

And finally in the notations of equation (1) this reads:

$$\begin{aligned} E_{\text{shell}}(R_1, R_1 - h_1, R_2, R_2 - h_2, d) = E_{\text{sphere}}(R_1, R_2, d) - E_{\text{sphere}}(R_1, R_2 - h_2, d + h_2) \\ - E_{\text{sphere}}(R_2, R_1 - h_1, d + h_1) \\ + E_{\text{sphere}}(R_1 - h_1, R_2 - h_2, d + h_1 + h_2) \end{aligned} \tag{5}$$

and since all terms in the right-hand side of equation (5) are known from equation (1), then equation (5) is analytic. Equation (5) describes the vdW energy between a spherical shell of thickness h_1 and external radius R_1 and a spherical shell of thickness h_2 and external radius R_2, when separated at the closest distance d apart.

Explicitly writing equation (5) may be redundant (and lengthy), however, approximating for the practical case when $R_j \gg d, h_j$, may give some physical insight to the way this function varies with the different variables. This is given in equation (5*a*):

$$E_{\text{shell}} = -\frac{AR_1R_2}{6(R_1 + R_2)} \left(\frac{1}{(d + h_1 + h_2)} - \frac{1}{(d + h_2)} - \frac{1}{(d + h_1)} + \frac{1}{d} \right)$$

$$-\frac{A}{6}\ln\left[\frac{d\,(d+h_1+h_2)}{(d+h_1)\,(d+h_2)}\right] \qquad R_j \gg d, h_j \tag{5a}$$

Equations (5) and (5a) correspond to the geometry described schematically in figure 1(b). Note that in the case when $d\sim h_1\sim h_2$, the logarithmic term in equation (5a) is negligible.

The force F_{shell} which corresponds to the energy E_{shell} is $F_{\text{shell}} = (\partial E_{\text{shell}}/\partial d)$. Writing the term for the force is straightforward (a derivative of the analytic equation (5)). To simplify the resulting expression (which is rather lengthy) we write an approximate expression for F_{shell} for the case of $R_j \gg d, h_j$. We first obtain $F_{\text{shell}} = (\partial E_{\text{shell}}/\partial d)$ and then neglect terms which are small compared to 1 (e.g. d/R_j and h_j/R_j or smaller). This yields:

$$F_{\text{shell}} = \frac{\partial E_{\text{shell}}}{\partial d} = -\frac{AR_1R_2}{6\,(R_1+R_2)} \times \left(\frac{1}{d^2} + \frac{1}{(d+h_1+h_2)^2} - \frac{1}{(d+h_1)^2} - \frac{1}{(d+h_2)^2}\right) \qquad R_j \gg d, h_j \tag{6}$$

The discussion of equation (6) is related to the next paragraph.

3. London–van der Waals energy between two parallel walls

Note that the expression for the force in equation (6) depends only on the geometrical average of the radii $R = R_1R_2/(R_1+R_2)$. At this regime of sizes ($R_j \gg d$) the Derjaguin approximation [3] holds, and the force over the radius corresponds to the energy per unit area E_A between two infinite planes which is readily derived in equation (7):

$$E_A = -\frac{A}{12\pi}\left(\frac{1}{d^2} + \frac{1}{(d+h_1+h_2)^2} - \frac{1}{(d+h_1)^2} - \frac{1}{(d+h_2)^2}\right). \tag{7}$$

Equation (7) describes the energy per unit area between a planar wall of thickness h_1 and a planar wall of thickness h_2 when separated by a distance d apart as shown in figure 2.

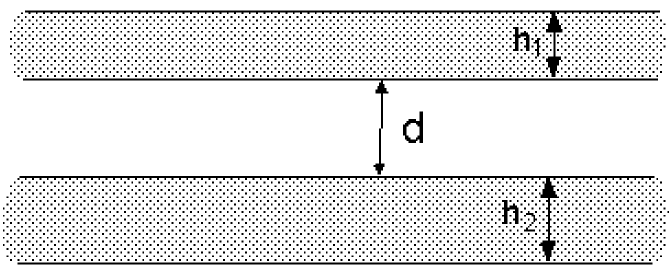


Figure 2. A cross-section of two parallel walls of finite thickness and infinite lateral dimensions.

There are two limiting cases to equation (7). One is the case when $h = h_1 = h_2$. This is written in equation (8), which may also be obtained by direct integration [6].

$$E_A = -\frac{A}{12\pi}\left(\frac{1}{d^2} + \frac{1}{(2h+d)^2} - \frac{2}{(h+d)^2}\right). \tag{8}$$

This case is particularly important in the field of membrane studies [6].

The other case is when $h_1 \to \infty$, then equation (7) obtains the form of equation (9):

$$E_A = -\frac{A}{12\pi}\left(\frac{1}{d^2} - \frac{1}{(d+h)^2}\right). \tag{9}$$

Equation (9) describes the energy per unit area between a wall of thickness h and a semi-infinite wall parallel to it and at a distance d apart as shown in figure 3. This expression is particularly important in wetting studies.

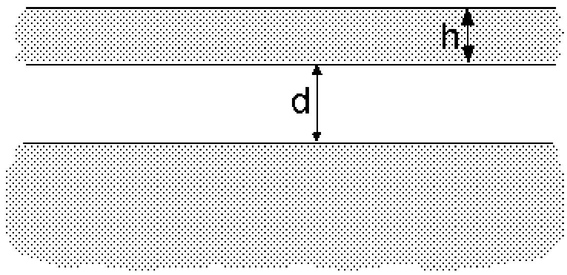


Figure 3. A cross-section of two parallel walls of infinite lateral dimensions, one of finite thickness and one of infinite thickness.

4. London–van der Waals energy between a shell and a sphere or a wall

The exact expression for a the vdW energy between a shell and a sphere was actually already obtained in equation (3), since the 'core' noted there is merely a sphere of a given radius. Writing equation (3) while substituting the word 'core' for the word 'sphere', and with the notations of equation (1) we get:

$$E_{\text{sphere}-\text{shell}}(R_1, R_2, R_2 - h, d) = E_{\text{sphere}}(R_1, R_2, d) - E_{\text{sphere}}(R_1, R_2 - h, d + h) \qquad (10)$$

Equation (10) describes the energy between a solid sphere of radius R_1 and a spherical shell of thickness h and external radius R_2, when separated by the closest distance d apart. Again we have limiting cases: first we discuss the case where $R_j \gg h, d$. This situation corresponds to the case shown in figure 4. In this case, by neglecting terms which are small compared to 1 (e.g. d/R_j and h/R_j or smaller), equation (10) reduces to:

$$E = -\frac{AR_1R_2}{6\,(R_1 + R_2)}\left(\frac{1}{d} - \frac{1}{(d+h)}\right) - \frac{A}{6}\ln\left[\frac{d}{(d+h)}\right] \qquad R_j \gg h, d. \qquad (10a)$$

Note that we could have obtain this result also from equation (5a).

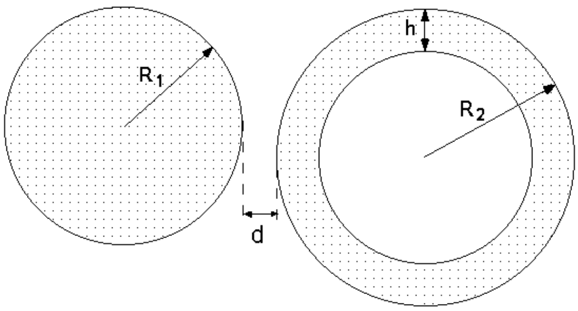


Figure 4. A cross-section of a solid sphere and a spherical shell.

Now we may readily obtain the case when $R_1 \gg h, d, R_2$, that is the energy between a spherical shell and a semi-infinite wall (see figure 5). This is obtained again from equation (10)

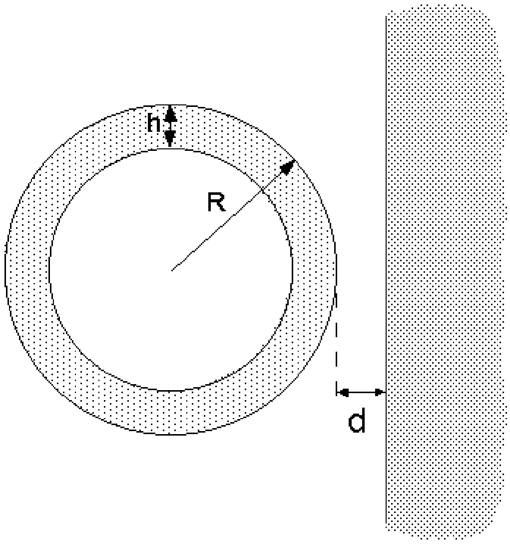


Figure 5. A cross-section of a spherical shell and a semi-infinite wall.

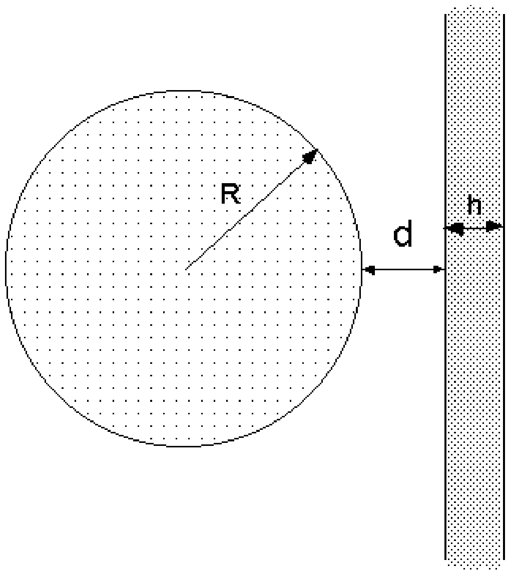


Figure 6. A cross-section of a solid sphere and a finite thickness wall with infinite lateral dimensions.

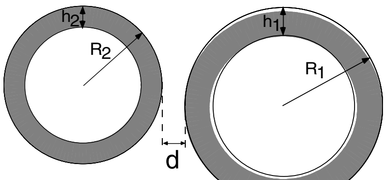
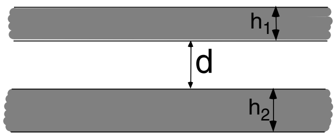
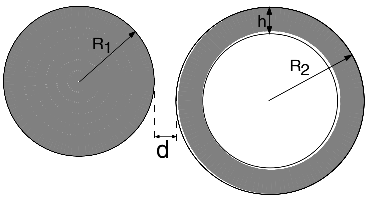
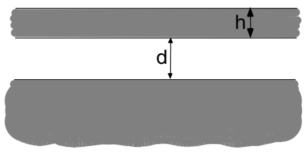
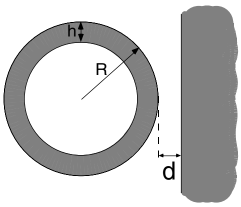
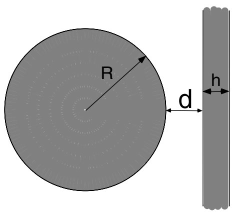
by neglecting terms small compared to R_1, (so R_1 is no longer in the function, and R_2 is written as R) and is written in equation (11):

$$E = -\frac{A}{6}\left(\frac{R}{(d+2R)} + \frac{h-R}{(d-h+2R)} + \frac{h-R}{(d+h)} + \frac{R}{d}\right) - \frac{A}{6}\ln\left[\frac{d\,(d-h+2R)}{(d+h)\,(d+2R)}\right]. \qquad (11)$$

Equation (11) reduces to equation (11a) when $R \gg h, d$:

$$E = -\frac{AR}{6}\left(\frac{1}{d} - \frac{1}{(d+h)}\right) - \frac{A}{6}\ln\left[\frac{d}{(d+h)}\right] \qquad R \gg h, d. \qquad (11a)$$

Table 1. A summary of some of the limiting cases calculated in this study.

Two spherical shells  $E=-\frac{AR_1R_2}{6(R_1+R_2)}\left(\frac{1}{(d+h_1+h_2)}-\frac{1}{(d+h_2)}-\frac{1}{(d+h_1)}+\frac{1}{d}\right)-\frac{A}{6}\ln\left[\frac{d(d+h_1+h_2)}{(d+h_1)(d+h_2)}\right]$	Two parallel walls  $E=-\frac{A}{12\pi}\left(\frac{1}{d^2}+\frac{1}{(d+h_1+h_2)^2}-\frac{1}{(d+h_1)^2}-\frac{1}{(d+h_2)^2}\right)$ (per unit area)
A sphere and a spherical shell  $E=-\frac{AR_1R_2}{6(R_1+R_2)}\left(\frac{1}{d}-\frac{1}{(d+h)}\right)-\frac{A}{6}\ln\left[\frac{d}{(d+h)}\right]$	Thin and a semi infinite walls  $E=-\frac{A}{12\pi}\left(\frac{1}{d^2}-\frac{1}{(d+h)^2}\right)$ (per unit area)
Spherical shell and semi-infinite wall  $E=-\frac{AR}{6}\left(\frac{1}{d}-\frac{1}{(d+h)}\right)-\frac{A}{6}\ln\left[\frac{d}{(d+h)}\right]$	A sphere and a wall  $E=-\frac{AR}{6}\left(\frac{1}{d}-\frac{1}{(d+h)}\right)-\frac{A}{6}\ln\left(\frac{d}{d+h}\right)$

Equations (11) and (11a) describe the interaction energy between a small spherical shell of external radius R and a thickness h and a semi-infinite wall.

The last case we discuss is when $R_2 \gg h, d, R_1$. This corresponds to the system shown in figure 6. In this case we get the following expression from equation (10):

$$E=-\frac{AR}{6}\left(\frac{1}{(d+2R)}-\frac{1}{(d+h+2R)}-\frac{1}{(d+h)}+\frac{1}{d}\right)-\frac{A}{6}\ln\left[\frac{d\,(2R+d+h)}{(d+h)\,(2R+d)}\right]. \quad (12)$$

For the common case when $R \gg d, h$ equation (12) is reduced to (12a):

$$E = -\frac{AR}{6}\left(\frac{1}{d} - \frac{1}{(d+h)}\right) - \frac{A}{6}\ln\left(\frac{d}{d+h}\right) \qquad R \gg d, h. \qquad (12a)$$

Equations (12) and (12a) describe the interaction energy between a wall (say a flat membrane) of thickness h and a solid sphere of radius R, when separated at a distance d apart. These may be important, e.g. in complex fluids when a micellar phase is in coexistence with a lamellar one, or in some cases of a hollow fibre enzymatic reactor [14] for the interaction of a substrate particle with an enzyme containing membrane. Comparing equations (12a) and (11a), we note that provided $R \gg d, h$ the interaction energy between a flat membrane of thickness h and a solid sphere of radius R has the same law as the interaction energy between a semi-infinite wall, and a spherical shell of external radius R, and a thickness h.

5. Summary

Table 1 summarizes some of the limiting cases calculated in this study. The general cases are omitted from this table, as the corresponding relations are rather lengthy, thus all the expressions which involve spherical objects in the table are subjected to large radii compared to the other sizes.

I wish to thank J Klein for useful discussions and for going over the eraly stages of the manuscript. I also acknowledge useful comments of S Safran, U Schwartz and A Weinstein from the Weizmann Institute and P Pincus and J Israelachvili from the University of California Santa Barbara.

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