General theory based on fluctuational electrodynamics for van der Waals interactions in colloidal systems

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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 van der Waals interactions in colloidal systems since it takes fully into account retardation, many-body, multipolar, and near-field 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 semiempirical corrections.[3,4,9–11] 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.[14–16]

Recently, a 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 and/or 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 *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[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 Ref. 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. 17 to the case of a colloidal crystal is to derive a semianalytical 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 Sec. II, we provide a brief overview of fluctuational electrodynamics and the Maxwell stress tensor. In Sec. 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 Sec. 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 ϵ_s and/or magnetic permeability μ_s different from those, ϵ_h and μ_h, of the surrounding homogeneous medium. According to classical electrodynamics, the exerted force **F** on a finite scatterer in the presence of electric **E** and magnetic **H** fields satisfying the Maxwell equations is obtained by integrating the time-average Maxwell stress tensor T_{ij} (Ref. 19) over the surface around the scatterer,

$$\langle F_i\rangle_t = \int_S \sum_j \langle \mathrm{T}_{ij}\rangle_t n_j dS, \tag{1}$$

where $\langle\cdots\rangle_t$ 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 $\langle \mathrm{T}_{ij}\rangle_t$ are given by

$$\langle \mathrm{T}_{ij}\rangle_t = \epsilon_h\epsilon_0\langle E_i(\mathbf{r},t)E_j(\mathbf{r},t)\rangle_t + \mu_h\mu_0\langle H_i(\mathbf{r},t)H_j(\mathbf{r},t)\rangle_t - \frac{1}{2}\delta_{ij}\left[\epsilon_h\epsilon_0\sum_{i'}\langle E_{i'}(\mathbf{r},t)E_{i'}(\mathbf{r},t)\rangle_t + \mu_h\mu_0\sum_{i'}\langle H_{i'}(\mathbf{r},t)H_{i'}(\mathbf{r},t)\rangle_t\right]. \tag{2}$$

δ_{ij} is the Kronecker symbol, and ϵ_0 and μ_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** and **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 $\langle E_i(\mathbf{r},t+\tau)E_j(\mathbf{r}',t)\rangle_t$ contained in Eq. (2) is calculated within the framework of fluctuational electrodynamics,[5,6] namely, from[20]

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

The quantity $W_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega)$ 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 neighboring scatterers at the same temperature T, W_{ij}, are provided by the fluctuation-dissipation theorem[21]

$$W_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega) = 4\omega\mu_h\mu_0c^2\,\mathrm{Im}\,G_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega)\times\hbar\omega\left[1+\frac{1}{\exp(\hbar\omega/k_BT)-1}\right], \tag{4}$$

where $\hbar$ is the reduced Planck's constant, k_B is the Boltzmann's constant, and $G_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega)$ 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 $\mathbf{r}'$. The time-correlation function $\langle H_i(\mathbf{r},t+\tau)H_j(\mathbf{r}',t)\rangle_t$ for the magnetic field is given similar to Eq. (3) with W_{ij}^{EE} substituted by

$$W_{ij}^{HH}(\mathbf{r},\mathbf{r}';\omega) = 4\omega\epsilon_h\epsilon_0c^2\,\mathrm{Im}\,G_{ij}^{HH}(\mathbf{r},\mathbf{r}';\omega)\times\hbar\omega\left[1+\frac{1}{\exp(\hbar\omega/k_BT)-1}\right]. \tag{5}$$

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 is the case for the calculation of the Casimir force between two semi-infinite slabs.[22] 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 electromagnetic field

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

$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re}[\mathbf{E}(\mathbf{r})\exp(-i\omega t)]. \tag{6}$$

In a homogeneous medium characterized by a dielectric function $\epsilon(\omega)\epsilon_0$ and a magnetic permeability $\mu(\omega)\mu_0$, where ϵ_0 and μ_0 are the electric permittivity and magnetic permeability of vacuum, Maxwell's equations imply that $\mathbf{E}(\mathbf{r})$ satisfies a vector Helmholtz equation, subject to the condition $\nabla\cdot\mathbf{E}=0$, 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 $\mathbf{E}(\mathbf{r})$ is given by[19]

$$\mathbf{E}(\mathbf{r}) = \sum_{l=1}^{\infty}\sum_{m=-l}^{l}\left\{a_{lm}^H f_l(qr)\mathbf{X}_{lm}(\hat{\mathbf{r}}) + a_{lm}^E\frac{i}{q}\nabla\times[f_l(qr)\mathbf{X}_{lm}(\hat{\mathbf{r}})]\right\}, \tag{7}$$

where a_{lm}^P $(P=E,H)$ are coefficients to be determined. $\mathbf{X}_{lm}(\hat{\mathbf{r}})$ are the so-called vector spherical harmonics[19] 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 $\mathbf{B}(\mathbf{r})$ can be readily obtained from $\mathbf{E}(\mathbf{r},t)$ using Maxwell's equations.[19,23]

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

In this section, we present a brief summary of the solution to the problem of EM scattering from a single sphere (Mie scattering theory[19,24]) 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 ϵ_s and/or magnetic permeability μ_s are different from those, ϵ_h and μ_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,

$$\mathbf{E}^0(\mathbf{r}) = \sum_L a_L^0 \mathbf{J}_L(\mathbf{r}), \quad (8)$$

where

$$\mathbf{J}_{Elm}(\mathbf{r}) = \frac{i}{q_h} \nabla \times j_l(q_h r)\mathbf{X}_{lm}(\hat{\mathbf{r}}), \quad \mathbf{J}_{Hlm}(\mathbf{r}) = j_l(q_h r)\mathbf{X}_{lm}(\hat{\mathbf{r}}), \quad (9)$$

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 Eq. (37) (Sec. III G) for $\mathbf{g}=\mathbf{0}$.

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: $h_l^+ \approx (-i)^l \exp(iq_h r)/iq_h r$ as $r \to \infty$, and appropriate expansion coefficients a_L^+. Namely,

$$\mathbf{E}^+(\mathbf{r}) = \sum_L a_L^+ \mathbf{H}_L(\mathbf{r}), \quad (10)$$

where

$$\mathbf{H}_{Elm}(\mathbf{r}) = \frac{i}{q_h} \nabla \times h_l^+(q_h r)\mathbf{X}_{lm}(\hat{\mathbf{r}}), \quad \mathbf{H}_{Hlm}(\mathbf{r}) = h_l^+(q_h r)\mathbf{X}_{lm}(\hat{\mathbf{r}}). \quad (11)$$

The wave field for $r > S$ is the sum of the incident and scattered waves, i.e., $\mathbf{E}^{out} = \mathbf{E}^0 + \mathbf{E}^+$. By applying the requirement that the tangential components of $\mathbf{E}$ and $\mathbf{H}$ 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:

$$a_L^+ = \sum_{L'} T_{LL'} a_{L'}^0, \quad (12)$$

where $T_{LL'}$ are the elements of the so-called scattering transition T matrix.[24] Equation (12) is valid for any shape of scatterer; explicit relations of the T matrix for scatterers of various shapes can be found elsewhere.[25,26]

The Green's tensor for a single sphere is given by[23]

$$G_{ii'}^{(s)}(\mathbf{r},\mathbf{r}') = -i\omega \frac{(\epsilon_h \mu_h)^{3/2}}{c_0^3} \sum_L [R_{L;i}(\mathbf{r}) \bar{I}_{L;i'}(\mathbf{r}') \Theta(r'-r) + I_{L;i}(\mathbf{r}) \bar{R}_{L;i'}(\mathbf{r}') \Theta(r-r')]. \quad (13)$$

The vector functions $R_{L;i}(\mathbf{r})$ and $\bar{R}_{L;i}(\mathbf{r})$ are dimensionless eigenfunctions of the wave operator

$$\mathbf{\Lambda}(\mathbf{r}) = \frac{c_0^2}{\epsilon(\mathbf{r})\mu(\mathbf{r})} \nabla \times \nabla \times \quad (14)$$

for a single scatterer which are regular at its center.[23,27] The vector functions $I_{L;i}(\mathbf{r})$ and $\bar{I}_{L;i}(\mathbf{r})$ are also eigenfunctions of operator (14) but they are infinite at the sphere center.[23,27] 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 ϵ_s and permeability μ_s centered at sites $\mathbf{R}_n$ in a homogeneous host medium described by ϵ_h and μ_h, respectively. In site-centered representation, the Green's tensor for the system of scatterers satisfies[23,27]

$$\sum_i [\omega^2 \delta_{i''i} - \Lambda_{i''i}(\mathbf{R}_n + \mathbf{r}_n)] G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'} + \mathbf{r}'_{n'}) = \delta_{i''i'} \delta(\mathbf{r}_n - \mathbf{r}'_{n'}) \delta_{nn'}, \quad (15)$$

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 $\Lambda_{i''i}(\mathbf{r})$ is given by Eq. (14). It can be verified that the Green's tensor satisfying Eq. (15) is the following:[23,27]

$$G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'} + \mathbf{r}'_{n'}) = G_{ii'}^{(s)n}(\mathbf{r}_n, \mathbf{r}'_{n'}) \delta_{nn'} - i\omega \frac{(\epsilon_h \mu_h)^{3/2}}{c^3} \times \sum_{LL'} \bar{R}_{L;i}^n(\mathbf{r}_n) D_{L'L}^{n'n} R_{L';i'}^{n'}(\mathbf{r}'_{n'}). \quad (16)$$

$G_{ii'}^{(s)n}(\mathbf{r}_n, \mathbf{r}'_{n'})$ is the Green's tensor for a single scatterer located at $\mathbf{R}_n$ and it is given by Eq. (13). The vector functions $R_{L;i}^n(\mathbf{r}_n)$ and $\bar{R}_{L;i}^n(\mathbf{r}_n)$ are the dimensionless eigenfunctions of the operator of Eq. (14) for the sphere at $\mathbf{R}_n$. $D_{LL'}^{nn'}$ 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 nth scatterer, after scattering in all possible ways (sequences) by the scatterers at all sites including the nth and n'th scatterers. The specific form of the $D_{LL'}^{nn'}$ 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[23]

$$D_{LL'}^{nn'} = \Omega_{LL'}^{nn'} + \sum_{n''} \sum_{L''} \sum_{L'''} D_{LL''}^{nn''} T_{L''L'''}^{n''} \Omega_{L'''L'}^{n''n'}. \quad (17)$$

The matrix $\Omega_{LL'}^{nn'}$ appearing in Eq. (17) is called free-space propagator and transforms an outgoing vector spherical wave about $\mathbf{R}_{n'}$ in a series of incoming vector spherical waves around $\mathbf{R}_n$.[23] The matrix $T_{LL'}^n$ is the scattering T matrix of a scatterer of general shape[25,26] located at $\mathbf{R}_n$.

E. Propagator for periodic arrays of scatterers

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

$$D_{LL'}^{nn'} = \frac{1}{v}\int_{BZ} d^q k \exp[i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_{n'})]D_{LL'}(\mathbf{k}), \quad (18)$$

where q is the space dimensionality, the integration in Eq. (18) is carried out within the Brillouin zone (BZ), $\mathbf{k}$ is the Bloch wave vector, and v is the BZ volume. $\mathbf{R}_n$ are the Bravais lattice vectors. $D_{LL'}(\mathbf{k})$ is given by

$$D_{LL'}(\mathbf{k}) = \Omega_{LL'}(\mathbf{k}) + \sum_{L''L'''} D_{LL''}(\mathbf{k})T_{L''L'''}\Omega_{L'''L'}(\mathbf{k}). \quad (19)$$

$T_{L''L'''}$ is the T matrix of the spheres. $\Omega_{LL'}(\mathbf{k})$ depend only on the crystal lattice and are known as structure constants, a term which is common in the Korringa-Kohn-Rostoker method[28] for the calculation of the electronic band structure of atomic solids. They can be found by Ewald-summation techniques.[29,30] Equations (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 scattering matrix $T_{0LL'}^{n}$) positioned at $\mathbf{R}_n$ 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.,

$$D_{LL'}^{nn'} = D_{0LL'}^{nn'} + \sum_{n''}\sum_{L''}\sum_{L'''} D_{LL''}^{nn''}\Delta T_{L''L'''}^{n''}D_{0L'''L'}^{n''n'}, \quad (20)$$

where $\Delta T_{L''L'''}^{n''} = T_{L''L'''}^{n''} - T_{0LL'}^{n}$ and $D_{0LL'}^{nn'}$ 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 two-dimensional (2D) periodicity with the associated lattice vectors given by

$$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2, \quad (21)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive vectors in the xy plane and $n_1, n_2 = 0, \pm 1, \pm 2, \pm 3, \ldots$. The corresponding 2D reciprocal lattice is defined by

$$\mathbf{g} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2, \quad (22)$$

where $m_1, m_2 = 0, \pm 1, \pm 2, \pm 3, \ldots$, and $\mathbf{b}_1$ and $\mathbf{b}_2$ are primitive vectors defined by

$$\mathbf{b}_i\cdot\mathbf{a}_j = 2\pi\delta_{ij}, \quad i,j = 1,2. \quad (23)$$

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 νth plane ($\nu = 1, 2, \ldots, N_p$) of a slab is written as a sum of three terms[31]

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

The matrix $D_{\nu;LL'}^{nm}$ represents all the possible scattering paths *within* the νth plane by which a wave outgoing from the mth sphere of this plane produces an incident wave on the nth 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.,

$$D_{\nu;LL'}^{nm} = \frac{1}{S_0}\int\int_{SBZ} d^2k_{\parallel}\exp(i\mathbf{k}_{\parallel}\cdot\mathbf{R}_{nm})D_{\nu;LL'}(\mathbf{k}_{\parallel}), \quad (25)$$

where

$$D_{\nu;LL'}(\mathbf{k}_{\parallel}) = \sum_{L''}[[\mathbf{I} - \mathbf{\Omega}(\mathbf{k}_{\parallel})\mathbf{T}_{\nu}]^{-1}]_{LL''}\Omega_{L''L'}(\mathbf{k}_{\parallel}), \quad (26)$$

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 $\Omega_{LL'}(\mathbf{k}_{\parallel})$ 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 nth sphere of the νth 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 νth plane. In the next section, 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. 31.

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

A wave outgoing from the nth sphere of the νth plane has the form of Eq. (10),

$$\mathbf{E}^{sc}(\mathbf{r}) = \sum_{L} b_L^{+}(n;\nu)\mathbf{H}_L(\mathbf{r}), \quad (27)$$

where $\mathbf{r}_{n\nu}$ is the position vector with respect to the center of the nth sphere of the νth plane. We can expand the wave of Eq. (27) into a sum of plane waves propagating or decaying away from the νth plane as follows.[31] To the right of the νth plane, we have

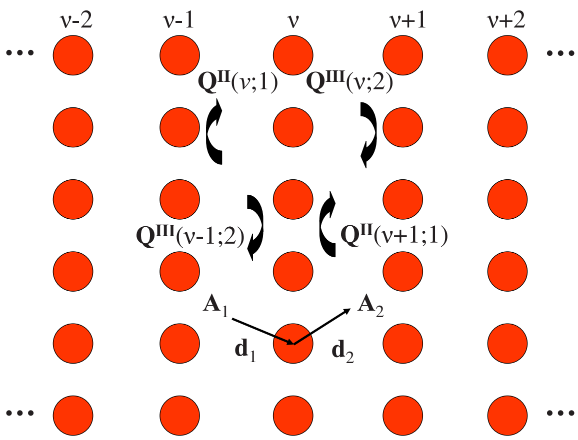

FIG. 1. (Color online) The **Q** matrices appearing in Eq. (39). The position vectors $\mathbf{d}_1$ and $\mathbf{d}_2$ of the νth layer along with the corresponding origins $\mathbf{A}_1$ and $\mathbf{A}_2$ are also shown.

$$\mathbf{E}^{out+}(\mathbf{r}) = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \sum_{\mathbf{g}} \mathbf{E}^{out+}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^+_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_2(\nu))], \tag{28}$$

with

$$E^{out+}_{\mathbf{g};i}(\mathbf{k}_\parallel) = \exp[-i(\mathbf{k}_\parallel\cdot\mathbf{R}_n - \mathbf{K}^+_{\mathbf{g}}\cdot\mathbf{d}_2(\nu))]\sum_L \Delta_{L;i}(\mathbf{K}^+_{\mathbf{g}})b^+_L(n;\nu), \tag{29}$$

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

$$\mathbf{E}^{out-}(\mathbf{r}) = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \sum_{\mathbf{g}} \mathbf{E}^{out-}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^-_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_1(\nu))], \tag{30}$$

with

$$E^{out-}_{\mathbf{g};i}(\mathbf{k}_\parallel) = \exp[-i(\mathbf{k}_\parallel\cdot\mathbf{R}_n + \mathbf{K}^-_{\mathbf{g}}\cdot\mathbf{d}_1(\nu))]\sum_L \Delta_{L;i}(\mathbf{K}^-_{\mathbf{g}})b^+_L(n;\nu), \tag{31}$$

where $\mathbf{A}_1(\nu)$ is a reference point to the left of the νth plane at $-\mathbf{d}_1(\nu)$ from its center (see Fig. 1). $\mathbf{K}^\pm_{\mathbf{g}}$ is given by $\mathbf{K}^\pm_{\mathbf{g}}=(\mathbf{k}_\parallel+\mathbf{g}, \pm[q^2-(\mathbf{k}_\parallel+\mathbf{g})^2]^{1/2})$, where the + and − signs define the sign of the z component of the wave vector. The coefficients $\Delta_{L;i}$ are given from Eqs. (19) and (20) of Ref. 32.

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 νth plane and the second (left part) consisting of all planes to the left of the $(\nu+1)$th plane (including the νth plane), to produce a set of plane waves incident on the νth plane from the right, which we can write formally as follows:

$$\mathbf{E}^{in-}(\mathbf{r}) = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \sum_{\mathbf{g}} \mathbf{E}^{in-}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^-_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_2(\nu))], \tag{32}$$

with

$$E^{in-}_{\mathbf{g};i}(\mathbf{k}_\parallel) = \sum_{\mathbf{g}',i'}\{\mathbf{Q}^{\mathrm{III}}(\nu;2)[\mathbf{I}-\mathbf{Q}^{\mathrm{II}}(\nu+1;1) \times\mathbf{Q}^{\mathrm{III}}(\nu;2)]^{-1}\}_{\mathbf{g}i;\mathbf{g}'i'}E^{out+}_{\mathbf{g}';i'}(\mathbf{k}_\parallel), \tag{33}$$

where $\mathbf{Q}^{\mathrm{II}}(\nu+1;1)$ and $\mathbf{Q}^{\mathrm{III}}(\nu;2)$ 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 νth plane and the second (right part) consisting of all planes to the right of the $(\nu-1)$th plane (including the νth plane), to produce a set of plane waves incident on the νth plane from the left, which we can write formally as follows:

$$\mathbf{E}^{in+}(\mathbf{r}) = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \sum_{\mathbf{g}} \mathbf{E}^{in+}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^+_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_1(\nu))], \tag{34}$$

with

$$E^{in+}_{\mathbf{g};i}(\mathbf{k}_\parallel) = \sum_{\mathbf{g}',i'}\{\mathbf{Q}^{\mathrm{II}}(\nu;1)[\mathbf{I}-\mathbf{Q}^{\mathrm{III}}(\nu-1;2) \times\mathbf{Q}^{\mathrm{II}}(\nu;1)]^{-1}\}_{\mathbf{g}i;\mathbf{g}'i'}E^{out-}_{\mathbf{g}';i'}(\mathbf{k}_\parallel), \tag{35}$$

where $\mathbf{Q}^{\mathrm{II}}(\nu;1)$ and $\mathbf{Q}^{\mathrm{III}}(\nu-1;2)$ are again the appropriate matrices, shown schematically in Fig. 1. A more detailed description of these matrices and the way these are calculated are to be found in Ref. 32. 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 νth plane in the manner of Eqs. (8) and (9). For a plane wave $\mathbf{E}^{in-}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^-_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_2(\nu))]$, incident on the νth plane from the right, the multipole coefficients are given by[32]

$$a^0_L(\mathbf{K}^-_{\mathbf{g}}) = \exp[-i\mathbf{K}^-_{\mathbf{g}}\cdot\mathbf{d}_2(\nu)]\sum_i A^0_{L;i}(\mathbf{K}^-_{\mathbf{g}})E^{in-}_{\mathbf{g};i}(\mathbf{k}_\parallel). \tag{36}$$

For a plane wave, $\mathbf{E}^{in+}_{\mathbf{g}}(\mathbf{k}_\parallel)\exp[i\mathbf{K}^+_{\mathbf{g}}\cdot(\mathbf{r}-\mathbf{A}_1(\nu))]$, incident on the νth plane from the left, the multipole coefficients are[32]

$$a^0_L(\mathbf{K}^+_{\mathbf{g}}) = \exp[i\mathbf{K}^+_{\mathbf{g}}\cdot\mathbf{d}_1(\nu)]\sum_i A^0_{L;i}(\mathbf{K}^+_{\mathbf{g}})E^{in+}_{\mathbf{g};i}(\mathbf{k}_\parallel), \tag{37}$$

where $A^0_{L;i}$ are given by Eqs. (12) and (13) of Ref. 32.

Finally, to obtain the wave incident on the central sphere of the νth 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 νth plane and it is given by multiplying the coefficients a^0_L of Eqs. (36) and (37) by the multiple-scattering matrix $[[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}]_{LL'}$ for the νth plane of spheres. We have

$$\sum_{L'} P^{0n}_{\nu;LL'} b^+_{L'}(n;\nu)$$

$$= \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \sum_{\mathbf{g}}\sum_{s=\pm}\sum_{L'} [[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}]_{LL'} a^0_{L'}(\mathbf{K}^s_{\mathbf{g}}) \tag{38a}$$

$$= \sum_{L'} \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \exp(-i\mathbf{k}_\parallel\cdot\mathbf{R}_n) \times [[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}\mathbf{\Gamma}_\nu]_{LL'} b^+_{L'}(n;\nu), \tag{38b}$$

where $\Gamma_{\nu;LL'}$ is a matrix defined by

$$\Gamma_{\nu;Plm,P'l'm'}(\mathbf{k}_\parallel;\omega) = \sum_{\mathbf{g},i}\sum_{\mathbf{g}',i'} \{\exp[-i(\mathbf{K}^-_{\mathbf{g}}-\mathbf{K}^+_{\mathbf{g}'})\cdot\mathbf{d}_2(\nu)] \times A^0_{Plm;i}(\mathbf{K}^-_{\mathbf{g}})[\mathbf{Q}^{\mathrm{III}}(\nu;2)[\mathbf{I}-\mathbf{Q}^{\mathrm{II}}(\nu+1;1) \times\mathbf{Q}^{\mathrm{III}}(\nu;2)]^{-1}]_{\mathbf{g}i;\mathbf{g}'i'}\Delta_{P'l'm';i'}(\mathbf{K}^+_{\mathbf{g}'}) + \exp[i(\mathbf{K}^+_{\mathbf{g}}-\mathbf{K}^-_{\mathbf{g}'})\cdot\mathbf{d}_1(\nu)]A^0_{Plm;i}(\mathbf{K}^+_{\mathbf{g}})[\mathbf{Q}^{\mathrm{II}}(\nu;1) \times[\mathbf{I}-\mathbf{Q}^{\mathrm{III}}(\nu-1;2)\mathbf{Q}^{\mathrm{II}}(\nu;1)]^{-1}]_{\mathbf{g}i;\mathbf{g}'i'}\Delta_{P'l'm';i'}(\mathbf{K}^-_{\mathbf{g}'})\}. \tag{39}$$

Therefore, from Eq. (38b), $P^{0n}_{\nu;LL'}$ is given by

$$P^{0n}_{\nu;LL'} = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel \exp(-i\mathbf{k}_\parallel\cdot\mathbf{R}_n)[[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}\mathbf{\Gamma}_\nu]_{LL'}. \tag{40}$$

Accordingly, the second term in Eq. (24) becomes[31]

$$\sum_n\sum_{L''}\sum_{L'''} P^{0n}_{\nu;LL''}T_{\nu;L''L'''}D^{n0}_{\nu;L'''L'} = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel[[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}\mathbf{\Gamma}_\nu\mathbf{T}_\nu\mathbf{D}_\nu]_{LL'}, \tag{41}$$

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

$$F^{00}_{\nu;LL'} = \frac{1}{S_0}\int\int_{SBZ} d^2k_\parallel[[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1} \times[\mathbf{\Omega}+\mathbf{\Gamma}_\nu(\mathbf{I}+\mathbf{T}_\nu[\mathbf{I}-\mathbf{\Omega}\mathbf{T}_\nu]^{-1}\mathbf{\Omega})]]_{LL'}. \tag{42}$$

IV. NUMERICAL EXAMPLE

The evaluation of the propagator, either from Eq. (25) or Eq. (42), 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 (42) is a relatively smooth function of $\mathbf{k}_\parallel$, 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[33] is very efficient. Using this formula, we managed good convergence with a total of 576 points in the SBZ.

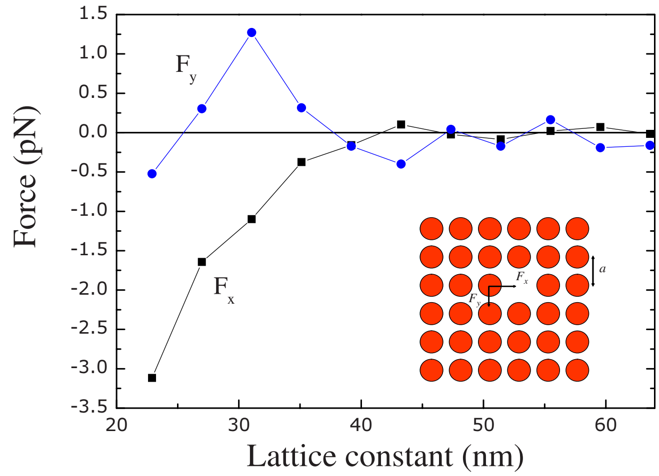

FIG. 2. (Color online) Inset: 2D square lattice of 10 nm polystyrene spheres containing a single defect (one missing sphere). Graph: the x (squares) and y (circles) components of the vdW force exerted on a single polystyrene nanosphere when its right neighboring sphere is missing.

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 afterward we perform the frequency integration, i.e., the vdW force F is calculated by integrating the force spectrum $F(\omega)$: $F=\int_0^\infty F(\omega)$. Both integrals are obtained numerically. We note that, in the Lifshitz theory for half spaces,[22] the frequency integration is done analytically using contour integration. The numerical integral over frequencies is convergent since, in the limit of $\omega\to\infty$, 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 $F(\omega)\to 0$ as $\omega\to\infty$.

We consider the case of a 2D square lattice (monolayer) of polystyrene nanospheres of radius of 10 nm. The dielectric function of the spheres, which is generally complex for high frequencies, is taken from numerical fit to experimental data.[4] We have calculated the force acting on a single polystyrene nanosphere when we remove one of its first neighboring 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 as clusters of colloidal particles, infinite periodic or defected crystals, and colloidal crystalline 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 where the continuum pictures of particle and medium dielectric properties pertain. 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 Poisson's equation in solids described by arbitrarily shaped, space-filling charges.[34] 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.

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