Non-local Effective Medium for the Electromagnetic Response of Colloidal Systems: a T-matrix Approach

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Abstract

We show the nonlocal nature of the effective electromagnetic response of a colloidal system with large particles and derive closed expressions for both, the effective nonlocal electric permittivity and the magnetic susceptibility.

Introduction

The effective-medium concept has been extremely useful for the electromagnetic treatment of colloidal and granular systems when the size of the inclusions is much less that the wavelength of the incident radiation [1]. When particles are not small compared to this wavelength the system becomes optically turbid. That is, in addition to the coherent field there is also a diffuse field. In this case there have been attempts [2] to derive an effective refractive index of a system consisting of randomly located identical spheres, in order to describe the propagation of the coherent beam. This effective refractive index turns out to be complex, in general, and the imaginary part takes account of both, optical absorption by the colloidal particles and scattering off the incident beam. One of the main assumptions in this derivation is that in case of nonmagnetic colloidal particles embedded in a nonmagnetic matrix, the effective medium is also nonmagnetic. In this case the full electromagnetic response of the system will be given only in terms of the effective electric permittivity ε_{eff}, or equivalently, in terms of its square root: the effective index of refraction $\tilde{n}_{eff}$.

Here we consider a boundless colloidal system composed by nonmagnetic identical spheres embedded in a nonmagnetic matrix and show, that in the case of particles whose size is comparable or larger that the wavelength of the incident radiation (large particles), the corresponding effective medium has a magnetic response. Thus, the full description of the electromagnetic response of the system for the coherent beam requires of both, the effective electric permittivity ε_{eff} and the effective magnetic permeability μ_{eff}. Besides providing explicit expressions for these quantities we show first that the effective medium is nonlocal (spatially dispersive), that is, the effective response functions ε_{eff} and μ_{eff} depend not only on the frequency of the incident beam but also on its wavevector. The importance of the results derived on this paper lies on the fact that in many applications in colloidal systems with large particles one finds that the concept of an effective medium is used rather carelessly.

Formalism

We consider a boundless colloidal system made of identical spherical nonmagnetic particles characterized by a radius a and frequency-dependent electric permittivity $\varepsilon_S(\omega)$. We also assume that on the average the system is homogeneous and isotropic. For simplicity in the presentation we will assume that the embedding matrix is vacuum. Our starting point is the equation for the electric field

$$\nabla \times \left(\nabla \times \vec{E} \right) - k_0^2 \vec{E} = i\omega \, \mu_0 \, \vec{J}^{ind} \tag{1}$$

where $i = \sqrt{-1}$, $k_0^2 = \omega^2 \varepsilon_0 \mu_0$ and $\vec{J}^{ind}$ is the *total* current density induced in the colloidal system by an external electromagnetic field oscillating with a single frequency ω. By total we mean all possible induced currents, and this includes not only conduction and polarization currents but even those closed currents that give rise to magnetic effects. We are using the SI system of units, thus ε_0 and μ_0 correspond to the permittivity and permeability of vacuum.

If one considers that the currents are induced in each of the N spheres of the colloidal system, the above equation can be written as

$$\vec{E}(\vec{r};\omega) = \vec{E}^{ext}(\vec{r};\omega) + i\omega\mu_0 \sum_{p=1}^{N} \overleftrightarrow{G}_0(\vec{r},\vec{r}\,';\omega) \cdot \vec{J}_p^{ind}(\vec{r}\,';\omega) \, d^3r' \tag{2}$$

where $\vec{E}$ is the total electric field (coherent plus diffuse), $\overleftrightarrow{G}_0$ is the free dyadic Green's propagator and the sum over p runs over all the particles in the system. The transition (dyadic) operator $\overleftrightarrow{T}$ (*T-matrix*) is now defined as

$$\vec{J}_p^{ind}(\vec{r};\omega) = \frac{1}{i\omega\mu_0}\int \overleftrightarrow{T}(\vec{r}-\vec{r}_p,\vec{r}'-\vec{r}_p;\omega)\cdot\vec{E}_p^E(\vec{r}\,';\omega)\,d^3r' \tag{3}$$

where $\vec{r}_p$ is the position vector of the p-th sphere and $\vec{E}_p^E$ is the field that excites it (exciting field). This field is defined as the external field plus the field scattered by all other particles but the p-th particle. We now use the effective-field approximation (EFA) in which the exciting field at each particle is approximated by the total average field, that is, $\vec{E}_p^E \approx \left\langle \vec{E} \right\rangle$, where $\langle ... \rangle$ denotes configurational average. The EFA is valid when the colloidal system is dilute.

The average induced current density within the EFA can be written as

$$\left\langle \vec{J}^{ind} \right\rangle (\vec{r};\omega) = \frac{N}{i\omega\mu_0}\int \langle T\rangle(\vec{r}-\vec{r}\,';\omega)\left\langle \vec{E} \right\rangle(\vec{r}\,';\omega)\,d^3r' \tag{4}$$

where $\left\langle \overleftrightarrow{T} \right\rangle(\vec{r}-\vec{r}\,';\omega) \equiv \left\langle \frac{1}{N}\sum_{p=1}^{N}\overleftrightarrow{T}(\vec{r}-\vec{r}_p,\vec{r}\,'-\vec{r}_p;\omega) \right\rangle$ is a function of $|\vec{r}-\vec{r}\,'|$ because we have assumed that the system is, on the average, homogeneous and isotropic. Let us recall that in this context $\left\langle \vec{E} \right\rangle$ is also called the *macroscopic* electric field. Eq. (4) shows explicitly the *nonlocal* nature of the electromagnetic response of the colloidal system; one of the main results of our work. Eq. (4) looks like a *nonlocal* Ohm's law with the kernel $(N/i\omega\mu_0)\left\langle \overleftrightarrow{T} \right\rangle(\vec{r}-\vec{r}\,';\omega)$ playing the role of an effective *nonlocal* conductivity.

We now transform the above relation into the momentum representation (p-representation), and write

$$\left\langle \vec{J}^{ind} \right\rangle (\vec{p};\omega) = \frac{1}{i\omega\,\mu_0}\,n_0\,\overleftrightarrow{T}(\vec{p},\vec{p};\omega)\cdot\left\langle \vec{E} \right\rangle(\vec{p};\omega) \tag{5}$$

Here $\vec{p}$ is the wavevector associated to the Fourier transformation in the momentum representation, $\overleftrightarrow{T}(\vec{p},\vec{p}\,') = \int d^3r \int d^3r'\, \exp[-i\vec{p}\cdot\vec{r}]\,\overleftrightarrow{T}(\vec{r},\vec{r}\,')\,\exp[-i\vec{p}\,'\cdot\vec{r}\,']$, we have taken $\sum_p \to (N/V)\int d^3r_p$ in the calculation of the configurational average, where V is the total volume of the system, and $n_0 \equiv N/V$. Note that in the EFA the average induced current density depends only on the transition operator of a single, isolated sphere. Also, we will be using the same symbol for quantities in the r- and p-representation, the difference being only in the arguments.

The transition operator $\overleftrightarrow{T}(\vec{p},\vec{p};\omega)$ can be decomposed as

$$\overleftrightarrow{T}(\vec{p},\vec{p};\omega) = T^L(p,\omega)\hat{p}\hat{p} + T^T(p,\omega)[\overleftrightarrow{1} - \hat{p}\hat{p}] \tag{6}$$

where the scalar functions $T^L(p,\omega)$ and $T^T(p,\omega)$ are called the longitudinal and transverse projections of $\overleftrightarrow{T}$. Here $\hat{p} \equiv \vec{p}/p$ is a unit vector along $\vec{p}$, thus $\hat{p}\hat{p}$ corresponds, in the momentum representation, to the longitudinal projection operator.

We now split the total induced current density as $\vec{J}^{ind} = \vec{J}_P + \vec{J}_M$ where $\vec{J}_P = -i\omega\vec{P}$ and $\vec{J}_M = i\vec{p}\times\vec{M}$ are defined in terms of the usual polarization and magnetization fields, $\vec{P}$ and $\vec{M}$. Then, the effective nonlocal electric permittivity and magnetic susceptibility of the colloidal system $\varepsilon_{eff}(p,\omega)$ and $\mu_{eff}(p,\omega)$ are defined through $\vec{P} = (\varepsilon_{eff}-\varepsilon_0)\left\langle \vec{E} \right\rangle$ and $\vec{M} = (\mu_{eff}/\mu_0 - 1)\,\vec{H}$, where $\vec{H}$ is the usual H-field that obeys $i\vec{p}\times\vec{H} = \vec{J}^{ext} - i\omega\varepsilon_{eff}\left\langle \vec{E} \right\rangle$. Note that all quantities here are in the p-representation. It is straightforward to show that the relationship between the pair of functions $\varepsilon_{eff}(p,\omega)$ and $\mu_{eff}(p,\omega)$, and $T^L(p,\omega)$ and $T^T(p,\omega)$ is given by

$$\tilde{\varepsilon}_{eff}(p,\omega) = 1 + \frac{n_0}{k_0^2}T^L(p,\omega) \quad \text{and} \quad \tilde{\mu}_{eff}(p,\omega) = \frac{1}{1-\dfrac{n_0}{p^2}\left[T^T(p,\omega)-T^L(p,\omega)\right]} \tag{7}$$

Thus a legitimate, *bona fide* magnetic response appears in the colloidal system whenever $T^T(p,\omega) \neq T^L(p,\omega)$. The idea that a colloidal system with nonmagnetic components might have a magnetic response was first pointed out by Bohren [3].

Calculation of the Transition Operator

In this section we calculate the longitudinal and transverse components of the transition operator. Although a calculation procedure for solving the integral equation for $\overleftrightarrow{T}(\vec{p},\vec{p}\,';\omega)$ in a spherical basis has been devised by Tsang and Kong [5], here we calculate $\overleftrightarrow{T}(\vec{p},\vec{p}\,'=\vec{p};\omega)$ directly by using an alternative procedure. We do this by considering in Eq. (3) a single, isolated sphere excited by a plane wave with wavevector $\vec{p}$, that is, $\vec{E}_p^{\,E}(\vec{r}\,';\omega) = \vec{E}^{ext} = \vec{E}_0 \exp[i\vec{p}\cdot\vec{r}]$. Then it is possible to show that in the p-representation one can write

$$\vec{J}^{ind}(\vec{p};\omega) = \frac{1}{i\omega\,\mu_0}\overleftrightarrow{T}(\vec{p},\vec{p};\omega)\cdot\vec{E}_0 \tag{8}$$

where $\overleftrightarrow{T}(\vec{p},\vec{p};\omega)$ is given at once in terms of $\vec{J}^{ind}(\vec{p};\omega)$. Note that the external plane wave is not a free electromagnetic wave but rather a plane wave that has associated, in general, an external charge density and an external current density.

Therefore, in order to calculate $\vec{J}^{ind}(\vec{p};\omega)$ we start by exciting a single, isolated sphere with an electromagnetic field $\vec{E}^{ext}$ (and H^{ext}), and then calculate the fields within the sphere (internal fields) using a spherical basis. In this calculation, the external and scattered fields are expanded in the usual way [4] but the appropriate expansion for the internal electric field, $\vec{E}^I$, looks like

$$\vec{E}^I(\vec{r};\omega) = \left(\frac{k_S^2-k_0^2}{k_S^2-p^2}\right)\sum_{n=1}^{\infty} E_n\left(c_n\vec{M}_{o1n}^{(1)} - id_n\vec{N}_{e1n}^{(1)}\right) + \frac{k_0^2-p^2}{k_S^2-p^2}\vec{E}^{ext} \tag{9}$$

with a similar expression for the internal H-field. Here $E_n = i^n E_0(2n+1)/n(n+1)$, the vector functions $\vec{M}_\alpha^{(1)}$ and $\vec{N}_\beta^{(1)}$ are the vector spherical harmonics [5], $k_S = \omega\sqrt{\varepsilon_S\mu_0}$, and the coefficients c_n and d_n are determined by imposing boundary conditions at the surface of the sphere, yielding

$$c_n = \frac{j_n(x_i)\,[x_0h_n(x_0)]' - h_n(x_0)\,[x_ij_n(x_i)]'}{j_n(x_S)\,[x_0h_n(x_0)]' - h_n(x_0)\,[x_Sj_n(x_S)]'};\;\; d_n = \frac{x_ij_n(x_i)\,[x_0h_n(x_0)]' - x_0^2h_n(x_0)\dfrac{1}{x_i}\,[x_ij_n(x_i)]'}{x_Sj_n(x_S)\,[x_0h_n(x_0)]' - x_0^2h_n(x_0)\dfrac{1}{x_S}\,[x_Sj_n(x_S)]'} \tag{10}$$

where $x_i \equiv pa$, $x_0 \equiv k_0a$, and $x_S = k_Sa$ are dimensionless variables and the prime denotes derivative with respect to the argument. The last term in the rhs of Eq. (9) takes account of the presence of the external sources associated to the external fields.

Since the induced current density within the sphere is given by $\vec{J}^{ind} = (\varepsilon_S/\varepsilon_0 - 1)\,\vec{E}^I$, where ε_S is the frequency-dependent electric permittivity of the sphere, one can use Eq. (8) to write

$$\overleftrightarrow{T}(\vec{p},\vec{p};\omega)\cdot\vec{E}_0 = k_0^2\left(\frac{\varepsilon_S(\omega)}{\varepsilon_0}-1\right)\int d^3r\,\vec{E}^I(\vec{r};\omega)\exp[-i\vec{p}\cdot\vec{r}] \tag{11}$$

We now perform this integral by using the expression of $\vec{E}^I(\vec{r};\omega)$ given by Eq. (9) and expand the exponential $\exp[-i\vec{p}\cdot\vec{r}]$ in a spherical basis in the usual way. By choosing $\vec{E}_0$ first perpendicular and then parallel to $\vec{p}$ one obtains directly $T^T(p,\omega)$ and $T^L(p,\omega)$, respectively. After a long but straightforward algebra we obtain for the transverse projection

$$\begin{aligned} T^T(p,\omega) =& \frac{4\pi}{3}x_0^2a\left(\frac{\varepsilon_S(\omega)}{\varepsilon_0}-1\right)(1-\xi) + 2\pi x_0^2a\left(\frac{\varepsilon_S(\omega)}{\varepsilon_0}-1\right)\xi \\ &\times\sum_{n=1}^{\infty}(2n+1)\left\{c_n\,I_2(n,n) + d_n\left[\frac{n+1}{x_i}I_1(n,\,n-1) + \frac{n}{x_i}I_1(n+1,\,n) - I_2(n+1,\,n-1)\right]\right\} \end{aligned} \tag{12}$$

where

$$I_2(n,m) \equiv \int_0^1 x^2 j_n(x_i x) j_m(x_S x)\, dx; \quad I_1(n,m) \equiv \int_0^1 x j_n(x_i x) j_m(x_S x)\, dx$$
$$I_2(n,n) \equiv \frac{1}{x_i^2 - x_S^2}\left[x_S j_n(x_i) j_{n-1}(x_S) - x_i j_{n-1}(x_i) j_n(x_S)\right] \quad \text{and} \quad \xi = \frac{k_S^2 - k_0^2}{k_S^2 - p^2} \tag{13}$$

Following the same procedure, we obtain for the longitudinal projection

$$T^L(p,\omega) = \frac{4\pi}{3} x_0^2 a \left(\frac{\varepsilon_S(\omega) - \varepsilon_0}{\varepsilon_S(\omega)}\right)\left[1 + \left(\frac{\varepsilon_S(\omega)}{\varepsilon_0} - 1\right)\sum_{n=1}^{\infty} 3n(n+1)(2n+1) d_n^L \frac{j_n(x_S)}{x_S}\frac{j_n(x_i)}{x_i}\right]$$

where

$$d_n^L = \frac{-x_0^2 h_n(x_0)\dfrac{1}{x_i} j_n(x_i)}{x_S j_n(x_S)\left[x_0 h_n(x_0)\right]' - x_0^2 h_n(x_0)\dfrac{1}{x_S}\left[x_S j_n(x_S)\right]'} \tag{14}$$

By inserting Eqs. (12)-(14) into Eq. (7) one obtains closed expressions for $\varepsilon_{eff}(p,\omega)$ and $\mu_{eff}(p,\omega)$.

Conclusion

We showed that the effective medium for the electromagnetic response for the coherent beam of a colloidal system with large inclusions is nonlocal (spatially dispersive), and that a colloidal system with nonmagnetic components has a (nonlocal) magnetic response. The physical origin of this response are the closed currents induced within the spheres. We also derive explicit closed expressions for both, the effective nonlocal electric permittivity $\varepsilon_{eff}(p,\omega)$ and the magnetic susceptibility $\mu_{eff}(p,\omega)$. A detailed numerical analysis of the spectral and nonlocal dependence of $\varepsilon_{eff}(p,\omega)$ and $\mu_{eff}(p,\omega)$, for a variety of colloidal and granular systems, will be presented elsewhere.

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