

The boundary element approach to Van der Waals interactions

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Abstract. We develop a boundary element method to calculate Van der Waals interactions for systems composed of domains of spatially constant dielectric response of a general boundary shape. We achieve this by rewriting the interaction energy expression presented in *Phys. Rev. B*, **62** (2000) 6997 exclusively in terms of surface integrals of surface operators. We validate this approach in the Lifshitz case and give numerical results for the interaction of two spheres as well as the van der Waals self-interaction of a uniaxial ellipsoid. Our method is simple to implement and is particularly suitable for a full, non-perturbative numerical evaluation of non-retarded van der Waals interactions between objects of a completely general shape.

PACS. 77.22.Ch Permittivity (dielectric function) – 02.70.Pt Boundary-integral methods – 71.45.-d Collective effects

1 Introduction

Van der Waals interactions are universal and pervade all of physics, being essential for understanding of, *e.g.*, surface melting of ice [1] as well as osmotic equilibria of biomatter [2]. Their formulation in the case of interacting bodies with highly symmetric shapes is relatively straightforward but the problem of van der Waals interactions between objects of general, low symmetry, shapes is difficult [3,4] and is related to the problem of shape dependence of eigenvalues of the wave (or, in the nonretarded limit, Laplace) equation in finite domains that has been consistently formulated and solved only for very restrictive conditions [5]. For general geometries the van der Waals interaction energy has been obtained mostly either in terms of a perturbation expansion in geometric deviations from the case of high symmetry or a perturbation expansion in the dielectric constant (see [6,7] and references therein). The result of Golestanian [7] is particularly germane for our point of departure since it deals with van der Waals interactions in general geometries. It is based on a path integral field formulation and expresses the van der Waals interaction as a perturbation series in the spatial

contrast of the polarizability profile $\epsilon - 1$. Another approach based on the path integral formulation that leads to an effective action is given in [8] A different approach, based on the correlation effect of the density functional theory, is proposed in [9] and leads to an approximate result for van der Waals interaction for general geometries in terms of an expansion in terms of $1 - \epsilon^{-1}$. Both these perturbation results lead to trace-log formulas that contain volume integrals across the whole space and are in general difficult to implement numerically.

Below we will give an easily implementable universal numerical method for calculating non-retarded Van der Waals interactions for systems that are comprised of general-shape domains of spatially constant dielectric response. The expression we derive for van der Waals interactions is applicable to a wide class of geometries and is based on a surface trace reformulation of the interaction energy [10]. It is not based on any series expansion and can inherently treat problems of strong interactions that go beyond the pairwise summation approximation. We use this new expression for the van der Waals interaction energy first to rederive the standard Lifshitz result for plane parallel geometry as well as the interaction between two spheres, and then, to show its strength and versatility, we treat the problem of self-interaction of a uni-axial ellipsoid.

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2 Reduction of dimensionality

In [10], the nonretarded zero temperature form of the Van der Waals energy of a dielectric medium is given as

$$F = \int_0^\infty \frac{du}{2\pi} \text{Tr} (\ln (1 + \epsilon^{-1} [\nabla, \epsilon] \cdot \nabla G)) = \int_0^\infty \frac{du}{2\pi} f(u), \quad (1)$$

where $\epsilon(\mathbf{r}, \mathbf{r}') = \epsilon(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ is the local dielectric response function, $G(\mathbf{r}, \mathbf{r}') = -1/4\pi|\mathbf{r} - \mathbf{r}'|$ is the scalar Green function of the Laplace operator and u is the imaginary frequency that ϵ depends on. In what follows we will always state out results in terms of a dimensionless single imaginary frequency contribution $f(u)$ to the interaction energy defined above. The expression $[\cdot, \cdot]$ is a commutator and the trace is to be understood as setting the initial and final point \mathbf{r} of the operator to be the same and then integrating over the space \mathbf{r} .

Let us furthermore assume that the space is partitioned into domains of constant ϵ . Let S denote the two-dimensional manifold that is the union of all the boundaries between the domains of different ϵ . For a local dielectric function $[\nabla, \epsilon(\mathbf{r}, \mathbf{r}')] = (\nabla\epsilon(\mathbf{r}))$ holds true and therefore

$$f(u) = \text{Tr} (\ln (1 + \epsilon^{-1} (\nabla\epsilon) \cdot \nabla G)). \quad (2)$$

If we introduce the implicit function that defines the boundary S as $\Sigma(\mathbf{r}) = 0$, then the gradient of the dielectric function is $\nabla\epsilon(\mathbf{r}) = \delta\epsilon \delta(\Sigma(\mathbf{r})) \nabla\Sigma(\mathbf{r}) = \delta\epsilon D_S(\mathbf{r}) \mathbf{n}_r$, where $\delta\epsilon$ is the jump in the dielectric constant going from the region of negative Σ to positive, \mathbf{n}_r is the surface normal and D_S is the surface delta function such that

$$\int d^3\mathbf{r} D_S(\mathbf{r})g(\mathbf{r}) = \oint dS g(\mathbf{r}) \quad (3)$$

for any function g . While all the operators defined thus far act on the full three-dimensional space, we will now show, that under the above assumptions they can be reduced to two-dimensional expressions that only operate on the boundaries between dielectrically homogeneous regions of space. Let us first write the trace

$$\text{Tr}(\ln(1 + T)) = \sum_{n=1}^{\infty} (-1)^{(n+1)} \frac{\text{Tr}(T^n)}{n} \quad (4)$$

as a series, where

$$T_{\mathbf{r},\mathbf{r}'} = D_S(\mathbf{r}) 2\Delta_r \mathbf{n}_r \cdot \nabla G_{\mathbf{r},\mathbf{r}'}, \quad (5)$$

and $\Delta = \frac{1}{2}\epsilon^{-1}\delta\epsilon$. While Δ is a function of the coordinate, it is by assumption a constant along any single boundary between two dielectrics. In a system with more than a single boundary we may have Δ 's that are different for different boundaries. The expression for Δ depends also on ϵ^{-1} , which is however ill defined on the boundary itself. As will be shown below, in order to have agreement with the Lifshitz case, one needs to set $\Delta = \frac{\epsilon_2 - \epsilon_1}{\epsilon_1 + \epsilon_2}$, if ϵ_2 is the dielectric constant of the material on the side of the boundary to which the normal \mathbf{n}_r is pointing, and ϵ_1 is the dielectric constant of the material on the opposite

side. While it gives the correct result also for the case of two spheres, there is as yet, however, no exact proof that this choice of Δ , plausible as it might be, is applicable to geometries of all curvatures.

The expression for the trace of a power of T is

$$\text{Tr}(T^n) = \int d^3\mathbf{r}^{(1)} \int d^3\mathbf{r}^{(2)} \dots \int d^3\mathbf{r}^{(n)} T_{\mathbf{r}^{(1)},\mathbf{r}^{(2)}} T_{\mathbf{r}^{(2)},\mathbf{r}^{(3)}} \dots T_{\mathbf{r}^{(n)},\mathbf{r}^{(1)}}. \quad (6)$$

By inserting the definition (5) and taking into account equation (3) we derive straightforwardly

$$\begin{aligned} \text{Tr}(T^n) = 2^n \oint dS^{(1)} \oint dS^{(2)} \dots \oint dS^{(n)} \\ [\Delta_{\mathbf{r}^{(1)}} \mathbf{n}_{\mathbf{r}^{(1)}} \cdot \nabla G_{\mathbf{r}^{(1)},\mathbf{r}^{(2)}}] [\Delta_{\mathbf{r}^{(2)}} \mathbf{n}_{\mathbf{r}^{(2)}} \cdot \nabla G_{\mathbf{r}^{(2)},\mathbf{r}^{(3)}}] \dots \\ \dots [\Delta_{\mathbf{r}^{(n)}} \mathbf{n}_{\mathbf{r}^{(n)}} \cdot \nabla G_{\mathbf{r}^{(n)},\mathbf{r}^{(1)}}]. \end{aligned} \quad (7)$$

The expressions for $\text{Tr}(T^n)$ are thus evidently reduced to surface integrals. The relevant operators can be therefore considered to act only on the surface S and not on the whole three-dimensional space. If we now define the main operator that acts between two points \mathbf{r}, \mathbf{r}' on the surface as

$$K_{\mathbf{r},\mathbf{r}'} = 2\Delta_r \mathbf{n}_r \cdot \nabla G_{\mathbf{r},\mathbf{r}'}, \quad (8)$$

defining at the same time the surface trace as

$$\text{Tr}_S A_{\mathbf{r},\mathbf{r}'} = \oint dS A_{\mathbf{r},\mathbf{r}'}, \quad (9)$$

we then see that $\text{Tr} T^n = \text{Tr}_S K^n$. This allows us to re-sum the equation (4) as

$$\text{Tr}(\ln(1 + T)) = \text{Tr}_S(\ln(1 + K)) \quad (10)$$

and therefore formulate the interaction energy expression succinctly as

$$f(u) = \text{Tr}_S \ln (1 + 2\Delta_r \mathbf{n}_r \cdot \nabla G_{\mathbf{r},\mathbf{r}'}) = \sum_i \ln |1 + \kappa_i|, \quad (11)$$

where the trace Tr_S now stands for an integral over the surface S rather than the whole space. In the last line we introduced the eigenvalues of the operator K , denoted by κ_i , and evaluated the trace as a sum over these eigenvalues. Alternatively, instead of computing the eigenvalues one might consider the expansion of the logarithm in terms of the traces of the power of K as given in equation (7). This might be considered as an expansion in multiple inductions, possibly leading to alternative numerical implementations. The second-order term, for example, corresponds to the pairwise summation approximation of the dispersion interaction.

3 The Lifshitz case

To test the above approach, let us consider the Lifshitz case of a planar slab of thickness ℓ composed of one dielectric, surrounded by different semi-infinite dielectrics

on either side. Let us define the normal \mathbf{n} to point outwards on the surface of the slab. The operator K does not have any contributions arising from the interaction of the elements of one wall with other elements of the same wall, since the gradient of the Green function between such two elements is perpendicular to the boundary normal.

Let the coordinates x, y lie in the plane of the slab and the z coordinate perpendicular to it. Let the eigenvector components be denoted as $\xi_i^{(j)}(x, y)$ with $j = 1, 2$ for the two boundaries. Due to the symmetry of the problem we may expect the solutions to take the form

$$\xi_i^{(Q,j)}(x, y) = \exp(iQx)\beta(j). \quad (12)$$

We choose the x -direction to be along the wave vector Q without loss of generality. Explicitly inserting the Green function expression into the eigenvalue equation

$$\kappa_i \xi_i = K \xi_i, \quad (13)$$

we obtain for $j \neq j'$

$$\kappa_i \beta(j) = -2\Delta_{j'} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dx_1 dy_1 \ell \exp(iQx_1) \beta(j')}{4\pi (x_1^2 + y_1^2 + \ell^2)^{\frac{3}{2}}}.$$

Integration over y_1 gives

$$\kappa_i \beta(j) = -2\Delta_{j'} \int_{-\infty}^{\infty} dx_1 \frac{\ell \exp(iQx_1) \beta(j')}{2\pi (x_1^2 + \ell^2)}. \quad (14)$$

The integration over x_1 requires contour integration depending on the sign of Q and yields the system of equations

$$\begin{aligned} \kappa_i \beta(1) &= -\Delta_2 \exp(-|Q|\ell) \beta(2), \\ \kappa_i \beta(2) &= -\Delta_1 \exp(-|Q|\ell) \beta(1), \end{aligned} \quad (15)$$

as we explicitly insert the two possibilities for j, j' . For a given Q this system has two eigenvalues, namely

$$\kappa_i = \pm \sqrt{\Delta_1 \Delta_2} \exp(-|Q|\ell). \quad (16)$$

We can therefore write the $f(u)$ (11) as

$$f(u) = \sum_Q \ln(1 - \Delta_1 \Delta_2 \exp(-2|Q|\ell)), \quad (17)$$

or equivalently, if Q s are assumed to fulfill periodic conditions on a flat plate of an area A , then taking this area to infinity, we get for the interaction energy

$$F/A = \int_0^{\infty} \frac{du}{2\pi} \int \frac{d^2Q}{(2\pi)^2} \ln(1 - \Delta_1 \Delta_2 \exp(-2|Q|\ell)), \quad (18)$$

which is exactly the non-retarded Lifshitz result [11].

4 Discretisation and numerical examples

In a general case, the equation (11) cannot be solved analytically but rather requires a proper discretization scheme

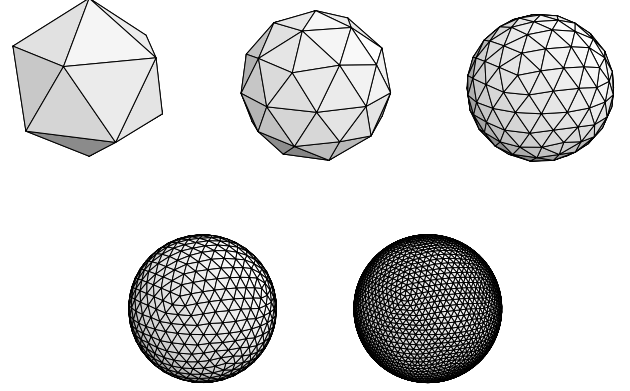


Fig. 1. The triangulation representation of a sphere as used in calculations. We start with an icosahedron and on each step subdivide each face into 4 smaller triangles. This triangulation is essential and allows us to use an explicit form for the solid angle $\Omega_{S_i}(\mathbf{r}')$.

for the operator (8) on the surface. Let us assume that the surface is split into a set of discrete boundary elements S_i , along which the eigenvectors of the operator K are constant. Higher-order schemes may of course be employed, but for clarity we will deal with this simplest example. It is worth noting that

$$h_{S_i, \mathbf{r}'} = \int_{S_i} dS_{\mathbf{r}} \mathbf{n}_{\mathbf{r}} \cdot \nabla G_{\mathbf{r}, \mathbf{r}'} = \frac{1}{4\pi} \Omega_{S_i}(\mathbf{r}'), \quad (19)$$

where $\Omega_{S_i}(\mathbf{r}')$ is the solid angle of the surface S_i as seen from the point \mathbf{r}' . To obtain the matrix elements of K , we also average above result over the surface S_j such that

$$K_{i,j} = \frac{2\Delta_{S_i}}{S_j} \int_{S_j} dS_{\mathbf{r}'} h_{S_i, \mathbf{r}'}. \quad (20)$$

The operators introduced thus far are not well defined for very short distances and lead to divergences that are due to the local dielectric response assumption [12]. These divergences can be regularized by a simple ansatz

$$\tilde{K}_{i,j} = K_{i,j} \left[1 - \exp\left(-\frac{d_{ij}^2}{2\sigma^2}\right) \right], \quad (21)$$

where d_{ij} is the distance between the centers of the boundary elements i and j and σ gives the estimate of the non-local response distance. By calculating the eigenvalues for a discrete matrix of this type, the interaction energy can then be calculated according to equation (11) using the approximate eigenvalues of \tilde{K} .

We test this method of calculation in two cases, namely the interaction between two dielectric spheres and the self-interaction of an uniaxial ellipsoid. In both cases we represent the spherical surfaces via a recursive subdivision of an icosahedron that limits towards a sphere, as shown in Figure 1. This triangulation procedure is extremely useful since in this case a closed expression exists for the solid angle $\Omega_{S_i}(\mathbf{r}')$ [13], which, for a triangle T_i with the vertices

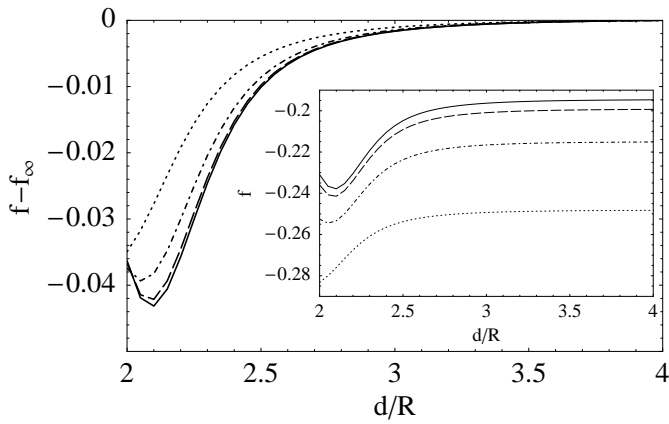


Fig. 2. The van der Waals interaction energy calculation for a pair of spheres of radius 1 with $\sigma = 0.2R$ and $\Delta = 1/2$ as a function of the separation d between the spheres as compared to the energy of two well-separated spheres. The inset shows the raw energy computation. The dotted lines represents the single, the dot-dashed line the double, the dashed line the triple and the full line the quadruple icosahedron subdivision of the two spheres.

\mathbf{r}_i , reads as

$$\Omega_{T_i}(\mathbf{r}') = 2 \tan^{-1} \left[\frac{\mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)}{(R_1 R_2 R_3 + R_1 \mathbf{R}_2 \cdot \mathbf{R}_3 + R_2 \mathbf{R}_3 \cdot \mathbf{R}_1 + R_3 \mathbf{R}_1 \cdot \mathbf{R}_2)} \right], \quad (22)$$

where $\mathbf{R}_i = \mathbf{r}_i - \mathbf{r}'$. Our reformulation of the van der Waals interaction energy was obtained exactly in terms of these solid angles, equation (11). The same triangulation procedure can be used for any other bounding surface.

The interaction energy calculation for a pair of spheres of radius R is given in Figure 2. In all calculations we use the value of $\Delta = 1/2$. We may see that the energy at large separation, that obviously corresponds to twice the self-interaction of individual spheres, is a relatively poorly convergent function of the degree of discretization. The convergence can be much improved by simply subtracting the self-interaction energy from the total energy with the result that the difference now converges a lot faster. The short-range kink in the interaction energy is a consequence of the short-range cutoff σ that represents the nonlocal dielectric response. The van der Waals interaction energy of two spheres can be also calculated analytically via the secular determinant of the field modes [12], yielding a closed-form expression with an error estimate of $\mathcal{O}(d^{-12})$, where d is the distance between the sphere centers. In Figure 3 we validate our result by comparing it to this expression. Obviously the large-distance behavior does not depend on the short-range cutoff, as indeed one would expect, and agrees pleasingly with the analytical result [12]. The short-range kink is displaced towards progressively smaller values of the separation as the short range cutoff is diminished, see Figure 3.

van der Waals self-interaction of a uniaxial ellipsoid is given in Figure 4 to illustrate the power of our approach. Again, convergence of the raw value of the energy as a

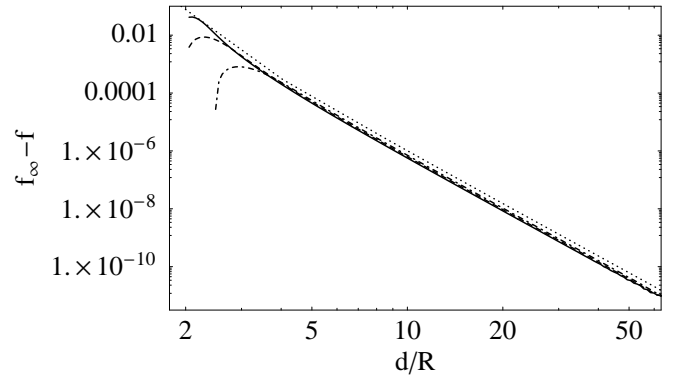


Fig. 3. The van der Waals energy as a function of the separation for the same system as in Figure 2 but with varying the cutoff $\sigma = 0.2R$ (full), $\sigma = 0.4R$ (dashed) and $\sigma = 0.8R$ (dot-dashed). All the results are given for the third subsequent icosahedron subdivision. The dotted line represents the analytical result [12].

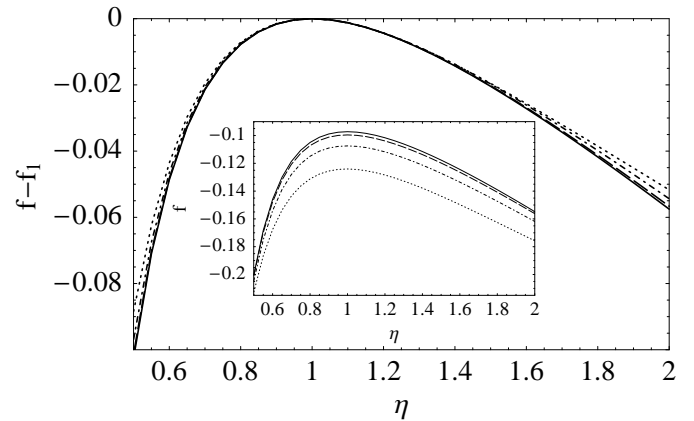


Fig. 4. The van der Waals energy contribution for a uniaxial ellipsoid of constant volume as a function of the main semi-axis half length relative to the energy of a sphere. The inset shows the raw free-energy computation. The dotted lines represents the single, the dot-dashed line the double, the dashed line the triple and the full line the quadruple icosahedron subdivision of the sphere used to obtain the ellipsoid.

function of the density of triangulation is slow, but if we subtract the energy of the spherical configuration the convergence is again much faster. We see that the spherical configuration has the highest van der Waals energy and is thus unstable. This shape instability is driven purely by shape-dependent van der Waals interactions under the assumption of a negligible surface energy contribution. In general, the exact location of the point of instability would depend on the dielectric discontinuity at the surface of the ellipsoid as well as on the surface tension and possibly on the elastic deformation energy [14]. Van der Waals interaction stabilization or destabilization of various shapes should be particularly important for systems of low or vanishing surface tension, such as complicated shapes of closed lipid vesicles, where good numerical estimates of these interactions for various non-trivial shapes arising in the shape phase diagram are extremely hard to get [15].

5 Conclusion

In this work we presented a general numerical method to calculate non-retarded zero-temperature van der Waals interactions for a class of systems that are composed of spatial domains of constant dielectric response. This was achieved by reformulating the interaction energy expression that contains volume traces in such a way that now it contains only surface ones. This reformulation yields itself to a straightforward numerical implementation based on multiple triangulation of the shapes of interacting bodies. We showed that the proposed method reduces to standard results for two plane parallel semi spaces and two spheres and that it can be used to shed light onto cases which have heretofore eluded an exact or even an approximate analysis.

Though our approach has been formulated in the framework of non-retarded zero-temperature van der Waals interactions, it appears to us that it should be quite straightforward to extend it also across the complete domain of spacings between interacting bodies as well as to the case of finite temperatures, where the frequency integral is simply turned into a Matsubara frequency summation.

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