A general theory for the van der Waals interactions in colloidal systems based on fluctuational electrodynamics

Vassilios Yannopapas

Department of Materials Science, University of Patras, GR-26504 Patras, Greece

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Abstract

A rigorous theory for the determination of the van der Waals interactions in colloidal systems is presented. The method is based on fluctuational electrodynamics and a multiple-scattering method which provides the electromagnetic Green’s tensor. In particular, expressions for the Green’s tensor are presented for arbitrary, finite, collections of colloidal particles, for infinitely periodic or defected crystals as well as for finite slabs of crystals. The presented formalism allows for ab initio calculations of the vdW interactions in colloidal systems since it takes fully into account retardation, many-body, multipolar and near-fields effects.

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I. INTRODUCTION

The van der Waals (vdW) interactions are particularly important in colloidal systems since, along with the electrostatic forces, they determine the structure of such systems. The stability of colloidal systems resulting from the interplay between the vdW and the electrostatic interactions is very well elucidated in the context of Derjaguin-Landau-Verwey-Overbeek theory.\(^1\) The vdW interactions which originate from the irreducible electromagnetic (EM) fluctuations of vacuum are usually calculated by means of the Hamaker approach,\(^2\) where the force stems from simple pairwise addition of the corresponding intermolecular forces,\(^3,4\) although the vdW interactions are not additive. A rigorous treatment of the vdW interactions based on fluctuational electrodynamics\(^5,6\) has been pioneered by Lifshitz\(^7\) for the case of two infinite half-spaces. The Lifshitz theory has been extended to the case of pairs of finite-sized objects such as spheres or cylinders (Derjaguin approximation)\(^4,8\) which is valid, however, for very short distances between the objects, in the nonretarded limit. In some cases, elements of the Lifshitz theory for half-spaces are incorporated within the Hamaker formula for the vdW force between two particles, in the form of semi-empirical corrections.\(^3,4,9,10,11\) By use of perturbation theory and the Clausius-Mossotti formula, Langbein\(^12,13\) developed a general formalism for the vdW force between two spheres which has been primarily applied to aerosol particles.\(^14,15,16\)

Recently, a new, rigorous theory based on fluctuational electrodynamics for the calculation of the vdW interactions among a collection of macroscopic bodies of finite size has been proposed.\(^17\) This theory is based on a multiple-scattering Green’s tensor formalism incorporated within the framework of fluctuational electrodynamics. More specifically, the vdW force results from the integration over the surface of the bodies of the Maxwell stress tensor of the vacuum/thermal EM field which is provided by the fluctuation-dissipation theorem and through this by the Green’s tensor of the classical EM field. The calculation of the Green’s tensor is based on an EM multiple scattering formalism for arbitrary collections of scatterers. The multiple-scattering Green’s tensor formalism offers a precise knowledge of the fluctuating EM field by going beyond the approximation of pairwise interactions between the scatterers and by taking into account the full multipole interactions between them. Furthermore, since it constitutes a solution to the inhomogeneous wave equation, retardation effects are included \textit{a priori} in the presented formalism. In addition, metallic
and dielectric particles are treated on an equal footing since the method in question also accounts for the magnetic-field vacuum fluctuations which cannot be neglected in the case of metallic particles. Finally, the effect of finite temperature can be easily addressed. We note that a different approach has been recently presented\textsuperscript{18} where the EM Green’s tensor entering the fluctuation-dissipation theorem is calculated by means of a finite-difference frequency-domain method.

When a particle is a member of a colloidal crystal and a net vdW force exerted on the particle is evident (e.g., in a finite slab of a colloidal crystal or in an infinite crystal containing point and/or line defects), it is calculated from a pairwise addition of the forces stemming from the all the other particles of the crystal. So, at first glance, an extension of the Ref.\textsuperscript{17} to the case of a colloidal system would be based on a pairwise summation of the (exact) force for a pair of particles. However, such an approach is only approximately correct since the vdW interactions are not additive. The way to extend the method of Ref.\textsuperscript{17} to the case of a colloidal crystal is to derive a semi-analytical expression of the EM Green’s tensor for the particular crystal. The knowledge of the EM Green’s tensor everywhere in space allows the calculation of the cross-spectral correlation functions of the vacuum EM field which are contained in the EM Maxwell stress tensor, by application of the fluctuation-dissipation theorem. By integrating the Maxwell stress tensor over the surface of the particle we obtain the vdW force. The paper is organized as follows. In section II we provide a brief overview of fluctuational electrodynamics and the Maxwell stress tensor. In section III we provide expressions for the EM Green’s tensor, (a) for arbitrary collections of a finite number of scatterers, (b) for infinite, periodic and defected crystals, and (c) for finite slabs of colloidal crystals. In section IV we apply the formalism to the case of a monolayer of polystyrene spheres containing a single defect. Section V concludes the paper.

II. VAN DER WAALS FORCE

A. Maxwell stress tensor

We consider a finite scatterer with electric permittivity $\epsilon_s$ and/or magnetic permeability $\mu_s$ different from those, $\epsilon_h$, $\mu_h$ of the surrounding homogeneous medium. According to classical electrodynamics, the exerted force $\mathbf{F}$ on a finite scatterer in the presence of electric
and magnetic $H$ fields satisfying the Maxwell equations is obtained by integrating the time-average Maxwell stress tensor $T_{ij}$ over the surface around the scatterer

$$\langle F_i \rangle_t = \int_S \sum_j \langle T_{ij} \rangle_t n_j dS \quad (1)$$

where $\langle .. \rangle_t$ denotes the time average, $n$ is the normal vector at the surface surrounding the object, and $i, j = x, y, z$. The components of the tensor $\langle T_{ij} \rangle_t$ are given by

$$\langle T_{ij} \rangle_t = \varepsilon_0 \varepsilon_0 \langle E_i(r, t) E_j(r, t) \rangle_t + \mu_0 \mu_0 \langle H_i(r, t) H_j(r, t) \rangle_t$$

$$- \frac{1}{2} \delta_{ij} \varepsilon_0 \varepsilon_0 \sum_i \langle E_i(r, t) E_i(r, t) \rangle_t + \mu_0 \mu_0 \sum_i \langle H_i(r, t) H_i(r, t) \rangle_t \right]. \quad (2)$$

$\delta_{ij}$ is the Kronecker symbol and $\varepsilon_0$, $\mu_0$ are the electric permittivity and magnetic permittivity of vacuum, respectively.

## B. Fluctuation-dissipation theorem

In the absence of other radiation sources, the fields $E, H$ are generated by the thermal radiation emitted from the same or neighboring scatterers at finite temperature (thermal fluctuations) or by vacuum radiation at zero temperature (zero-point fluctuations). The time-correlation function $\langle E_i(r, t + \tau) E_j(r', t) \rangle_t$ contained in Eq. (2) is calculated within the framework of fluctuational electrodynamics, namely from

$$\langle E_i(r, t + \tau) E_j(r', t) \rangle_t = \text{Re} \left[ \int_0^\infty \frac{d\omega}{2\pi} \exp(i\omega\tau) W_{ij}^{EE}(r, r'; \omega) \right]. \quad (3)$$

The quantity $W_{ij}^{EE}(r, r'; \omega)$ is the cross-spectral correlation function for the electric field. For a system at thermal equilibrium, i.e., the scatterer, the surrounding medium and its neighbouring scatterers at the same temperature $T$, $W_{ij}$ is provided by the fluctuation-dissipation theorem

$$W_{ij}^{EE}(r, r'; \omega) = 4\omega \mu_0 \varepsilon_0 c^2 \text{Im} G_{ij}^{EE}(r, r'; \omega) \hbar \omega \left[ 1 + \frac{1}{\exp(h\omega/k_B T) - 1} \right], \quad (4)$$

where $\hbar$ is the reduced Planck’s constant, $k_B$ is the Boltzmann’s constant and $G_{ij}^{EE}(r, r'; \omega)$ is the component of the full Green’s tensor $G_{ij}$ which provides the electric field at $r$ due to an electric dipole source at $r'$. The time-correlation function $\langle H_i(r, t + \tau) H_j(r', t) \rangle_t$ for the magnetic field is given similar to Eq. (3) with $W_{ij}^{EE}$ substituted by

$$W_{ij}^{HH}(r, r'; \omega) = 4\omega \varepsilon_0 \varepsilon_0 c^2 \text{Im} G_{ij}^{HH}(r, r'; \omega) \hbar \omega \left[ 1 + \frac{1}{\exp(h\omega/k_B T) - 1} \right]. \quad (5)$$
We note that, the final value of the vdW force acting on a scatterer is obtained by subtracting from Eq. (1) the force which remains in the absence of the scatterer as it is the case for the calculation of the Casimir force between two semi-infinite slabs. However, in vacuum, the Green’s tensor and the corresponding Maxwell stress tensor, Eq. (2), are constant in space and their integral over a closed surface is zero. From the above, it is obvious that the central quantity which essentially determines the force acting on the scatterer is the EM Green’s tensor.

III. ELECTROMAGNETIC GREEN’S TENSOR

A. Multipole expansion of the EM field

Let us consider a harmonic EM wave, of angular frequency \( \omega \) which is described by its electric-field component

\[
E(r, t) = \text{Re} [E(r) \exp(-i \omega t)].
\]

In a homogeneous medium characterized by a dielectric function \( \epsilon(\omega)\epsilon_0 \) and a magnetic permeability \( \mu(\omega)\mu_0 \), where \( \epsilon_0, \mu_0 \) are the electric permittivity and magnetic permeability of vacuum, Maxwell equations imply that \( E(r) \) satisfies a vector Helmholtz equation, subject to the condition \( \nabla \cdot E = 0 \), with a wave number \( q = \omega/c \), where \( c = 1/\sqrt{\mu \epsilon \mu_0 \epsilon_0} = c_0/\sqrt{\mu \epsilon} \) is the velocity of light in the medium. The spherical-wave expansion of \( E(r) \) is given by

\[
E(r) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left\{ a_{Elm} f_l(qr) X_{lm}(\hat{r}) + a_{Elm}^* \frac{i}{q} \nabla \times \left[ f_l(qr) X_{lm}(\hat{r}) \right] \right\},
\]

where \( a_{lm}^P (P = E, H) \) are coefficients to be determined. \( X_{lm}(\hat{r}) \) are the so-called vector spherical harmonics and \( f_l \) may be any linear combination of the spherical Bessel function, \( j_l \), and the spherical Hankel function, \( h_l^+ \). The corresponding magnetic induction, \( B(r) \), can be readily obtained from \( E(r, t) \) using Maxwell’s equations.

B. Scattering from a single scatterer and the corresponding Green’s tensor

In this subsection we present a brief summary of the solution to the problem of EM scattering from a single sphere (Mie scattering theory) along with the expression for the single-sphere Green’s tensor. We consider a sphere of radius \( S \), with its center at the origin.
of coordinates, and assume that its electric permittivity $\epsilon_s$ and/or magnetic permeability $\mu_s$ are different from those, $\epsilon_h$, $\mu_h$ of the surrounding homogeneous medium. An EM plane wave incident on this scatterer is described, respectively, by Eq. (7) with $f_l = j_l$ (since the plane wave is finite everywhere) and appropriate coefficients $a_L^0$, where $L$ denotes collectively the indices $Plm$. That is,

$$E^0(r) = \sum_L a_L^0 J_L(r)$$

(8)

where

$$J_{Elm}(r) = i\frac{q_h}{q_h} \nabla \times j_l(q_hr)X_{lm}(\hat{r}), \quad J_{Hlm}(r) = j_l(q_hr)X_{lm}(\hat{r})$$

(9)

and $q_h = \sqrt{\epsilon_h\mu_h\omega/c_0}$. The coefficients $a_L^0$ depend on the amplitude, polarization and propagation direction of the incident EM plane wave and are given by Eqs. (37) (subsection III G) for $g = 0$.

Similarly, the wave that is scattered from the sphere is described by Eq. (7) with $f_l = h_l^+$, which has the asymptotic form appropriate to an outgoing spherical wave: $h_l^+ \approx (-i)^l\exp(iq_hr)/iq_hr$ as $r \to \infty$, and appropriate expansion coefficients $a_L^+$. Namely,

$$E^+(r) = \sum_L a_L^+ H_L(r)$$

(10)

where

$$H_{Elm}(r) = i\frac{q_h}{q_h} \nabla \times h_l^+(q_hr)X_{lm}(\hat{r}), \quad H_{Hlm}(r) = h_l^+(q_hr)X_{lm}(\hat{r}).$$

(11)

The wavefield for $r > S$ is the sum of the incident and scattered waves, i.e., $E^{\text{out}} = E^0 + E^+$. By applying the requirement that the tangential components of $E$ and $H$ be continuous at the surface of the scatterer, we obtain a relation between the expansion coefficients of the incident and the scattered field, as follows:

$$a_L^+ = \sum_{L'} T_{LL'} a_{L'}^0,$$

(12)

where $T_{LL'}$ are the elements of the so-called scattering transition $T$-matrix.\textsuperscript{22} Eq. (12) is valid for any shape of scatterer; explicit relations of the $T$-matrix for scatterers of various shapes can be found elsewhere.\textsuperscript{23,24}

The Green’s tensor for a single sphere is given by\textsuperscript{25}

$$G_{ii}^{(s)}(r, r') = -i\omega \frac{\epsilon_h\mu_h}{c_0^3} \sum_L \left[ R_{L;i}(r) \overline{R}_{L;i'}(r') \Theta(r - r') + I_{L;i}(r) \overline{I}_{L;i'}(r') \Theta(r - r') \right]$$

(13)
The vector functions $R_{L;i}(r), \overline{R}_{L;i}(r)$ are dimensionless eigenfunctions of the wave operator
\[
\Lambda(r) = \frac{c_0^2}{\epsilon(r)\mu(r)} \nabla \times \nabla \times
\]
for a single scatterer which are regular at its center.\textsuperscript{25,26} The vector functions $I_{L;i}(r), \overline{I}_{L;i}(r)$ are also eigenfunctions of the operator (14) but they are infinite at the sphere center.\textsuperscript{25,26} The Green’s tensor of Eq. (13) will be the basis for the construction of the corresponding tensor for a collection of spheres.

C. Green’s tensor for many scatterers

We consider a collection of $N$ nonoverlapping scatterers described by a permittivity $\epsilon_s$ and permeability $\mu_s$ centred at sites $\mathbf{R}_n$ in a homogeneous host medium described by $\epsilon_h, \mu_h$, respectively. In site-centered representation, the Green’s tensor for the system of scatterers satisfies\textsuperscript{25,26}
\[
\sum_i \left[ \omega^2 \delta_i - \Lambda_{\nu_i}(\mathbf{r}_n + \mathbf{r}_n) \right] G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'}, \mathbf{r}_{n'}) = \delta_{i'i} \delta(\mathbf{r}_n - \mathbf{r}_{n'}) \delta_{nn'}
\]
where $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$, $\mathbf{r}_{n'} = \mathbf{r}' - \mathbf{R}_{n'}$, and $i, i' = x, y, z$. The operator $\Lambda_{\nu_i}(\mathbf{r})$ is given by Eq. (14). It can be verified that the Green’s tensor satisfying Eq. (15) is the following\textsuperscript{25,26}
\[
G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'}, \mathbf{r}_{n'}) = G_{ii'}^{(s)}(\mathbf{r}_n, \mathbf{r}_{n'}) \delta_{nn'} - i\omega \frac{(\epsilon_h \mu_h)^{3/2}}{c^3} \sum_{LL'} \overline{R}_{L;i}(\mathbf{r}_n) D^{n}_{L'i} R^{n'}_{L'i'}(\mathbf{r}_{n'}).
\]
$G_{ii'}^{(s)}(\mathbf{r}_n, \mathbf{r}_{n'})$ is the Green’s tensor for a single scatterer located at $\mathbf{R}_n$ and it is given by Eq. (13). The vector functions $R^n_{L;i}(\mathbf{r}_n), \overline{R}^n_{L;i}(\mathbf{r}_n)$ are the dimensionless eigenfunctions of the operator of Eq. (14) for the sphere at $\mathbf{R}_n$. $D^{n}_{LL'}$ are propagator functions that represent the contributions of all possible paths by which a wave outgoing from the $n'$-th scatterer produces an incident wave on the $n$-th scatterer, after scattering in all possible ways (sequences) by the scatterers at all sites including the $n$-th and $n'$-th scatterers. The specific form of the $D^{n}_{LL'}$ propagator functions depends on the geometrical arrangement of the scatterers.

D. Propagator for an arbitrary collection of scatterers

For an arbitrary collection of a finite number $N$ of scatterers, the $D$-propagator is given by\textsuperscript{25}
\[
D^{nn'}_{LL'} = \Omega^{nn'}_{LL'} + \sum_{n''} \sum_{L''} \sum_{L'''} D^{n'n''}_{LL'''} T^{n''}_{L'''} \Omega^{n''n'}_{L'L''}.
\]
The matrix $\Omega_{LL'}^{nn'}$ appearing in Eq. (17) is called free-space propagator and transforms an outgoing vector spherical wave about $R_{n'}$ in a series of incoming vector spherical waves around $R_n$. The matrix $T_{LL'}^n$ is the scattering $T$-matrix of a scatterer of general shape, located at $R_n$.

**E. Propagator for periodic arrays of scatterers**

For the case of an infinite number of same spheres arranged periodically, in one- (1D), two- (2D) or three (3D) dimensions, the propagator $D_{LL'}^{nn'}$ is given as a Fourier transform

$$D_{LL'}^{nn'} = \frac{1}{v} \int_{BZ} d^q k \exp[i k \cdot (R_n - R_{n'})]D_{LL'}(k),$$

where $q$ is the space dimensionality, the integration in Eq. (18) is carried out within the Brillouin Zone (BZ), $k$ is the Bloch wavevector, and $v$ is the BZ volume. $R_n$ are the Bravais lattice vectors. $D_{LL'}(k)$ is given by

$$D_{LL'}(k) = \Omega_{LL'}(k) + \sum_{L''L'''} D_{LL''}(k)T_{L''L'''}\Omega_{L''L'}(k).$$

$T_{L''L'''}$ is the $T$-matrix of the spheres. $\Omega_{LL'}(k)$ depend only on the crystal lattice and are known as structure constants a term which is common in the Korringa-Kohn-Rostoker method for the calculation of the electronic band structure of atomic solids. They can be found by Ewald-summation techniques. Eqs. (4) and (5) require the calculation of the Green’s tensor [via Eq. (16)] for an infinitely periodic lattice of scatterers; therefore, only the $D_{LL'}^{00}$ component (that for the central unit cell) is needed since all spheres are equivalent for the case of a Bravais lattice with one sphere per unit cell.

We note that the propagator of Eq. (19) does not yield a net nonzero vdW force, since it corresponds to an infinitely periodic system. However, the propagator of Eq. (19) can be used as a basis for calculating the corresponding propagator of a system containing, e.g., one or more point defects (not symmetrically distributed within the crystal), in which case a net vdW force emerges. If, for example, the colloidal particles (described by a a scattering matrix $T_{0LL'}^n$) positioned at $R_n$ in an otherwise periodic crystal, are substituted by other, different particles, each of them described by a scattering matrix $T_{LL'}^n$, the propagator of the defected system is given similar to Eq. (17), i.e.,

$$D_{LL'}^{nn'} = D_{0LL'}^{nn'} + \sum_{n''} \sum_{L''} D_{LL'''}^{nn''} \Delta T_{L''L'''}^{nn''} D_{0L''L'}^{nnn'}.$$
where $\Delta T_{L''L'''}^{n'} = T_{L''L'''}^{n'} - T_{0LL'}^{0}$ and $D_{0LL'}^{n'}$ is the propagator of the periodic system given by Eqs. (18) and (19).

F. Propagator for finite slabs

In reality, the colloidal systems are not infinitely periodic but they are actually slabs consisting of a finite number of planes of particles (scatterers). In this case, the vdW force exerted on a given scatterer depends on the position of the plane within which it is located and can therefore be very different for a scatterer on a surface plane than a scatterer at an innermost plane. In the following lines, we will provide a formalism for the propagator for a slab consisting of $N_p$ planes of scatterers. It is assumed that all the planes of the slab have the same 2D periodicity with the associated lattice vectors given by

$$R_n = n_1a_1 + n_2a_2,$$

where $a_1$ and $a_2$ are primitive vectors in the $xy$ plane and $n_1, n_2 = 0, \pm 1, \pm 2, \pm 3, \cdots$. The corresponding 2D reciprocal lattice is defined by

$$g = m_1b_1 + m_2b_2$$

where $m_1, m_2 = 0, \pm 1, \pm 2, \pm 3, \cdots$ and $b_1, b_2$ are primitive vectors defined by

$$b_i \cdot a_j = 2\pi\delta_{ij}, \ i, j = 1, 2. \quad (23)$$

Although each plane of the slab must have the same 2D periodicity, the spheres within each of the $N_p$ planes can be different in terms of shape, size or refractive index.

The propagator for a scatterer residing at the $\nu$-th plane ($\nu = 1, 2, \cdots, N_p$) of a slab is written as a sum of three terms

$$F_{\nu;LL'}^{00} = D_{\nu;LL'}^{00} + \sum_n \sum_{L''} P_{\nu;LL'}^{0n} T_{\nu;L''L'''}^{n} D_{\nu;LL'}^{n0} + P_{\nu;LL'}^{00} \quad (24)$$

The matrix $D_{\nu;LL'}^{n0}$ represents all the possible scattering paths within the $\nu$-th plane by which a wave outgoing from the $m$-th sphere of this plane produces an incident wave on the $n$-th sphere of the same plane, after scattering in all possible ways by all the spheres of this plane including the central sphere (every sphere represented by the scattering matrix $T_{\nu;LL'}$). It is given by application of Eq. (18) to a 2D periodic lattice, i.e.,
\[ D_{\nu;LL'}^{nm} = \frac{1}{S_0} \int \int_{SBZ} d^2k_\parallel \exp(i k_\parallel \cdot \mathbf{R}_{nm}) D_{\nu;LL'}(k_\parallel) \]  

(25)

where

\[ D_{\nu;LL'}(k_\parallel) = \sum_{LL''} \left[ \left[ I - \Omega(k_\parallel) \mathbf{T}_\nu \right]^{-1} \right]_{LL''} \Omega_{LL''}(k_\parallel) \]  

(26)

where \( \mathbf{R}_{nm} = \mathbf{R}_n - \mathbf{R}_m \), \( S_0 \) is the area of the Surface Brillouin Zone (SBZ) corresponding to Eq. (22), and \( \Omega_{LL'}(k_\parallel) \) are the 2D structure constants.

The matrix \( P_{\nu;LL'}^{0n} \) appearing in the second and third terms of Eq. (24) represents all scattering paths by which an outgoing wave from the \( n \)-th sphere of the \( \nu \)-th plane exits from that plane to produce an incident wave on the central sphere of the same plane after scattering in all possible ways by all the planes of spheres of the slab, including the \( \nu \)-th plane. In the next subsection we will present a summary of the derivation of \( P_{\nu;LL'}^{0n} \) and \( F_{\nu;LL'}^{00} \), which is given in detail in Ref. 30.

**G. Calculation of \( P_{\nu;LL'}^{0n} \) and \( F_{\nu;LL'}^{00} \)**

A wave outgoing from the \( n \)-th sphere of the \( \nu \)-th plane has the form of Eq. (10)

\[ \mathbf{E}^{sc}(\mathbf{r}) = \sum_L b^+_L(n; \nu) \mathbf{H}_L(\mathbf{r}) \]  

(27)

where \( \mathbf{r}_{nm} \) is the position vector with respect to the center of the \( n \)-th sphere of the \( \nu \)-th plane. We can expand the wave of Eq. (27) into a sum of plane waves propagating or decaying away from the \( \nu \)-th plane as follows.\(^{30}\) To the right of the \( \nu \)-th plane we have

\[ \mathbf{E}^{out +}(\mathbf{r}) = \frac{1}{S_0} \int \int_{SBZ} d^2k_\parallel \sum_g \mathbf{E}^{out +}_g(k_\parallel) \exp[i \mathbf{K}_g^+ \cdot (\mathbf{r} - A_2(\nu))] \]  

(28)

with

\[ \mathbf{E}^{out +}_g(k_\parallel) = \exp[-i(\mathbf{k}_\parallel \cdot \mathbf{R}_n - \mathbf{K}_g^+ \cdot \mathbf{d}_2(\nu))] \sum_L \Delta_{L,i}(\mathbf{K}_g^+) b^+_L(n; \nu) \]  

(29)

where \( i = 1, 2 \). \( A_2(\nu) \) is a reference point on the right of the \( \nu \)-th plane at \( \mathbf{d}_2(\nu) \) from its center (see Fig. 1). To the left of the \( \nu \)-th plane we have

\[ \mathbf{E}^{out -}(\mathbf{r}) = \frac{1}{S_0} \int \int_{SBZ} d^2k_\parallel \sum_g \mathbf{E}^{out -}_g(k_\parallel) \exp[i \mathbf{K}_g^- \cdot (\mathbf{r} - A_1(\nu))] \]  

(30)
with

\[ E_{g;i}^{\text{out}}(k) = \exp[-i(k \parallel \cdot R_n + K_g \cdot d_1(\nu))] \sum_L \Delta_{L;i}(K_g^-) b_L^+(n;\nu) \]  

(31)

where \( A_1(\nu) \) is a reference point to the left of the \( \nu \)-th plane at \( -d_1(\nu) \) from its center (see Fig. 1). \( K_g^\pm \) is given by

\[ K_g^\pm = \left( k \parallel + g, \pm \left[q^2 - (k \parallel + g)^2\right]^{1/2}\right), \]

where the +,− sign defines the sign of the \( z \) component of the wavevector. The coefficients \( \Delta_{L;i} \) are given from Eqs. (19) and (20) of Ref. 31.

The plane waves of Eq. (28) will be multiply reflected between two parts of the slab, the first (right part) consisting of all planes to the right of the \( \nu \)-th plane, and the second (left part) consisting of all planes to the left of the \( (\nu + 1) \)-th plane (including the \( \nu \)-th plane), to produce a set of plane waves incident on the \( \nu \)-th plane from the right, which we can write formally as follows

\[ E^{in}(r) = \frac{1}{S_0} \int \int_{SBZ} d^2 k \parallel \sum_g E_{g;i}^{in}(k) \exp[iK_g \cdot (r - A_2(\nu))] \]  

(32)

with

\[ E_{g;i}^{in}(k) = \sum_{g',i'} \left\{ Q^{III}(\nu;2)[I - Q^{II}(\nu + 1;1)Q^{III}(\nu;2)]^{-1}\right\}_{g;g'i'} E_{g;i'}^{out}(k) \]  

(33)

where \( Q^{II}(\nu + 1;1) \) and \( Q^{III}(\nu;2) \) are the appropriate matrices which determine the reflection (diffraction) of a plane wave by the left and the right parts of the slab respectively, as defined above. These matrices are shown schematically in Fig. 1.

Similarly, the plane waves of Eq. (30) will be multiply reflected between two parts of the slab, the first (left part) consisting of all planes to the left of the \( \nu \)-th plane and the second (right part) consisting of all planes to the right of the \( (\nu - 1) \)-th plane (including the \( \nu \)-th plane), to produce a set of plane waves incident on the \( \nu \)-th plane from the left, which we can write formally as follows

\[ E^{in}(r) = \frac{1}{S_0} \int \int_{SBZ} d^2 k \parallel \sum_g E_{g;i}^{in}(k) \exp[iK_g \cdot (r - A_1(\nu))] \]  

(34)

with

\[ E_{g;i}^{in}(k) = \sum_{g',i'} \left\{ Q^{II}(\nu;1)[I - Q^{III}(\nu - 1;2)Q^{II}(\nu;1)]^{-1}\right\}_{g;g'i'} E_{g;i'}^{out}(k) \]  

(35)

where \( Q^{II}(\nu;1) \) and \( Q^{III}(\nu - 1;2) \) are again the appropriate matrices, shown schematically in Fig. 1. A more detailed description of these matrices and the way these are calculated is
to be found in Ref. 31. We note that for \( \nu = 1(N) \) we have only waves incident from the right (left).

Each plane wave in Eqs. (32) and (34) can be expanded in spherical waves about the central sphere of the \( \nu \)-th plane in the manner of Eqs. 3 and 9. For a plane wave \( E^\text{in}_{g}^-(k) \exp[iK_g^- \cdot (r - A_2(\nu))] \), incident on the \( \nu \)-th plane from the right, the multipole coefficients are given by 31

\[
a_L^0(K_g^-) = \exp[-iK_g^- \cdot d_2(\nu)] \sum_i A_{L,i}^0(K_g^-) E^\text{in}_{g,i}^-(k)
\]

And for a plane wave, \( E^\text{in}_{g}^+(k) \exp[iK_g^+ \cdot (r - A_1(\nu))] \), incident on the \( \nu \)-th plane from the left, the multipole coefficients are 31

\[
a_L^0(K_g^+) = \exp[iK_g^+ \cdot d_1(\nu)] \sum_i A_{L,i}^0(K_g^+) E^\text{in}_{g,i}^+(k).
\]

where \( A_{L,i}^0 \) are given by Eqs. (12) and (13) of Ref. 31.

Finally, to obtain the wave incident on the central sphere of the \( \nu \)-th plane, which derives from the outgoing wave of Eq. (27), we must add to the waves given by Eqs. (32) and (34) that which is due to the wave scattered from all the other spheres of the \( \nu \)-th plane and it is given by multiplying the coefficients \( a_L^0 \) of Eqs. (36) and (37) by the multiple-scattering matrix \( [I - \Omega T_\nu]^{-1} \) for the \( \nu \)-th plane of spheres. We have

\[
\sum_{L'} P_{\nu,LL'}^{0n} b_{L'}^+(n; \nu) = \frac{1}{S_0} \int \int_{SBZ} d^2k_l \sum_{s=\pm} \sum_{L'} \left[I - \Omega T_\nu\right]_{LL'}^{-1} a_{L'}^0(K_g^+) \]

\[
\sum_{L'} \frac{1}{S_0} \int \int_{SBZ} d^2k_l \exp(-ik_l \cdot R_n) \left[I - \Omega T_\nu\right]_{LL'}^{-1} \Gamma_{\nu,LL'} b_{L'}^+(n; \nu)
\]

where \( \Gamma_{\nu,LL'} \) is a matrix defined by

\[
\Gamma_{\nu,Plm,Pl'm'}(k_L; \omega) = \sum_{g,i} \sum_{g',i'} \left\{ \exp[-i(K_g^- - K_g^+) \cdot d_2(\nu)] A_{Plm;i}^0(K_g^-) \right. \\
\times \left. \left[ Q^{II}(\nu; 2) [I - Q^{II}(\nu + 1; 1)Q^{II}(\nu; 2)]^{-1} \right]_{g;i,g'i'} \Delta_{Pl'm';i'}^{P'P'}(K_g^+) \right. \\
+ \exp[i(K_g^- - K_g^+) \cdot d_1(\nu)] A_{Plm;i}^0(K_g^+) \right. \\
\times \left. \left[ Q^{II}(\nu; 1) [I - Q^{II}(\nu - 1; 2)Q^{II}(\nu; 1)]^{-1} \right]_{g;i,g'i'} \Delta_{Pl'm';i'}^{P'P'}(K_g^-) \right\}
\]

(40)
Therefore, from Eq. (39), $P^{0n}_{\nu;LL'}$ is given by

$$P^{0n}_{\nu;LL'} = \frac{1}{S_0} \int \int_{SBZ} d^2 k_{\parallel} \exp(-i k_{\parallel} \cdot R_n) \left[ [I - \Omega T_{\nu}]^{-1} T_{\nu} \right]_{LL'} \tag{41}$$

Accordingly the second term in Eq. (24) becomes

$$\sum_n \sum_{L''} \sum_{L''' \neq L''} P^{0n}_{\nu;LL''} T_{\nu;L'L''} D^{00}_{\nu;LL''} = \frac{1}{S_0} \int \int_{SBZ} d^2 k_{\parallel} \left[ [I - \Omega T_{\nu}]^{-1} \Gamma_{\nu} T_{\nu} D_{\nu} \right]_{LL'} \tag{42}$$

where $D_{\nu;LL'}(k_{\parallel})$ is given by Eq. (26). Finally, the matrix $F^{00}_{\nu;LL'}$, defined by Eq. (24), is given by

$$F^{00}_{\nu;LL'} = \frac{1}{S_0} \int \int_{SBZ} d^2 k_{\parallel} \left[ [I - \Omega T_{\nu}]^{-1} \Gamma_{\nu} (I + T_{\nu} [I - \Omega T_{\nu}]^{-1} \Omega) \right]_{LL'} \tag{43}$$

**IV. NUMERICAL EXAMPLE**

The evaluation of the propagator, either from Eq. (25) or Eq. (13), requires a numerical integration over the entire SBZ. Using symmetry to reduce the area of integration to a part of SBZ is not profitable in the present case. However, when one deals with scatterers whose dielectric function contains a positive imaginary part, the intergrand in Eqs. (25) or (43) is a relatively smooth function of $k_{\parallel}$, and the integration can be performed without much difficulty by subdividing the SBZ (a square in our example) into small squares, within which a nine-point integration formula is very efficient. Using this formula we managed good convergence with a total of 576 points in the SBZ.

When computing the vdW for $T = 0$, we first integrate the Maxwell stress tensor for a specific frequency over the surface of the body and afterwards we perform the frequency integration, i.e., the vdW force $F$ is calculated by integrating the force spectrum $F(\omega)$:

$$F = \int_{0}^{\infty} F(\omega) \, d\omega.$$  

Both integrals are obtained numerically. We note that, in the Lifshitz theory for half-spaces, the frequency integration is done analytically using contour integration. The numerical integral over frequencies is convergent since, in the limit of $\omega \rightarrow \infty$, the refractive index of most materials tends to unity and the corresponding Green’s tensor of the system tends to that of vacuum which is constant in space. However, the integral over a closed surface of a constant tensor vanishes and therefore $F(\omega) \rightarrow 0$ as $\omega \rightarrow \infty$.

We consider the case of a 2D square lattice (monolayer) of polystyrene nanospheres of radius 10 nm. The dielectric function of the spheres which is generally complex for high
frequencies is taken from numerical fit to experimental data. We have calculated the force acting on a single polystyrene nanosphere when we remove one of its first neighbouring spheres (see inset of Fig. 2). In this case, we first calculate the propagator for the periodic square lattice from Eqs. (25) and (26) (which yields vanishing net vdW force) and then make use of Eq. (20).

In Fig. 2 we show the net vdW force ($x$- and $y$- components) for different lattice constants $a$ of the underlying 2D square lattice. While each of the components oscillates from positive to negative values, it is evident that there exists a value of the lattice constant $a$, namely $a \simeq 47$ nm, where the net force is zero and this particular sphere rests in equilibrium. Overall, the magnitude of the vdW force decreases with the lattice constant, as expected.

V. CONCLUSION

We have presented a method for the calculation of the vdW forces in colloidal systems such clusters of colloidal particles, infinite periodic or defected crystals, and colloidal crystals slabs. The method is based on the fluctuation-dissipation theorem which relates the cross-spectral correlation functions entering the formula for the vdW force (integral of the Maxwell stress tensor over the particle surface) with the EM Green’s tensor of the system of particles (scatterers). The calculation of the Green’s tensor is based on a rigorous multiple-scattering formalism for EM waves. The accuracy stems from the fact that it does not include any kind of approximations apart from the unavoidable cutoffs in the angular momentum expansion and/or in the plane-wave expansion of the EM field. As such, the method includes all essential multipole terms beyond the dipole term in the EM response of the scatterers and is valid for any distance between the scatterers. By including $a$ priori all the possible multiple-scattering processes of the vacuum fluctuations, the method, naturally, accounts for all possible many-body interactions between the scatterers and therefore goes beyond the approximation of pairwise interactions.

Finally, we note that a theoretical approach, analogous to the multiple-scattering treatment for the wave equation, has been developed for solving the Poisson equation in solids described by arbitrarily shaped, space-filling charges. By combining this electrostatic multiple-scattering approach with the vdW theory presented in this work, one can devise a
general, first-principles theory for the determination of colloidal structure.

* Electronic address: vyannop@upatras.gr

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\[ Q_{II}^{\nu;1} \]

\[ Q_{III}^{\nu;2} \]

\[ Q_{III}^{\nu-1;2} \]

\[ Q_{II}^{\nu+1;1} \]

\[ \mathbf{A}_1 \]

\[ \mathbf{d}_1 \]

\[ \mathbf{d}_2 \]

\[ \mathbf{A}_2 \]

FIG. 1: The \( Q \)-matrices appearing in Eq. (40). The position vectors \( \mathbf{d}_1, \mathbf{d}_2 \) of the \( \nu \)-th layer along with the corresponding origins \( \mathbf{A}_1, \mathbf{A}_2 \) are also shown.
FIG. 2: (Color online) Inset: 2D square lattice of 10 nm polystyrene spheres containing a single defect (one missing sphere). Graph: the $x$- (squares) and $y$- (circles) component of the vdW force exerted on a single polystyrene nanosphere when its right neighboring sphere is missing.