First-Principles Theory of van der Waals Forces between Macroscopic Bodies

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We present a first-principles method for the determination of the van der Waals interactions for a collection of finite-sized macroscopic bodies. The method is based on fluctuational electrodynamics and a rigorous multiple-scattering method for the electromagnetic field. As such, the method takes fully into account retardation, many-body, multipolar, and near-fields effects. By application of the method to the case of two metallic nanoparticles, we demonstrate the breakdown of the standard $1/r^2$ distance law as the van der Waals force decays exponentially with distance when the nanoparticles are too close or too far apart.

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The van der Waals (vdW) interactions between macroscopic particles have attracted a great deal of attention in recent years due to the advances in nanoscience. The physical origin of the vdW interactions are the irreducible electromagnetic (EM) fluctuations of vacuum [1,2]. Historically, Hamaker [3] extended the intermolecular vdW force to macroscopic bodies by the simple pairwise summation of those vdW interactions between the molecules of the interacting bodies [4]. Because the original London–van der Waals force, the basis for Hamaker's treatment, did not take the finiteness of the speed of light (retardation effects) into account, from the outset it pertained only for small distances. For large separations between the macroscopic bodies, retardation effects come into play and a more general theory of the vdW force is needed. The first approach dealing with such effects was given by Casimir and Polder [5] who derived an analytic formula of the retarded vdW force between two neutral atoms. Later on, Lifshitz [6] developed a general theory of the vdW forces between macroscopic entities which was based on fluctuational electrodynamics [1,2] and the condensed phase material properties of the interacting bodies rather than the polarizabilities of their isolated molecular constituents. Less involved derivations of the Lifshitz formula in the retarded [7] and nonretarded limit [8,9] have also been reported. A third approach was given by Dzyaloshinskii and Pitaevskii [10] based on quantum field diagrammatic techniques. From the above methods, the Lifshitz theory provides the most physically transparent picture, but, so far, it has been applied primarily to planar geometries.

Here, we focus on macroscopic objects of finite size, such as spheres, aiming to provide a rigorous EM theory for the vdW forces between such objects. A precise knowledge of the vdW forces can be very important in colloidal science, where usually the vdW force among the constituent micro- or nanoparticles relies on the approximation of pairwise forces within the Hamaker (nonretarded) approach [4]. 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 [4,11,12]. Alternative approaches [9,13–15] calculate the iterated dipole interactions among the interacting bodies modeled as comprised of discrete, molecular Drude oscillators, in one case, or as dielectric spheres interacting via multipolar interactions. By employing perturbation theory and the Clausius-Mosotti relation to replace the molecular polarizabilities by the dielectric permittivity, $\epsilon(\omega)$, Langbein [13] derived expressions for the electric multipole interactions of spheres to all orders (including retardation).

In this Letter we present a rigorous theory based on fluctuational electrodynamics for the calculation of the vdW interactions among a collection of macroscopic bodies of finite size. The vdW force is provided by the fluctuation-dissipation theorem and hence by the Green's tensor of the classical EM field based on an EM *multiple-scattering formalism* for arbitrary collections of scatterers. This formalism goes beyond the approximation of pairwise interactions between the scatterers and takes into account the *full multipole interactions* between them. Furthermore, since it constitutes a solution of the inhomogeneous wave equation, *retardation effects* are included *a priori*. We also note that the presented method treats metallic and dielectric particles on an equal footing since it 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 consider a finite scatterer with electric permittivity ϵ_s and/or magnetic permeability μ_s different from those, ϵ_h, μ_h of the surrounding homogeneous medium. According to classical electrodynamics, the exerted force $\mathbf{F}$ on a finite scatterer in the presence of electric $\mathbf{E}$ and magnetic $\mathbf{H}$ fields satisfying the Maxwell equations is obtained by integrating the time-average Maxwell stress tensor T_{ij} [16] over the surface around the scatterer: $\langle F_i \rangle_t = \int_S \sum_j \langle T_{ij} \rangle_t n_j dS$ where $\langle .. \rangle_t$ denotes the time average, $\mathbf{n}$ 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

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

δ_{ij} is the Kronecker symbol and ϵ_0, μ_0 are the electric permittivity and magnetic permeability of vacuum, respectively. In the absence of other radiation sources, the fields $\mathbf{E}$, $\mathbf{H}$ 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 $\langle E_i(\mathbf{r},t+\tau)E_j(\mathbf{r}',t)\rangle_t$for $\tau = 0$ contained in Eq. (1) is calculated within the framework of fluctuational electrodynamics [1,2], namely, from [17]

$$\langle E_i(\mathbf{r},t+\tau)E_j(\mathbf{r}',t)\rangle_t = \mathrm{Re}\int_0^\infty \frac{d\omega}{2\pi}e^{i\omega\tau}W_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega). \quad (2)$$

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} is provided by the fluctuation-dissipation theorem [1,2,17]; i.e., $W_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega) = 4\omega\mu_h\mu_0c^2\mathrm{Im}G_{ij}^{EE}(\mathbf{r},\mathbf{r}';\omega)\times[\hbar\omega + \Theta(\omega,T)]$, where $\Theta(\omega,T) = \hbar\omega/[\exp(\hbar\omega/k_BT) - 1]$, $\hbar$ 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 $\mathbf{r}$ due to an electric-dipole source at $\mathbf{r}'$. $\langle H_i(\mathbf{r},t+\tau)H_j(\mathbf{r}',t)\rangle_t$ is given similarly to Eq. (2) with W_{ij}^{EE} substituted by $W_{ij}^{HH}(\mathbf{r},\mathbf{r}';\omega) = 4\omega\epsilon_h\epsilon_0c^2\mathrm{Im}G_{ij}^{HH}(\mathbf{r},\mathbf{r}';\omega)\times[\hbar\omega + \Theta(\omega,T)]$.

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, μ_h, respectively. In site-centered representation, the Green's tensor for the system of scatterers satisfies [18,19]

$$\sum_i[\omega^2\delta_{i''i} - \Lambda_{i''i}(\mathbf{R}_n + \mathbf{r}_n)]G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'} + \mathbf{r}'_{n'}) = \delta_{i''i'}\delta(\mathbf{r}_n - \mathbf{r}'_{n'})\delta_{nn'}, \quad (3)$$

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 $\mathbf{\Lambda}(\mathbf{r}) = c^2/[\epsilon(\mathbf{r})\mu(\mathbf{r})]\nabla\times\nabla\times$ and c is the speed of light in vacuum. It can be verified that the Green's tensor satisfying Eq. (3) reads [18,19]

$$G_{ii'}(\mathbf{R}_n + \mathbf{r}_n, \mathbf{R}_{n'} + \mathbf{r}'_{n'}) = G_{ii'}^{(s)n}(\mathbf{r}_n, \mathbf{r}'_{n'})\delta_{nn'} - i\omega\frac{(\epsilon_h\mu_h)^{3/2}}{c^3}\sum_{LL'}\bar{R}_{L;i}^n(\mathbf{r}_n)D_{L'L}^{n'n}R_{L';i'}^{n'}(\mathbf{r}'_{n'}). \quad (4)$$

The index L denotes collectively the indices Plm, where $l = 1, 2, \ldots$ is the angular-momentum number, m the magnetic number ($-l \le m \le l$) and $P = E, H$ denotes the two independent polarization modes. $G_{ii'}^{(s)n}(\mathbf{r}_n, \mathbf{r}'_{n'})$ is the Green's tensor for a single scatterer located at $\mathbf{R}_n$ [18]. $D_{LL'}^{nn'}$ 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. They are given by [18]

$$D_{LL'}^{nn'} = \Omega_{LL'}^{nn'} + \sum_{n''}\sum_{L''}\sum_{L'''}D_{LL''}^{nn''}T_{L''L'''}^{n''}\Omega_{L'''L'}^{n''n'}. \quad (5)$$

$\Omega_{LL'}^{nn'}$ transforms an outgoing vector spherical wave about $\mathbf{R}_{n'}$ into a series of incoming vector spherical waves around $\mathbf{R}_n$ [18]. The vector functions $R_{L;i}^n(\mathbf{r}_n)$, $\bar{R}_{L;i}^n(\mathbf{r}_n)$ are the dimensionless eigenfunctions of $\Lambda_{i''i}(\mathbf{r})$ for a single scatterer which are regular at its center [18]. Finally, the matrix $T_{LL'}^n$ is the scattering T matrix [18] of a scatterer of general shape, located at $\mathbf{R}_n$. For the Green's tensors G_{ij}^{EE} and G_{ij}^{HH} contained in W_{ij}^{EE} and W_{ij}^{HH}, the appropriate trace of Eq. (4) should be taken.

For computing convenience, in the actual calculation of the vdW force 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 $F(\omega)$: $F = \int_0^\infty F(\omega)$. Both integrals are obtained numerically. We note that, in the Lifshitz theory for half-spaces [20] or point dipoles [21], 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 $\omega \to \infty$.

The accuracy of the presented method stems from the fact that it involves a minimum of assumptions, apart from an unavoidable cutoff $l_{\max}$ in the angular-momentum expansion of the EM field and the implicit use of the semiclassical approximation in the coupling of the fields and particles. As such, the method includes all essential electric and magnetic multipole terms as well as the important surface-plasmon contributions for conductors in the EM response of the scatterers and is valid for any distance between the scatterers. In contrast, both magnetic and plasmon contributions are omitted in Langbein's and re-

lated work, [9,14,21], thereby restricting their applicability. When more than two scatterers are present, the multiple-scattering process described by Eq. (5) includes all possible many-body interactions between the scatterers and therefore goes beyond the approximation of pairwise interactions which is usually employed in molecular-dynamics simulations. Since the presented formalism allows for a first-principles calculation of the vdW force between macroscopic bodies such as micro- and nanoparticles (the formalism depends only on the dielectric function of the bodies), one can devise a corresponding first-principles molecular-dynamics method for such particles by analogy to the Car-Parrinello molecular-dynamics method for atoms and molecules [22].

We apply the presented theory to the case of two spherical metallic nanoparticles of radius $S = 10$ nm whose dielectric function is described by a Drude-type formula $\epsilon_s(\omega) = 1 - \omega_p^2/[\omega(\omega + i\tau^{-1})]$ where ω_p is the bulk plasma frequency and τ the relaxation time of the conduction-band electrons of the metal. We have chosen $\hbar\omega_p = 9.2$ eV which corresponds to the bulk plasma frequency of silver. The losses are taken to be $\hbar\tau^{-1} = 0.11$ eV which contains both the bulk value and the correction due to the scattering of the metal electrons at the particle boundary [23]. The particles are assumed to be held at zero temperature ($T = 0$), since the dominant contribution to the vdW force stems from the vacuum fluctuations in the optical region where the finite-temperature (thermal) contribution is negligible. Had the contribution to the vdW force originated from the near-infrared or infrared regime, the thermal contribution would have been more appreciable [24]. Practically, the spectral contribution to the integral of Eq. (2) for $\omega > \omega_p$ is vanishingly small. This is in agreement with the cutoff of $\omega_c = c/a_0$ for the intermolecular vdW force introduced by Lu and Marlow [25], where a_0 is the characteristic molecular size (in our case the characteristic length is $a_0 = c/\omega_p$).

In Fig. 1 we show the force spectrum $F(\omega)$ for various particle separations r. As expected, the force spectrum decreases with increasing distance. The distinct features of $F(\omega)$ stem from the surface-plasmon resonances of the individual metal nanoparticles occurring at $\tilde{\omega}_l \simeq \omega_p\sqrt{l/(2l+1)}$, $l = 1, 2, \ldots$. Hence, the low frequency peak corresponds to the dipolar surface plasmon, the next peak to the quadrupolar one while the rest of the surface plasmons are more or less submerged to a single peak. The curve for $r = 2.5$ nm converges for angular-momentum cutoff $l_{\max} = 11$ while the other curves for $l_{\max} = 7$. As the particles come closer, the contribution of the higher-multipolar terms in the force spectrum becomes much more significant than the dipolar one, a result that is consistent with the characteristic rapid decrease of multipolar potentials with increasing separation and the literature on multipolar, molecular van der Waals interactions. Moreover, the magnetic-field vacuum fluctuations become equally important as the electric-field ones for separations larger than approximately 4 nm. The above findings reveal the inadequacy of the electric-dipole approximation in this case. However, if a constant permittivity ϵ_s is assumed over the given frequency region instead of the Drude-type one, the electric-dipole contribution is dominant and higher-multipoles provide small corrections to the vdW force, in agreement with Ref. [13].

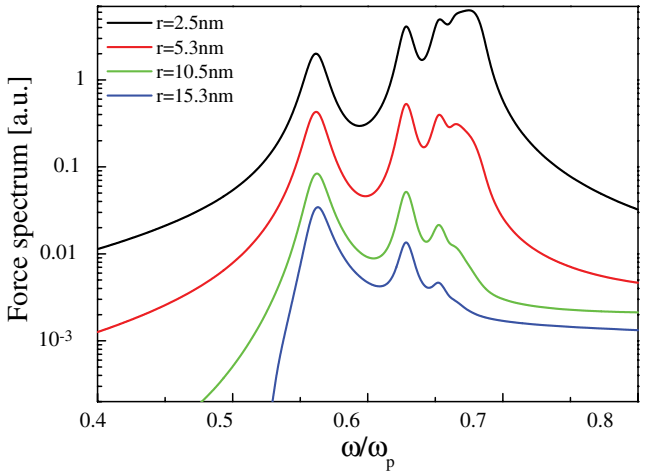

FIG. 1 (color online). Spectrum $F(\omega)$ of the vdW force between two silver nanospheres ($S = 10$ nm) for various surface-to-surface distances.

By integrating $F(\omega)$ over frequencies we obtain the vdW force for a certain interparticle distance. In Fig. 2 we show the vdW force between the two silver nanoparticles as a function of their surface-to-surface distance. From Fig. 2(a) it is obvious that we have deviations from a power-law behavior which would have been manifested as a straight line in a log-log plot: according to the

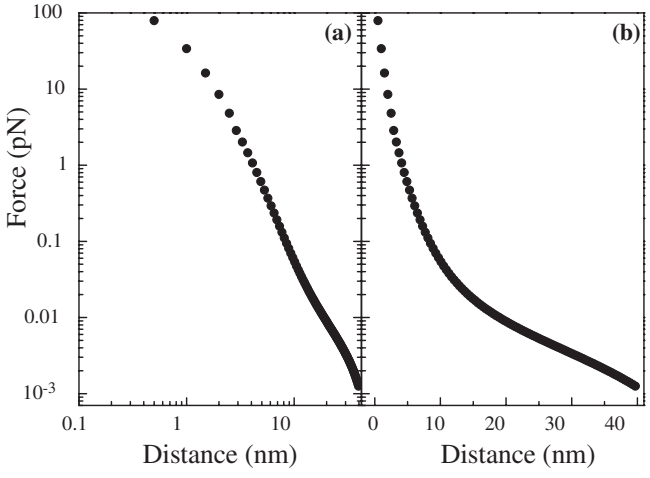

FIG. 2. vdW force between two silver nanospheres of radius $S = 10$ nm as a function of their surface-to-surface distance, in log-log scale (a) and log-linear scale (b).

Hamaker approach, the nonretarded vdW force between two macroscopic spheres decreases as $1/r^2$ with distance r. By comparing Figs. 2(a) and 2(b), we identify approximately three different regimes in terms of the distance dependence of the force. The first regime is $0 < r \lesssim 3$ nm, the second $10 \lesssim r \lesssim 20$ nm, and the third is $r \gtrsim 20$ nm. In the *first regime*, $0 < r \lesssim 3$ nm, the force decreases exponentially as it is evident from the linearity of the curve of Fig. 2(b) within this range of distances. The corresponding decay length is about 0.8 nm. The exponential decay is also evident in the force spectrum $F(\omega)$. To the best of our knowledge, an exponential decay for the vdW force for such small separations has not been reported in literature, and it must be near-field effect. A similar exponential behavior has been observed for the thermal emission spectrum from a planar surface [26] and it has been attributed to the evanescent modes of the EM field (near-field modes) which are dominant for short distances from the surface. However, for such short distances, the atomic structure of the particles becomes evident and a more accurate description of the vdW interaction possibly requires a microscopic treatment which accounts for Born repulsive forces stemming from exchange and electrostatic interactions [27]. In the *second regime*, $10 \lesssim r \lesssim 20$ nm, the curve of Fig. 2(a) is linear and the vdW force decreases approximately as $1/r^{5/2}$. This is again remarkably different from the $1/r^2$ Hamaker behavior. Similar deviations from the standard integer exponents have been reported for the nonretarded vdW force between anisotropic nanostructures [28]. The region from $3 \lesssim r \lesssim 10$ nm is a crossover regime where neither an exponential nor a power-law function can be successfully fitted. Last, in the *third regime*, $r \gtrsim 20$ nm, the force decreases again exponentially with a decay length of about 10 nm. The much faster decay of the force in this regime is attributed to the retardation effects which become important for such separations. In the electric-dipole approximation, the retarded vdW potential becomes larger than the nonretarded one for separations $r \gtrsim c/2\omega$ [21,29]. Since the main contribution to $F(\omega)$ is generated by the surface-plasmon resonances, i.e., around $\omega/\omega_p = 1/\sqrt{3}$, the threshold of retardation effects in our case ($\hbar\omega_p = 9.2$ eV) is $r \simeq 18.5$ nm. The breakdown of the vdW power law due to retardation has been also predicted for aerosol particles [15].

In conclusion, we have presented a first-principles method for the calculation of the vdW forces between finite-sized macroscopic objects, based on the fluctuation-dissipation theorem and a rigorous multiple-scattering theory. The formalism is applied to the case of the vdW force between two metal nanoparticles. We have shown that the higher-multipolar contribution to the force is dominant for small particle separations and that dramatic deviations from the standard $1/r^2$ power-law occur as a result of near-field and retardation effects.

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