Optical extinction, refractive index, and multiple scattering for suspensions of interacting colloidal particles

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Abstract

We provide a general microscopic theory of the scattering cross-section and of the refractive index for a system of interacting colloidal particles, exact at second order in the molecular polarizabilities. In particular: a) we show that the structural features of the suspension are encoded into the forward scattered field by multiple scattering effects, whose contribution is essential for the so-called "optical theorem" to hold in the presence of interactions; b) we investigate the role of radiation reaction on light extinction; c) we discuss our results in the framework of effective medium theories, presenting a general result for the effective refractive index valid, whatever the structural properties of the suspension, in the limit of particles much larger than the wavelength; d) by discussing strongly-interacting suspensions, we unravel subtle anomalous dispersion effects for the suspension refractive index.

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I. STATEMENT OF THE PROBLEM

Scattering methods have long been a basic tool for the investigation of colloidal systems. The recent development of optical correlation techniques[1–4] that, by successfully combining scattering and real-space visualization, allow to probe the microscopic Brownian dynamics still retaining the spatial resolution proper of a microscope, calls however for a critical reassessment of the relation between scattering and imaging. A detailed analysis of the effects of the propagation through a scattering medium on the amplitude and phase of the transmitted wavefront is also of primary importance for digital holographic techniques[5].

The effect on the transmitted wavefront of the transit though a scattering medium can be expressed by stating that the forward scattering pattern consists in a faithful reproduction of the incident field that spatially superimposes with the transmitted radiation, but with a different phase. The interference between this "simulacrum" of the incident field and the portion of the field which passes through the medium without being scattered yields *both* its phase delay in traversing the medium (thus fixing its refractive index) and, adding to the non-radiative power loss due to absorption, the power reduction of the transmitted field. For what concerns power loss, this is explicitly treated by the so-called "Optical Theorem" (OT), a general and extremely useful result that holds true not only for electromagnetic radiation but also for matter waves [6]. Consider the simple case of a plane wave with wave-vector $\mathbf{k}_i = (\omega/c)\,\hat{\mathbf{k}}_i$, where $\hat{\mathbf{k}}_i$ is a unit vector specifying the incident direction, and polarized with the electric field along $\mathbf{n}_i$, $\mathbf{E}_i(\mathbf{r}, t) = \mathbf{n}_i E_i \exp[i(\mathbf{k}_i \cdot \mathbf{r} - \omega t)]$, which encounters a scattering and absorbing medium confined in a finite region of space around the origin. In far field, the radiation scattered along $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$ with wavevector $\mathbf{k}_s = k_s\hat{\mathbf{r}}$ can be written as

$$\mathbf{E}_s(\mathbf{r}, t) = \mathbf{n}_s E_i \frac{iS(\mathbf{k}_s, \mathbf{k}_i)}{kr} e^{i(k_s r - \omega t)}, \tag{1}$$

where $\mathbf{n}_s$ is a vector normal to $\mathbf{k}_s$, which depends on both n_i and k_s, and $S(\mathbf{k}_s, \mathbf{k}_i)$, called the scattering amplitude, takes in general complex values. Then, the OT states that the extinction cross section is given by [32]

$$\sigma_{ext} = \frac{4\pi}{k^2}(\mathbf{n}_i \cdot \mathbf{n}_s)\text{Re}[S(\mathbf{k}_s = \mathbf{k}_i)] \tag{2}$$

This rather surprising result, which basically shows that evaluating the total extinction (due to scattering and, possibly, absorption) of the radiation traversing the medium requires

to know the scattering amplitude *only* in the forward direction $\mathbf{k}_i$, can be rather easily obtained [7] by considering that, at steady state, the change in the total energy density within a spherical region containing the whole scattering medium is solely due to the dissipative absorption processes taking place within it, and by equating the latter to the incident plus scattered energy flow through the spherical surface.[33]

Most presentations of the OT consider an incoming plane wave and a single scattering particle. Here we assume that the scattering volume contains a large number of particles in Brownian motion. The field scattered in any direction, except for zero-scattering angle, is the sum of many uncorrelated fields, it is a random process with zero-average and a two-dimensional Gaussian probability density. On the contrary, the fields scattered by individual particles in the forward direction have all the same phase, that is, the forward scattered wave exactly reproduces the wavefront of the incident wave. In this paper we will only deal with an incident plane wave, but the OT can be generalized to an arbitrary incident field (for instance, a gaussian beam) by considering the angular spectrum of the latter and applying Eq. (2) to each plane wave component. Of course, in such a case the relation between extinction and forward scattering amplitude applies only to the *whole* far-field diffraction pattern.

The forward scattering amplitude contains *more* information than what simply conveyed by the OT. To see this, it is sufficient to recall that, in a macroscopic description of the passage of radiation though a material, the effects of propagation can be fully embodied into a complex refractive index $\tilde{n} = n + in'$, whose real and imaginary parts are respectively related to dispersion and power loss. Then, *both* n and n' can be formally linked to the real and imaginary parts of $S(\mathbf{k}_s = \mathbf{k}_i)$. Yet, such a relation would be of little practical interest unless we are able to evaluate $S(\mathbf{k}_s = \mathbf{k}_i)$, which is the *overall* forward scattering amplitude, in terms of the specific microscopic scattering and absorption events taking place in the medium. Strenuous efforts to derive the macroscopic optical properties of a molecular fluid from microscopic scattering events have spangled the history of physical optics (for a review of the early attempts, see for instance the books by Rosenfeld [8] and Fabelinskii [9]), culminating in a series of impressive contributions by Hynne and Bullough [10–12], in which a rigorous many-body electrodynamic theory is used to obtain consistent expressions for the refractive index, the extinction coefficient, and the scattering cross section. Unfortunately, this powerful analysis, which was performed with a very sophisticated formalism and ba-

sically no approximation, leads to rather cumbersome general results that, as a matter of fact, yield manageable expressions only for rather dilute real gases, where interactions are accounted for only at the level of the second virial coefficient in a density expansion.

The situation looks however much more promising if we consider a *particulate* medium, namely, a collection of individual scatterers, such as a suspension of colloidal particles dispersed in a weakly scattering, non-absorbing solvent. Our problem can then be rephrased as follows: is there any way to relate the real and imaginary part of the refractive index of the whole dispersion to the scattering properties of the *individual* scatterers? In the simple case of a thin slab of a medium consisting of a dispersion of identical scatterers illuminated by a monochromatic plane wave, the OT provides a straightforward affirmative answer to this question, at least provided that two basic assumptions are satisfied: [13]

1. The scatterers are *randomly arranged*, namely, they do not display any structural correlation. This implies that the physical particles acting as scatterers interact very weakly, so that any correlations in density fluctuations can be neglected.

2. The incident field "seen" by a particle coincides with the *external* radiation, namely, any additional contribution due to the surrounding scatterers is neglected. Provided that we carefully specify that these contributions may be due not only to radiating, but also to quasi-static fields in the near-zone, which would actually be the case for those scatterers that lying a distance $r \lesssim \lambda$ from the particle, this loosely means that "multiple scattering" effects are negligible.

In this case, assuming for simplicity that the scatterers are optically isotropic, and indicating with θ the polar angle with respect to the direction of $\mathbf{k}_i$, Eq. (2) reduces to

$$\sigma_{ext} = \frac{4\pi N}{k^2} \text{Re}[s(0)], \tag{3}$$

where $N = \rho V$ is the particle number in the volume V, $k = 2\pi/\lambda$, and $s(0)$ is the amplitude of the field scattered in the forward direction $\theta = 0$ by each *single* particle. This simpler relation can be obtained by considering that i) for independent particles, σ_{ext} is the sum of the single-particle cross sections; ii) in the forward direction (and *only* in this direction) the scattering amplitudes are additive too, because all scattering contributions add *in phase*, regardless of the positions of the particles in the scattering volume. By evaluating the phase

shift in propagation through the slab, the real and imaginary parts of the effective refractive index of the medium are then easily found to be[34]

$$\begin{cases} n = 1 - \dfrac{2\pi\rho}{k^3}\mathrm{Im}[s(0)] \\ n' = \dfrac{2\pi\rho}{k^3}\mathrm{Re}[s(0)] \end{cases} \tag{4}$$

It is useful to recall that, when $n' \neq 0$, the intensity of a plane wave propagating in the medium along z decreases as $I = I_0 \exp(-\gamma z)$, where the extinction coefficient

$$\gamma = 2kn' = \frac{4\pi\rho}{k^2}\mathrm{Re}[s(0)] = \frac{\sigma_{ext}}{V} \tag{5}$$

is simply the extinction cross section per unit volume.

Eq. 4 has been used to investigate the effects of particle size on refractive index and extinction by using the expression for scattering amplitude obtained from the general Mie theory for light scattering from non-interacting spherical particles.[14]. However, repulsive and attractive interparticle forces are well known to strongly affect (the former by increasing, the latter by reducing) the transmittance of light through a colloid. Moreover, Eq. (4) suggests that also the real part n of the refractive index should not be immune from interaction effects. It is then very tempting to scrutinize whether an effective refractive index could be defined in the interacting case too, provided that the expression for the single-particle forward scattering amplitude is suitably revisited to account for the structure of the medium.

The goal of this work is to extend the OT approach to the case of interacting colloidal particles, and to apply our results to investigate the contribution of correlations to the refractive index of a suspension. We shall confine our investigation to suspensions of spherical particles in the colloidal size range that, though possibly concentrated in terms of particle volume fraction ϕ, are still dilute in terms of number density $\rho = \phi/v$, where v is the volume of a single particle. This restriction allows to describe interparticle forces using simple model pair potentials and correlation functions, an approach which is generally unsuited to properly describe the structure of dense molecular fluids. In addition, we shall systematically adopt the lowest order approximation for the optical properties of the scatterers in which interactions effects do nevertheless show up which, as we shall see, amounts to a second order approximation in the optical polarizability α. Even within these approximations, however, an explicit evaluation of $S(0)$ casts new light on the optical mechanism leading to the formation of the transmitted wavefront, and highlights a rather unexpected role

played by multiple scattering, usually just regarded as a nuisance in light scattering studies. A key result of our investigation is indeed that, when considering the radiation strictly scattered in the *forward* direction, the contribution from multiple scattering events, even when negligible at finite q, is conversely found to be crucial to figure out why the forward scattering amplitude, and therefore light extinction, depends on interparticle interactions.

This paper is then organized as follows. The microscopic approach we use and the approximations we make are introduced in Section II, where we first evaluate the electric field in the forward direction due to the superposition of the incident field with the waves generated by *point-like* oscillating particles. By considering a slab geometry, we show that a microscopic expression for the refractive index of a suspension of uncorrelated point-like particles is fully consistent *at all orders* with the high frequency limit of the Clausius-Mossotti (CM) formula, namely, the Lorentz-Lorenz expression[15]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\rho\alpha, \tag{6}$$

provided that the expression for the dipole polarizability includes the contribution from the reaction radiation field, namely, the self-action of the dipole on itself.

The correlation contribution to the scattering amplitude and to the refractive index for the general case of a homogeneous but *correlated* distribution of point-like dipoles is derived in Section III, and used to check that the forward scattering amplitude is rigorously linked to σ_{ext} by the Optical Theorem. Such an explicit comparison yields an interesting conceptual consequence: particle spatial correlations are "encoded" into the forward scattering amplitude only via the additional contribution to the incident field brought in by the secondary fields scattered by those dipole lying within a close-by region with a size comparable to the correlation range of the medium. In particular, we discuss the limits of validity of the CM approximation in terms of the ratio of the correlation length ξ of the system to the wavelength λ of the incident light.

In Section IV, we first extend the former results to a system of particles of finite size in vacuum, comparing in particular the limits for small and large particle size both in the absence (IV A) and in the presence (IV B) of interparticle interactions. Extension of these results to the case of particles dispersed in a solvent is made in Section IV C, where we show that this is straightforward provided that the latter is assumed to be an uncorrelated dielectric medium. In Section IV D we frame our results within the context of effective

medium theories, which is made, showing in particular that a very general result for the effective *static* dielectric constant, which is exact at 2nd order in polarizability whatever the structural correlations of the suspension, fails in the optical regime when $\lambda \ll \xi$, and has to be substituted by a novel, equally general expression for the effective refractive index. Illustrative examples of the contribution of interparticle interactions to the concentration dependence of the refractive index are presented in Section IV E for the specific case of hard-sphere interactions. In particular, by investigating the strongly correlated case of a colloidal fluid in equilibrium with a colloidal crystal, we show that, whenever the peak of the structure factor $S(q)$ falls within the detectable q-range, the refractive index displays a peculiar "anomalous dispersion" region where it behaves similarly to the refractive index of a Lorentz oscillator close to resonance. Experimental conditions in which these effects could be observed are finally discussed in Section IV F.

II. SYSTEM OF POINT-LIKE PARTICLES

The purpose of this Section is to describe the total field scattered by a system of point-like polarizable particles (namely, simple dipoles) by explicitly taking into account the contribution to the incident field on each single dipole due both the other surrounding dipoles *and* to the self-action of the dipole on itself. Consider then a collection of N oscillating dipoles made of a mobile charge e and a fixed charge $-e$ located at fixed positions $\mathbf{R}_i$, with a spatial distribution to be specified later. Defining the instantaneous dipole moment of a given particle as

$$\mathbf{p}(t) = \mathbf{p}_0 \mathrm{e}^{-\mathrm{i}\omega t}, \tag{7}$$

the electric field in $\mathbf{r}$ generated by the oscillating dipole placed at the origin has the form [7]

$$E_d^\mu(\mathbf{r}, t) = \mathrm{e}^{\mathrm{i}(kr-\omega t)} k^3 \Gamma^{\mu\nu}(\mathbf{r}) \, p_0^\nu, \tag{8}$$

where $k = \omega/c$, the radial unit vector is $n^\mu = r^\mu/r$, and the dimensionless matrix $\Gamma(\mathbf{r})$ is defined by

$$\Gamma^{\mu\nu}(\mathbf{r}) = (3n^\mu n^\nu - \delta^{\mu\nu}) \left[\frac{1}{(kr)^3} - \mathrm{i}\frac{1}{(kr)^2} \right] - \frac{1}{kr} (n^\mu n^\nu - \delta^{\mu\nu}). \tag{9}$$

Here and in the following, Greek superscripts refer to the spatial components (x, y, z) and the summation over repeated Greek indices is understood. It is useful to observe right from the start that the 2nd and 3rd term in $\Gamma^{\mu\nu}(\mathbf{r})$, which respectively account for the field in the

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so-called "intermediate" and "radiation" zones,[7] are of order r/λ and $(r/\lambda)^2$ with respect to the electrostatic part decaying as r^{-3}. When we take into account spatial correlations, the relative contribution of these two terms will be found to increase with the correlation length ξ of the system.

If we include the presence of an external linearly polarized plane wave of the form

$$E_0^\mu(\mathbf{r}, t) = \mathscr{E}^\mu \mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{10}$$

with $k^\mu \mathscr{E}^\mu = 0$, the total electric field, due to the external source and the collection of dipoles, is then

$$
\begin{align}
E^\mu(\mathbf{r}, t) &= E_0^\mu(\mathbf{r}, t) + \sum_j E_d^\mu(\mathbf{r} - \mathbf{R}_j, t) \tag{11} \\
&= E_0^\mu(\mathbf{r}, t) + k^3 \sum_j \mathrm{e}^{\mathrm{i}k|\mathbf{r}-\mathbf{R}_j|} \Gamma^{\mu\nu}(\mathbf{r} - \mathbf{R}_j)\, p_{0j}^\nu\, \mathrm{e}^{-\mathrm{i}\omega t} \tag{12}
\end{align}
$$

where $\mathbf{E}_d(\mathbf{r} - \mathbf{R}_j, t)$ is the contribution to the electric field in $\mathbf{r}$ due to the dipole in $\mathbf{R}_j$. Now we introduce the polarizability α by assuming that the moment $\mathbf{p}_j$ of the dipole in $\mathbf{R}_j$ is proportional to the local electric field due to the *other* charges (i.e. the dipoles represent polarizable point-like objects):

$$\mathbf{p}_j(t) = \mathbf{p}_{0j}\, e^{-\mathrm{i}\omega t} = \alpha\, \mathbf{E}_j(\mathbf{R}_j, t) \tag{13}$$

where the subscript j in $\mathbf{E}_j(\mathbf{R}_j, t)$ means that the contribution due to the dipole in $\mathbf{R}_j$ has to be subtracted, and α depends in general on the frequency ω.

Yet, as we already mentioned, a consistent treatment requires to take also into account the action on the oscillating charge of the field emitted by itself, namely, of the so-called "radiation reaction field" which, in the absence of non-radiative dissipation, provides the only mechanism for power loss. The question of the back-reaction of the radiated field onto the motion of a charge is one of the most challenging problem in electrodynamics, since it leads to an equation, originally derived by Lorentz[16] and then generalized to the relativistic case by Abraham and Dirac[17], which, containing the derivative of $\ddot{\mathbf{r}}$, causes serious diffi-culties due the appearance of "runaway" solutions showing an exponential increase of $\ddot{\mathbf{r}}$ even in the absence of external fields. Nevertheless, for a charge *oscillating* at non-relativistic speed, the ingenious approach devised by Lorentz safely allows to include radiation reaction effects at lowest order by introducing an imaginary additive contribution to the particle

polarizability[13]

$$\alpha \to \tilde{\alpha} = \alpha \left[1 + i \frac{2}{3} k^3 \alpha \right] \tag{14}$$

In the following, the physical counterpart of the elementary dipoles we introduced will be atoms or molecules excited at a frequency ω far from any electronic or vibrational transition, so that α will be taken as a *real* quantity.

Since we are considering point-like dipoles, the only intrinsic length scale in the problem is the wavelength λ of the incident radiation. It is then suitable to define a dimensionless polarizability $\alpha_d = \tilde{\alpha}k^3$ (where the subscript d stands for "dipoles") that, substituted into Eq. (12) using (14), yields:

$$E^\mu(\mathbf{r}, t) = E_0^\mu(\mathbf{r}, t) + \alpha_d \sum_j e^{ik|\mathbf{r}-\mathbf{R}_j|} \Gamma^{\mu\nu}(\mathbf{r} - \mathbf{R}_j) E_j^\nu(\mathbf{R}_j, t) \tag{15}$$

This is an equation for the electric field $\mathbf{E}(\mathbf{r}, t)$, which can be solved by iteration. To second order in the scaled polarizability α_d the explicit solution is:

$$\begin{aligned}
E^\mu(\mathbf{r}, t) = \ & E_0^\mu(\mathbf{r}, t) + \alpha_d \sum_j e^{-ik|\mathbf{r}-\mathbf{R}_j|} \Gamma^{\mu\nu}(\mathbf{r} - \mathbf{R}_j) E_0^\nu(\mathbf{R}_j, t) + \\
& \alpha_d^2 \sum_{j\neq l} e^{ik|\mathbf{r}-\mathbf{R}_j|} e^{ik|\mathbf{R}_j-\mathbf{R}_l|} \Gamma^{\mu\nu}(\mathbf{r} - \mathbf{R}_j) \Gamma^{\nu\sigma}(\mathbf{R}_j - \mathbf{R}_l) E_0^\sigma(\mathbf{R}_l, t)
\end{aligned} \tag{16}$$

The second order approximation in α_d given by Eq. (16) will be particularly useful in what follows both to describe a system of interacting dipoles, and to extend our results to the case of finite-size particles in Section IV, where, in the case of non-interacting colloids, we shall also check for consistency with the exact Mie results obtained within a continuum approach. However, it is interesting to point out that Eq. (15) is also the starting point of a *non-perturbative* investigation of the dispersion relation which characterizes the medium, which fully justifies the CM relation for a system of uncorrelated dipoles, and actually generalized it to account for the extinction contribution brought in by radiation reaction effects. For a monochromatic perturbation, the time dependence is factorized as

$$E_j^\mu(\mathbf{r}, t) = E_j^\mu(\mathbf{r}) e^{-i\omega t} \tag{17}$$

Moreover, by evaluating the electric field at the position of the ith particle and subtracting the singular contribution bue to the ith dipole, we get:

$$E_i^\mu(\mathbf{R}_i) = E_0^\mu(\mathbf{R}_i) + \bar{\alpha} \sum_{j\neq i} e^{ik|\mathbf{R}_i-\mathbf{R}_j|} \Gamma^{\mu\nu}(\mathbf{R}_i - \mathbf{R}_j) E_j^\nu(\mathbf{R}_j) \tag{18}$$

For given positions of the N dipoles of the medium $(\mathbf{R}_1 \cdots \mathbf{R}_N)$, this is a set of linear equations for the $3N$ unknowns $E_i^\mu(\mathbf{R}_i)$. Here we want to analyze the possible solutions in the bulk, i.e., the monochromatic waves which can propagate in the medium. Consider then a planar slab of thickness h, placed orthogonally to the direction of propagation z of an incident plane wave polarized along x, $E_0^x(\mathbf{r}) = \epsilon_0 e^{ikz}$. The field *inside* the slab at the position Z_i along the optical axis of the i-th particle, averaged on the positions of all the other particles, can always be written as the superposition of two counter-propagating components (the transmitted and the reflected wave)

$$E_i^x(\mathbf{R}_i) = \epsilon^+ e^{iqZ_i} + \epsilon^- e^{-iqZ_i}, \tag{19}$$

where q is a complex quantity to be specified later representing the average wave vector of the propagating field inside the medium. By substituting this parametrization into Eq. (18) and introducing the pair distribution function $g(\mathbf{r})$, we obtain

$$\epsilon^+ e^{iqz} + \epsilon^- e^{-iqz} = \epsilon_0 e^{ikz} + \bar{\alpha}\rho \int d\mathbf{r}'\, g(\mathbf{r} - \mathbf{r}') e^{ik|\mathbf{r} - \mathbf{r}'|} \Gamma^{xx}(\mathbf{r} - \mathbf{r}') \left[\epsilon^+ e^{iqz'} + \epsilon^- e^{-iqz'}\right] \tag{20}$$

where ρ is the number density of particles in the system. We anticipate that the adopted procedure is in fact correct to second order in an expansion in powers of the molecular polarization, while it neglects three body correlations.

The domain of integration in Eq. (20) coincides with the whole volume of the slab. Note that $g(0) = 0$ due to the presence of a hard core: this guarantees that the constraint $j \neq i$ in Eq. (18) is correctly implemented. Next we write $g(\mathbf{r}) = 1 + h(r)$, where $h(r)$ is non-zero only at short range (i.e. only for r comparable to the molecular diameter). The first contribution ($g(\mathbf{r}) = 1$) accounts for the average particle distribution, while the residual term, containing $h(r)$, provides the correlation contribution to the propagating wave. Let us examine the uncorrelated term with the supplementary *caveat* to exclude an infinitesimal neighborhood of $\mathbf{r} = 0$. By explicitly performing the integrals we obtain the following set of four consistency conditions:

$$\frac{\epsilon^+}{k - q} + \frac{\epsilon^-}{k + q} = -\frac{k^2 \epsilon_0}{2\pi\bar{\alpha}\rho} \tag{21}$$

$$\frac{\epsilon^+ e^{-i(k+q)h}}{k + q} + \frac{\epsilon^- e^{i(k-q)h}}{k - q} = 0 \tag{22}$$

$$\frac{\epsilon^\pm}{k + q} + \frac{\epsilon^\pm}{k - q} - \frac{2}{3}\frac{\epsilon^\pm}{k} = -\frac{k^2 \epsilon^\pm}{2\pi\bar{\alpha}\rho} \tag{23}$$

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which are necessary and sufficient for the validity of Eq. (20) for all z. The condition expressed by Eq. (21) is equivalent to the extinction theorem: the incident wave of wave-vector k does not propagate in the medium because it is exactly canceled by the contribution of the oscillating dipoles. Moreover, together with Eq. (22), it provides the amplitudes of the waves propagating in the direction of the incident signal (ϵ^+) and in the opposite direction (ϵ^-). Finally, the last two equations (23) allow to fix the wave-vector q of the wave at frequency $\omega = kc$ propagating inside the medium. By defining the complex refractive index $\tilde{n}$ via $q = \tilde{n}k$, the final result is:

$$\frac{\tilde{n}^2 - 1}{\tilde{n}^2 + 2} = \frac{4\pi}{3}\alpha_d\rho_d = \frac{4\pi}{3}\tilde{\alpha}\rho \tag{24}$$

where $\rho_d = k^{-3}\rho$ is a dimensionless dipole density. Notably, Eq. (24) is a generalized Clausius–Mossotti (or, better, Lorentz-Lorenz) relation for the *complex* refractive index $\tilde{n}$, which includes the effects of radiation reaction through the imaginary part of $\tilde{\alpha}$. Expanding $\tilde{n}$ at second order in $\tilde{\alpha}\rho$, using (14) with α real, and equating the real and imaginary parts, we obtain

$$\begin{cases} n = 1 + 2\pi\alpha\rho + \dfrac{2}{3}(\pi\alpha\rho)^2 \\ n' = \dfrac{4\pi}{3}\rho k^3\alpha^2 \end{cases} \tag{25}$$

The real part coincides with the expansion at 2nd order of the usual CM formula, whereas the dissipative radiation-reaction term contribute *only* to attenuation. When this result is inserted into Eq. (4), it yields an explicit expression for the scattering amplitude of a *single* non-interacting dipole

$$s_0(0) = \frac{2}{3}k^6\alpha^2 - ik^3\alpha, \tag{26}$$

to leading order in α (linear for the imaginary, and quadratic for the real part). From the OT we then get the correct extinction cross section $\sigma_{ext} = (8\pi/3)N\alpha^2 k^4$ for Rayleigh scattering from independent particles with a size much smaller than λ.

III. CORRELATED FLUID OF POINT-LIKE DIPOLES

We now consider a correlated dielectric medium starting from the general expression (20). The weight function $h(\mathbf{r} - \mathbf{r}')$ is appreciably different from zero only in a small neighborhood of $\mathbf{r}$, therefore if the observation point $\mathbf{r}$ is placed in the bulk, we can extend the integral to the whole space, neglecting the effects of the boundary surfaces. The resulting consistency

condition, which corrects the Lorentz-Lorentz formula (24) for a correlated fluid, is obtained by including into Eq. (21–23) a correlation integral $C(q, k)$:

$$1 = 4\pi\tilde{\alpha}\rho \left[\frac{1}{\tilde{n}^2 - 1} + \frac{1}{3} + C(q, k) \right] \tag{27}$$

$$C(q, k) = \frac{k^3}{4\pi} \int d\mathbf{r}\, e^{-iqz} h(r) \Gamma^{xx}(\mathbf{r}) e^{ikr} \tag{28}$$

where, as usual, an infinitesimal neighborhood of $r = 0$ is excluded from the integration domain. By introducing the Fourier transforms, the correlation integral can be expressed as

$$C(q, k) = \frac{1}{2q^2} \int \frac{d\mathbf{p}}{(2\pi)^3} h(p) \left[\frac{k^2q^2 + (q^2 - \mathbf{p} \cdot \mathbf{q})^2}{|\mathbf{q} - \mathbf{p}|^2 - k^2 + i\eta} - \frac{q^2}{3} \right] \tag{29}$$

where the complex wavevector $\mathbf{q} = \tilde{n}\mathbf{k}$ is directed along z. Eq. (27), with the definition (29), implicitly relates the complex refraction index $\tilde{n}$ to the microscopic (complex) polarizability $\tilde{\alpha}$ in a correlated fluid of number density ρ. To *second* order in the scaled polarizability, the correlation integral (29) can be evaluated at $\mathbf{q} = \mathbf{k}$. In this case, Equation (27) explicitly provides $\tilde{n}$ as a function of $\tilde{\alpha}$ with the result:

$$\tilde{n}^2 = 1 + \frac{4\pi\tilde{\alpha}\rho}{1 - 4\pi\tilde{\alpha}\rho \left[\frac{1}{3} + C(k, k) \right]} \tag{30}$$

which reduces to (24) for $C = 0$ and represents an approximate, non perturbative expression of the complex refractive index of a correlated medium. Expanding again to second order, we obtain the exact lowest order correction to the refractive index in a correlated fluid:

$$\tilde{n} = 1 + 2\pi\tilde{\alpha}\rho + \frac{2}{3}(\pi\tilde{\alpha}\rho)^2 + 8(\pi\tilde{\alpha}\rho)^2 C. \tag{31}$$

Recalling that $\tilde{\alpha}\rho = \alpha_d \rho_d$, we point out that this expansion can be regarded as valid at second order in α_d with *no restriction* on the value of the scaled density ρ_d (namely, it is not a low-density expansion). The formal expressions of the real and imaginary part of C read:

$$\text{Im}\, C = \frac{1}{16\pi k^3} \int_0^{2k} dp\, ph(p) \left[2k^4 - k^2 p^2 + \frac{p^4}{4} \right] \tag{32}$$

$$\text{Re}\, C = \frac{1}{16\pi^2 k^3} \int_0^\infty dp\, ph(p) \left[\frac{8}{3} k^3 p - kp^3 + \left(2k^4 - k^2 p^2 + \frac{p^4}{4} \right) \ln \frac{p + 2k}{|p - 2k|} \right]$$

Here and in the following we drop the momentum dependence of the correlation integral, setting $C = C(k, k)$. To this order of approximation, both the refractive index $\tilde{n}$ and the

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forward scattering amplitude $S(0)$ acquire an *additive* contribution due to correlations:

$$\begin{cases} \delta S(0) = -i\tilde{\alpha}^2 k^3 V C \\ \delta\tilde{n} = 2\pi\tilde{\alpha}^2 C \end{cases} \tag{33}$$

where V is the volume of the sample. Notably, if we define an excess scattering amplitude *per particle*, $\delta s(0) = \delta S(0)/N$, so that $s(0) = s_0(0) + \delta s(0)$, Eq. (4) remains then formally valid, although of course the effective forward scattering amplitude $s(0)$ actually depends on ρ and on the specific structure of the medium via the correlation integral C.

It is useful to point out that the correlation contribution to the imaginary part n' of the refractive index in Eq. (32) depends *only* on those values of p that are smaller than the maximum wave-vector $2k$ (corresponding to a scattering angle $\theta = \pi$) falling within the experimentally detectable range. Although this is seemingly not the case for $\mathrm{Re}\,C$, we shall see in Section IV E that the actual occurrence or not of a peak of the structure factor $S(q)$ within the accessible range $q \leq 2k$ *does* appreciably influence the value of the refractive index n. Notice also that Eq. (31) provides a quantitative explanation of the reason why the Lorentz-Lorenz expression for the refractive index of a *molecular* fluid is often a very good approximation, even in the presence of consistent correlations. For $k\xi \ll 1$, where ξ is the correlation length defined as the distance where $h(r)$ becomes negligible,[35] the correlation coefficient C is indeed easily found to behave as $(k\xi)^2 \sim (\xi/\lambda)^2$. Then, provided that ξ is of the order of the molecular size (which is usually the case, unless the system is close to a critical point), correlation corrections are small.

Expression (33) can be readily shown to be fully consistent with the Optical Theorem. We first evaluate the real part of Eq. (33) through Eq. (32), retaining the correlation contribution and radiation-reaction effects:

$$\mathrm{Re}[S(0)] = N\,\alpha^2 \left\{ \frac{2}{3}k^6 + \frac{\rho}{4} \int_0^{2k} \mathrm{d}q\, qh(q) \left[2k^4 - k^2q^2 + \frac{q^4}{4} \right] \right\} \tag{34}$$

where the first term comes from radiation reaction in the first order contribution, while the second from Eq. (32). It is convenient to change the integration variable to $q = 2k\sin(\theta/2)$ with $\theta \in (0,\pi)$. Eq. (34) then becomes

$$\begin{aligned} \mathrm{Re}[S(0)] &= N\alpha^2 k^6 \left\{ \frac{2}{3} + \frac{\rho}{4} \int_0^{\pi} \mathrm{d}\theta\, \sin\theta(1 + \cos^2\theta)h(q) \right\} \\ &= N\frac{\alpha^2 k^6}{4} \int_0^{\pi} \mathrm{d}\theta\, \sin\theta(1 + \cos^2\theta)[1 + \rho\,h(q)] \end{aligned} \tag{35}$$

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Calling θ the scattering angle and φ is the angle between the scattering plane and the polarization vector, the differential cross section for Rayleigh scattering from a collection of dipoles is given by [7]:

$$\frac{d\sigma}{d\Omega} = N\alpha^2 \left(\frac{\omega}{c}\right)^4 (1 - \sin^2\theta \cos^2\varphi)\,[1 + \rho\, h(q)], \tag{36}$$

where $q = 2k\sin(\theta/2)$ and, for a harmonically bound oscillator of elementary charge e excited at a frequency ω much lower than its natural frequency ω_0, $\alpha = -e^2/(m\omega_0^2)$. Putting again $s(0) = S(0)/N$, we immediately verify via an integration of Eq. (36) on the solid angle $d\Omega = \sin\theta\, d\theta\, d\varphi$, namely, by averaging over all possible orientations of the incident field with respect to the scattering plane, that Eq. (3) is satisfied by our final expression (35).

IV.   COLLOIDAL SUSPENSIONS

Up to now we considered just point-like polarizable particles, i.e. particles whose size is much smaller than the wavelength of the incident field. However, if we are interested in colloidal suspensions, we have to deal with polarizable spheres whose size may be comparable to or even larger than the optical wavelength. To this aim, we model each particle p as a homogeneous dielectric sphere of radius a made of M polarizable molecules. On a microscopic scale, the system is again described by a collection of point-like dipoles, whose spatial distribution clusters however into spherical units centered around the position of the center of mass of each single colloidal particle. The derivation of the previous Sections is therefore still valid, provided the polarizability α is the microscopic polarizability of each molecule, the density ρ is the number density of molecules, related to the colloidal particle density ρ_p by $\rho_p = \rho/M$ and the distribution function $h(r)$ has a non-trivial structure, appropriate for the underlying "cluster fluid".

Let us consider a collection of N spherical particles, characterized by a normalized probability distribution $P_p(\mathbf{R}_1 \cdots \mathbf{R}_N)$. Each polarizable molecule is identified by its position $\mathbf{r}_m^l$, where $l = 1 \cdots N$ labels the colloid and $m = 1 \cdots M$ the specific molecule in the colloid. If the molecules are homogeneously distributed inside each sphere in an uncorrelated way, their probability density in space is given by:

$$P(\{\mathbf{r}_m^l\}) = \int d\mathbf{R}_1 \cdots d\mathbf{R}_N\, P_p(\mathbf{R}_1 \cdots \mathbf{R}_N) \prod_{l,m} \frac{\theta\left(a - |\mathbf{r}_m^l - \mathbf{R}_l|\right)}{v} \tag{37}$$

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where $\theta(x)$ is the Heaviside step function and $v = (4\pi/3)a^3$ is the particle volume. The molecular distribution enters our expressions through the correlation integral Eq. (28) where we used the standard definition of radial distribution function:[18]

$$\rho^2\, g(\mathbf{R} - \mathbf{R}') = \left\langle \sum_{i \neq j} \delta(\mathbf{R} - \mathbf{R}_i)\, \delta(\mathbf{R}' - \mathbf{R}_j) \right\rangle \tag{38}$$

Now, this expression must be generalized to:

$$\rho^2\, g(\mathbf{r} - \mathbf{r}') = \left\langle \sum_{(l,m) \neq (l',m')} \delta(\mathbf{r} - \mathbf{r}_m^l)\, \delta(\mathbf{r}' - \mathbf{r}_{m'}^{l'}) \right\rangle \tag{39}$$

where the average is taken according to the probability distribution (37). In performing the average, we must consider two possibilities in the summation over particle pairs:

- $l = l'$ (and then $m \neq m'$). These terms take into account spatial correlations among molecules inside the same sphere, induced by their confinement. The resulting contribution to $\rho^2 g(\mathbf{r} - \mathbf{r}')$ is:

$$\rho\, M\, \frac{1}{v^2} \int d\mathbf{R}\, \theta\left(a - |\mathbf{r} - \mathbf{R}|\right) \theta\left(a - |\mathbf{r}' - \mathbf{R}|\right) \tag{40}$$

  The convolution integral is easily performed in Fourier space by introducing the form factor

$$F(q) = \frac{1}{v} \int d\mathbf{R}\, \theta\left(a - r\right) e^{i\mathbf{q}\cdot\mathbf{R}} = \frac{j_1(qa)}{qa}, \tag{41}$$

  where

$$j_1(x) = 3\, \frac{\sin x - x \cos x}{x^3}$$

  is the 1st order spherical Bessel function of the first kind.

- $l \neq l'$. This term takes into account the correlations between molecules belonging to different colloids. The resulting contribution is:

$$\rho^2\, \frac{1}{v^2} \int d\mathbf{R} d\mathbf{R}'\, g_p(\mathbf{R} - \mathbf{R}')\, \theta\left(a - |\mathbf{r} - \mathbf{R}|\right) \theta\left(a - |\mathbf{r}' - \mathbf{R}'|\right) \tag{42}$$

  where $g_p(r)$ is the distribution function of the colloidal particles.

In summary, our final expressions for the correlation contribution to the refractive index (32) are still valid with the substitution

$$\rho^2\, h(q) \to M^2\, \rho_p\, F(q)^2\, \left[1 + \rho_p\, h_p(q)\right]. \tag{43}$$

We note two main differences with respect to the previous expressions: *i*) the presence of the form factor $F(q)^2$ and *ii*) the additive contribution (the unity in the square bracket). The latter takes care of the scattering from pairs of molecules inside the same colloid, which in turns provides the second order contribution in the Mie scattering of each colloidal particle. [36] It is also important to notice that we have in this case an *intrinsic* structural length scale, given by the particle size a. It is then suitable to perform the expansion in terms of the particle polarization per unit volume $\alpha_p = M\alpha/v$, a dimensionless quantity that plays the same role as α_d for point-like dipoles. Substituting (43) into the correlation integral (28), we find at 2nd order in α_p:

$$\tilde{n} = 1 + 2\pi\phi\,\alpha_p + 2\pi\left(\frac{\pi}{3}\phi^2 + \widetilde{C}\phi\right)\alpha_p^2 \tag{44}$$

where we have defined a dimensionless complex *correlation factor* $\widetilde{C} = C_r + \mathrm{i}C_i$, with:

$$C_r = \frac{v}{4\pi k^3}\int_0^\infty \mathrm{d}q\,qF^2(q)\left[1 + \rho_p h(q)\right]\left[\frac{8}{3}k^3q - kq^3 + \left(2k^4 - k^2q^2 + \frac{q^4}{4}\right)\ln\frac{q+2k}{|q-2k|}\right]$$

$$C_i = \frac{v}{4k^3}\int_0^{2k}\mathrm{d}q\,qF^2(q)\left[1 + \rho_p h_p(q)\right]\left[2k^4 - k^2q^2 + \frac{q^4}{4}\right]. \tag{45}$$

We stress again that Eq. (44) is valid, at second order in α_p/v, for *any* value of ϕ.

For the real part n of the refractive index and the extinction coefficient $\gamma = 2kn'$, which are the experimentally observed quantities, Eq. (44) yields:

$$\begin{cases} n = 1 + 2\pi\phi\,\alpha_p + 2\pi\left(\frac{\pi}{3}\phi^2 + C_r\phi\right)\alpha_p^2 \\ \gamma = 4\pi k\phi C_i\,\alpha_p^2 \end{cases} \tag{46}$$

For an easier comparison with the experimental data, and to check for consistency in the absence of interparticle interactions with the continuum Mie theory, it is useful to introduce the index of refraction n_p of the material constituting the colloidal particle. Expanding the CM equation inside the particle at second order in the refractive index contrast $\Delta n_p = n_p - 1$, the particle polarizability per unit volume is easily found to be given by

$$\alpha_p = \frac{1}{4\pi}\left[2\Delta n_p - \frac{(\Delta n_p)^2}{3}\right]. \tag{47}$$

Retaining for consistency only terms to order $(\Delta n_p)^2$, Eq. (46) becomes:

$$\begin{cases} n = 1 + \phi\,\Delta n_p + \left[\frac{\phi - 1}{3} + \frac{C_r}{\pi}\right]\frac{\phi}{2}(\Delta n_p)^2 \\ \gamma = \frac{k\phi}{\pi}C_i\,(\Delta n_p)^2 = \frac{2\phi}{\lambda}C_i\,(\Delta n_p)^2 \end{cases} \tag{48}$$

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Notice that for $C_r = 0$ the refractive index is given by:

$$n = 1 + \left(1 - \frac{\Delta n_p}{6}\right) \Delta n_p \phi + \mathcal{O}(\phi^2) \tag{49}$$

which therefore differs at *first* order in ϕ, even in the absence of both intra- and inter-particle correlations, from the simple expression $n = 1 + \Delta n_p \phi$, obtained by volume-averaging the refractive indices of particle and solvent (which is conversely correct for polarizabilities).

For what follows, it is also useful to introduce, as customary in light scattering theory, an "efficiency factor" Q_{ext}, defined as the ratio of σ_{ext} to the total geometric cross–section $N\pi a^2$ of the particles. Taking into account the definition of γ in (5), we have:

$$Q_{ext} = \frac{\sigma_{ext}}{N\pi a^2} = \frac{4a}{3\phi}\gamma, \tag{50}$$

so that, from the second of (48):

$$Q_{ext} = \frac{\sigma_{ext}}{N\pi a^2} = \frac{4ka}{3\pi} C_i (\Delta n_p)^2. \tag{51}$$

A.   Non-interacting particle limit and comparison with Mie theory

We first examine the limit, denoted by the superscript "0", in which inter-particle correlations can be neglected, that is obtained by setting $h(q) \equiv 0$ in Eq. (45):

$$\begin{cases} C_r^0 = \dfrac{1}{3x^3} \displaystyle\int_0^\infty dy\, yF^2(y) \left[\dfrac{8}{3}x^3 y - xy^3 + \left(2x^4 - x^2y^2 + \dfrac{y^4}{4}\right) \ln \dfrac{y + 2x}{|y - 2x|}\right] \\ C_i^0 = \dfrac{\pi}{3x^3} \displaystyle\int_0^{2x} dy\, yF^2(y) \left[2x^4 - x^2y^2 + \dfrac{y^4}{4}\right], \end{cases} \tag{52}$$

where $x = ka$ and $y = qa$. This single-particle approximation will be compared to the Mie solution, expanded at 2nd order in Δn_p. It is worth considering the cases of particles much smaller or much larger than the wavelength separately.

a.   Small particles ($x \ll 1$)   In the limit $x \to 0$, the real and imaginary parts of the correlation factor in (52) are easily found to be:

$$\begin{cases} C_r^0 \underset{x\to 0}{\longrightarrow} \dfrac{88\pi}{75} x^2 \\ C_i^0 \underset{x\to 0}{\longrightarrow} \dfrac{8\pi}{9} x^3 \end{cases} \tag{53}$$

Substituting in Eq. (48, 51), we find the limiting behaviour:

$$
\begin{cases}
n^0 \xrightarrow[x \to 0]{} 1 + \phi\, \Delta n_p - \dfrac{(\Delta n_p)^2}{6}\, \phi(1 - \phi) + \dfrac{44}{75}(\Delta n_p)^2 \phi\, x^2 \\
\gamma^0 \xrightarrow[x \to 0]{} \dfrac{8}{9}\, k x^3 \phi\, (\Delta n_p)^2 \\
Q^0_{ext} \xrightarrow[x \to 0]{} \dfrac{32}{27}\, x^4\, (\Delta n_p)^2
\end{cases}
\tag{54}
$$

where in the first equation we have also retained the lowest-order dependence on x, for later convenience. Reassuringly, Q^0_{ext} coincides with the efficiency factor for Rayleigh scatterers, namely, for particles much smaller than the wavelength.[13] It is also very interesting to notice that, using Eq. (4) the real part of the scattering amplitude can be written

$$
\mathrm{Re}\, s^0(0) = \frac{8}{27}(\Delta n_p)^2 x^6 = (2/3)\,(v\alpha_p)^2\, k^6,
\tag{55}
$$

which, comparing with Eq. (26), is identical to the radiation reaction contribution from a single, *point-like* dipole of polarizability $v\alpha_p$. This result is equivalent to the brilliant conclusion reached by Lorentz: the radiation reaction from a spherical radiator with fixed polarizability does not depend on its size, provided that the latter is much smaller than the wavelength. It also clarifies, however, a subtle feature of the general results obtained in the former Section. In deriving Eq. (44), we have actually disregarded the radiation reaction term of each polarizable molecule because, due to the presence of the dimensionless factor $\alpha k^3 \ll 1$ in Eq. (14), this gives a negligible contribution to the scattering of the whole colloidal particle. Surprisingly, therefore, while the extinction from a distribution of uncorrelated point-like dipoles is *solely* due to radiation reaction, when the same dipoles "cluster" into uniform spherical particles this contribution becomes vanishingly small. The microscopic approach we followed shows that it is again multiple scattering (in the generalized sense stated in Section I) that, due to internal correlations, generates a "collective" radiation reaction effect, leading to finite extinction.

    b.   Large particles ($x \gg 1$).   In the opposite case $x \to \infty$, the real and imaginary part of the correlation factor in Eq. (52) can be readily evaluated at leading order in x in terms of simple integrals of $j_1(y)$ with the result:

$$
\begin{cases}
C^0_r \xrightarrow[x \to \infty]{} \dfrac{7\pi}{3} \\
C^0_i \xrightarrow[x \to \infty]{} \dfrac{3\pi}{2}\, x
\end{cases}
\tag{56}
$$

which, using Eq. (48), yields

$$
\begin{cases}
n^0 \xrightarrow[x\to\infty]{} 1 + \phi\Delta n_p + \phi\left(1 + \dfrac{\phi}{6}\right)(\Delta n_p)^2 \\[3mm]
\gamma^0 \xrightarrow[x\to\infty]{} \dfrac{3\phi}{2a}\,x^2(\Delta n_p)^2 = 2\pi\rho a^4 k^2(\Delta n_p)^2 \\[3mm]
Q^0_{ext} \xrightarrow[x\to\infty]{} 2x^2(\Delta n_p)^2
\end{cases}
\tag{57}
$$

The expression for γ^0 and Q^0_{ext} in (57) are however quite suspicious: in fact, they highlight a severe limit in the quadratic expansion we use. Indeed, from (57) Q^0_{ext} grows without limits with x, whereas in Mie theory $Q^0_{ext} \xrightarrow[x\to\infty]{} 2$, whatever the value (even complex) of the particle refractive index.[37] Actually, the efficiency factor in (57) coincides with the value obtained in the Rayleigh–Gans (RG) approximation of the exact Mie solution, which requires both Δn_p *and* the maximum phase delay $\delta = 2x\Delta n_p$ that the incident field undergoes in traversing the particle to be small.[13] The second condition, in particular, is equivalent to assume that the incident radiation on each volume element of the particle coincides with the external field. In our description, this means that, for $\delta \ll 1$, internal multiple scattering contributions are negligible, so that intra-particle correlations are only related to the geometrical arrangement of the elementary scatterers expressed by the form factor. Moreover, since for large particles $Q^0_{ext} \simeq \delta^2/2$, the RGD condition is met only when $Q^0_{ext} \ll 1$, namely, when the extinction cross-section is substantially smaller than the geometrical "shadow" of the particle.

As a matter of fact, in the double limit $x \to \infty$, $\Delta n_p \to 0$, made by keeping δ finite, known in the light scattering jargon as the "anomalous diffraction" limit, it is possible to find an *exact* solution for $s(0)$, given in our notation by (see Section 11.22 in van de Hulst[13]):

$$
s(0) = x^2\left(\frac{1}{2} + \mathrm{i}\,\frac{\mathrm{e}^{\mathrm{i}\delta}}{\delta} + \frac{1 - \mathrm{e}^{\mathrm{i}\delta}}{\delta^2}\right),
\tag{58}
$$

which yields, for the efficiency factor:

$$
Q^0_{ext}(\delta) = \frac{4}{x^2}\,\mathrm{Re}\,s(0) = 2 - \frac{4}{\delta}\sin(\delta) + \frac{4}{\delta^2}(1 - \cos\delta),
\tag{59}
$$

Whereas $Q^0_{ext}(\delta) \xrightarrow[\delta\to0]{} \delta^2/2$, for $\delta \gg 1$ the scattering cross section per particle $\pi a^2 Q^0_{ext}$ correctly converges to twice the geometrical shadow. This finite limiting value, which does *not* depend on Δn_p[38] and corresponds to the limit of diffraction optics, can be recovered only by resumming *all* orders in Δn_p, however small they are, and is therefore missing in our analysis. Technically, this is due to the fact that the Mie solution, expressed as a

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series depending on the two parameters n_p and x, is not absolutely convergent, therefore, exchanging the limits $x \to \infty$ and $n_p \to 1$ is therefore not permitted.
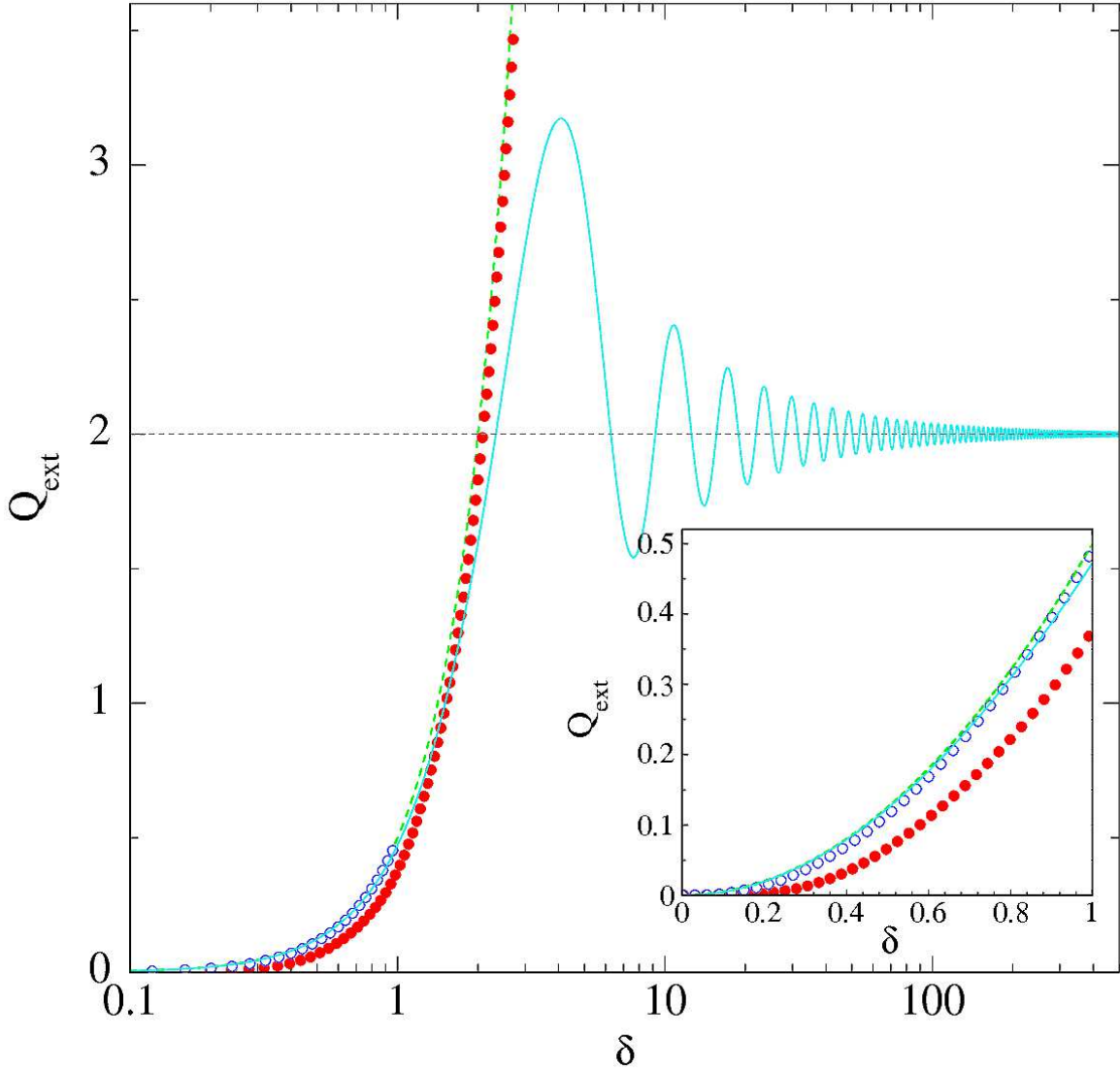

FIG. 1: Comparison between of the efficiency factor Q_{ext}^0 obtained from Eq. (59) (full line), and the 2nd order approximation in Δn_p from Eq. (51, for $\Delta n_p = 0.05$ (open dots) and $\Delta n_p = 0.2$ (full dots). The broken line shows the Rayleigh–Gans approximation $Q_{ext}^0 = \delta^2/2$. The region with $\delta \leq 1$ is expanded in the inset.

The efficiency factor obtained from Eq. (59), whose complex oscillating behavior can be regarded as the effect of the interference between the transmitted and the diffracted fields, is contrasted in Fig. 1 with the full numerical solution of Eq. (51) in the absence of inter-particle correlations, $Q_{ext}^0 = (2\Delta n_p/3\pi) \, C_i^0 \, \delta$. The plot shows that, for $\Delta n_p = 0.05$, the latter is very

close to the RG limit given by Eq. (57). As shown in the inset, the range of validity of our 2nd order approximation shows extends up to values of $\delta \simeq 1$ or, equivalently, for values of the efficiency factor $Q_{ext}^0 \lesssim 0.5$. Notice, however, that for the larger value $\Delta n_p = 0.2$, included for later convenience, differences are more marked.

Luckily, the evaluation of *dispersion* effects does not arguably suffer from this limitation. Indeed, the expression refractive index in (57) does *not* depend on the particle size, and should give the correct limiting behavior for $x \rightarrow \infty$ (at 2nd order in Δn_p). This is also suggested from the limiting behavior of the refractive index obtained from (58) using Eq. (4):

$$n = 1 + \phi \Delta n_p - (2/5)\, x^2 (\Delta n_p)^3 + \mathcal{O}(\Delta n_p^5),$$

which does not contain terms in $(\Delta n_p)^2$, and depends on particle size only at order $(\Delta n_p)^3$ and higher. Trusting this ansatz, in what follows we shall mainly focus on the effect of interparticle interactions on the refractive index of the suspension, limiting the discussion of extinction properties to dispersions of particles with a size $a \lesssim \lambda/(4\pi \Delta n_p)$.

B.   Refractive index of interacting colloids: an exact limit

For small particles, including interparticle interactions does not substantially modify the behavior of the refractive index given by Eq. (54), since the real part of the correlation factor is still found to be proportional to x^2. Yet, C_r specifically depends on the nature of interparticle forces: the case of hard-sphere suspensions will be discussed in Section IV E.

Remarkably, however, in the opposite limit of $ka \rightarrow \infty$ the real part of the correlation integral can be analytically evaluated at *any* particle volume fraction. In fact, in this limit Eq. (45) becomes

$$C_r = \frac{7v}{6\pi} \int_0^\infty dq\, q^2 F(q)^2 \left[1 + \rho_p h(q)\right] \tag{60}$$

which, by use of the convolution theorem can be written as

$$C_r = \frac{7\pi}{3v} \int d\mathbf{r} \int d\mathbf{r}'\, \theta(r-a)\,\theta(r'-a)\left[\delta(\mathbf{r}-\mathbf{r}') + \rho_p\, h(\mathbf{r}-\mathbf{r}')\right] \tag{61}$$

where use has been made of the definition of the form factor $F(q)$ in (41). The domain limitation induced by the presence of the θ function, implies that $|\mathbf{r}-\mathbf{r}'| < 2a$ and therefore $h(\mathbf{r}-\mathbf{r}') = -1$ in the whole integration domain for colloids provided of a hard core

contribution. This immediately yields:

$$C_r = \frac{7\pi}{3}(1 - \phi) = (1 - \phi)C_r^0 \tag{62}$$

When this result is substituted in the general expression (48) for the real part of the refractive index, we obtain the *exact* limit of n for $ka \to \infty$ to second order in the particle polarizability:

$$n = 1 + \phi\Delta n_p + \phi(1 - \phi)(\Delta n_p)^2 \tag{63}$$

Note that this asymptotic result is valid for *any* specific form of the interparticle interactions, provided the latter contain a hard core contribution.

C.   Inclusion of the solvent

The former results have been obtained for particles suspended in a vacuum. Nevertheless, once the refractive index has been expressed in terms of continuum electrodynamics quantities such as n_p, inclusion of the effects of a solvent, acting as a homogeneous, non-absorbing medium of refractive index n_s, is straightforward. Eq. (54) and (63) retain indeed their validity provided that we simply make the substitutions $n \to n/n_s$, $n_p \to n_p/n_s$. Besides, in the presence of the solvent the incident wave-vector should be written as $k = 2\pi n_s/\lambda$. Putting $\Delta n_{ps} = n_p - n_s$, the general expression for the complex refractive index in Eq. (48) becomes:

$$\frac{\tilde{n}}{n_s} = 1 + \phi\frac{\Delta n_{ps}}{n_s} + \frac{\phi}{2}\left[\frac{\phi - 1}{3} + \frac{\tilde{C}}{\pi}\right]\left(\frac{\Delta n_{ps}}{n_s}\right)^2. \tag{64}$$

Note that Eq. (64) is a 2nd order expansion in $\Delta n_{ps}/n_s$, which does not require $n_p - 1 \ll 1$ and $n_s - 1 \ll 1$ separately. In the limits $ka = 0$ and $ka \to \infty$ we have therefore:

$$n = n_s + \phi\Delta n_{ps} - \frac{\phi(1 - \phi)}{6n_s}(\Delta n_{ps})^2 \quad (ka = 0) \tag{65}$$

$$n = n_s + \phi\Delta n_{ps} + \frac{\phi(1 - \phi)}{n_s}(\Delta n_{ps})^2 \quad (ka \to \infty) \tag{66}$$

A note of caution is however appropriate, since the continuum electrodynamics approach fully neglects fluctuations. It is then worth wondering whether this simple way to account for the presence of the solvent holds true also in the presence of correlations, by considering again the problem in a microscopic perspective. This is done in Appendix IV C, where we explicitly show that Eq. 65 is rigorously true only provided that the solvent is regarded as a uniform, uncorrelated dielectric medium.

D. Effective medium approach

A colloidal suspension of particles at volume fraction ϕ in a solvent at volume fraction $1 - \phi$ is actually a composite medium. It is then useful to try and frame our results within the problem of "homogenization" of a heterogeneous medium, which basically consists in mapping the latter into a homogeneous structure by defining "effective", global material properties.[19] For what follows it is useful to point out that most of the approaches has addressed the case where these material properties are response functions to an external field which is uniform, or slowly-varying over the length scales that characterize the microscopic structure of the heterogeneous medium. This is the case of the static dielectric constant, but also of several other physical quantities such as the thermal and low-frequency electric conductivities, or even of mechanical quantities such as the elastic stress tensor.

In the case of a very dilute suspension of spherical particles in a solvent, the problem is conceptually analogous to the discussion of a system of uncorrelated point dipoles made in Section II, provided that each particle is attributed a polarizability per unit volume $\alpha_p = (\epsilon_p - \epsilon_s)/(\epsilon_p + 2\epsilon_s)$. It is therefore not surprising that Maxwell, who first explicitly tackled this problem,[39] obtained a result that can be written, for the case of the effective dielectric constant ϵ^* we are discussing

$$\frac{\epsilon^*}{\epsilon_s} = \frac{1 + 2\beta\phi}{1 - \beta\phi}, \tag{67}$$

where $\beta = (\epsilon_p - \epsilon_s)/(\epsilon_p + 2\epsilon_s)$, which is strictly related to the CM equation. [19] As Maxwell already pointed out, however, Eq. (67) is valid only at first order in ϕ, hence it should consistently be written:

$$\frac{\epsilon^*}{\epsilon_s} = 1 + 3\frac{\epsilon_p - \epsilon_s}{\epsilon_p + 2\epsilon_s}\phi + \mathrm{o}(\phi), \tag{68}$$

A straightforward way to prove (68) consists in noticing that, from the definition of the effective dielectric constant and indicating with $\mathbf{E}_0$ an external uniform field, we must have[20]

$$(\epsilon^* - \epsilon_s)\mathbf{E}_0 = \frac{1}{V}\int_V d\mathbf{r}\,[\mathbf{D}(\mathbf{r}) - \epsilon_s\mathbf{E}(\mathbf{r})] = \rho_p \int_v d\mathbf{r}\,(\epsilon_p - \epsilon_s)\,\mathbf{E}(\mathbf{r}),$$

where $\mathbf{E}(\mathbf{r})$ and $\mathbf{D}(\mathbf{r})$ are the local, fluctuating electric and displacement fields, V is sample volume, and the last equality is because the averaged quantity differs from zero only within particle volume v. Then, *if* we assume that the field incident on particles coincides with the external field (namely, if we neglect the additional contributions due to the other particles),

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the field inside a dielectric sphere is also uniform, and given by $\mathbf{E}(\mathbf{r}) \equiv [3\epsilon_s/(\epsilon_p + 2\epsilon_s)]\mathbf{E}_0$, wherefrom Eq. (68) immediately follows.

In the presence of correlations, expressions which are valid to higher order in ϕ can be found only for specific geometries, although rigorous upper and lower limits for ϵ^*, such as the Hashin-Shtrikman bonds, can be given.[19] A very interesting situation is however that of a "weakly inhomogeneous" medium, which for the present purposes we identify with a suspension of colloidal particles made of a material with dielectric constant ϵ_p, which does not differ too much from the dielectric constant ϵ_s of the suspending medium. Denoting by $\bar{\epsilon} = \phi\epsilon_p + (1-\phi)\epsilon_s$ the volume average of the dielectric constants (which is the expression at lowest order in $\Delta\epsilon_{ps} = \epsilon_p - \epsilon_s$ for the dielectric constant of the mixture), and by $\overline{(\delta\epsilon)^2} = \overline{\epsilon^2} - (\bar{\epsilon})^2 = \phi(1-\phi)(\Delta\epsilon_{ps})^2$ its mean square fluctuation, one finds, at second order in $\Delta\epsilon_{ps}$,[19–21]

$$\epsilon^* = \bar{\epsilon} - \frac{\overline{(\delta\epsilon)^2}}{3\bar{\epsilon}} = \bar{\epsilon} - \frac{\phi(1-\phi)}{3\bar{\epsilon}}(\Delta\epsilon_{ps})^2. \tag{69}$$

Notice that this expression, originally derived by Braun[21] using an approach closely resembling the one we used in Section II, is valid *whatever* the spatial correlations of the particles and, in particular, for any value of the particle volume fraction ϕ. Remarkably, Eq. (69) also coincides with the 2nd order expansion in $\Delta\epsilon_{ps}$ of Eq. (67), a result which has however been derived in the *uncorrelated*, single-particle limit $\phi \to 0$. This means that, at this order of approximation in $\Delta\epsilon_p$, the static dielectric constant is not affected by correlations.[40]

As we anticipated, however, Eq. (69) requires the applied electric field to be *slowly-varying* on the microscopic structural length scales of the suspension (the particle size, or in general the correlation length for interacting particles): it is then very useful to investigate whether Eq. (69) still holds at *optical* frequencies, namely, for the refractive index $n = \sqrt{\epsilon}$. This is readily found to be true in the limit $ka \to 0$, where, according to Eq. (53), C_r^0 vanishes as $(ka)^2$: it is indeed easy to show that Eq. (69), written in terms of the refractive indices $n_p = \sqrt{\epsilon_p}$, $n_s = \sqrt{\epsilon_s}$, and expanded at second order in Δn_{ps}, coincides with Eq. (65). Hence, at 2nd order in the polarizability difference, the refractive index of a suspension of particles small compared to the wavelength satisfies the Lorentz-Lorenz equation at *any* volume fraction. According to our results, this does not hold true for finite values of ka, where system-specific effects of the intra- and inter-particle correlations should be expected. Remarkably, however, a distinct limiting behavior, which is still independent from the nature

and strength of particle interactions (provided that the latter have a hard-core contribution) and valid for any volume fraction, is reached at large ka. Notice in particular that not only the amplitude, but also the *sign* of the quadratic correction in Eq. (66) differs from the CM expression. Eq. (66) is then a very general result for the effective refractive index of a weakly inhomogeneous 2-components medium that, at variance with Eq. (65), applies when the field varies on much shorter spatial scales than the microscopic correlation length of the system. The fact that is does not depend on the structural organization of the medium, but only on the volume fractions of the two components, suggests that is should also be obtained from phenomenological but more general arguments.

E. Correlation effects on the refractive index for hard spheres

For intermediate values of x, correlation effects on the refractive index become system-specific: it is particularly instructive to examine these effect for a fluid of monodisperse hard spheres of radius a. Consider first the single-particle (Mie) limit discussed in Section IV A, where only intra-particle correlations are taken into account. The inset A in Fig. 2 shows that, in agreement with Eq. (53) and (56), the real part C_r^0 of the correlation factor, which vanishes for $x \to 0$ (the "Clausius–Mossotti" limit), progressively grows with x, asymptotically approaching the value $C_r^0 = 7\pi/3$. As we already mentioned, even in the presence of inter-particle interactions C_r retains, for small values of ka, a quadratic behavior, $C_r = cx^2$. For hard spheres, Inset B shows that, to a good degree of approximation, the slope c decreases exponentially up to $\phi \simeq 0.4$, starting from the value $C_r^0 = 88\pi/75$ given by Eq. (53). The fractional contribution C_r/C_r^0 due to *inter*-particle correlation is conversely shown in the body of Fig. 2 as a function of the particle volume fraction, for several values of x. Starting from the limiting behavior shown in inset B (dotted line), C_r/C_r^0 is seen to rapidly approach, by increasing x, the asymptotic behavior $C_r/C_r^0 = 1 - \phi$ given by Eq. (62). For $x \gtrsim 5$, as a matter of fact, C_r is a remarkably linear function of particle volume fraction, showing that for large x only the Mie contribution and excluded volume effects are relevant. For $1.5 \lesssim x \lesssim 2$, however, the trend of C_r/C_r^0 versus ϕ is rather peculiar: for instance, the curve for $x = 1.6$, which at low ϕ lies below the curve for $x = 2.5$ as expected, crosses the latter at $\phi \simeq 0.3$, reaching a consistently higher value at the maximum packing fraction $\phi \simeq 0.5$ of the stable fluid phase.
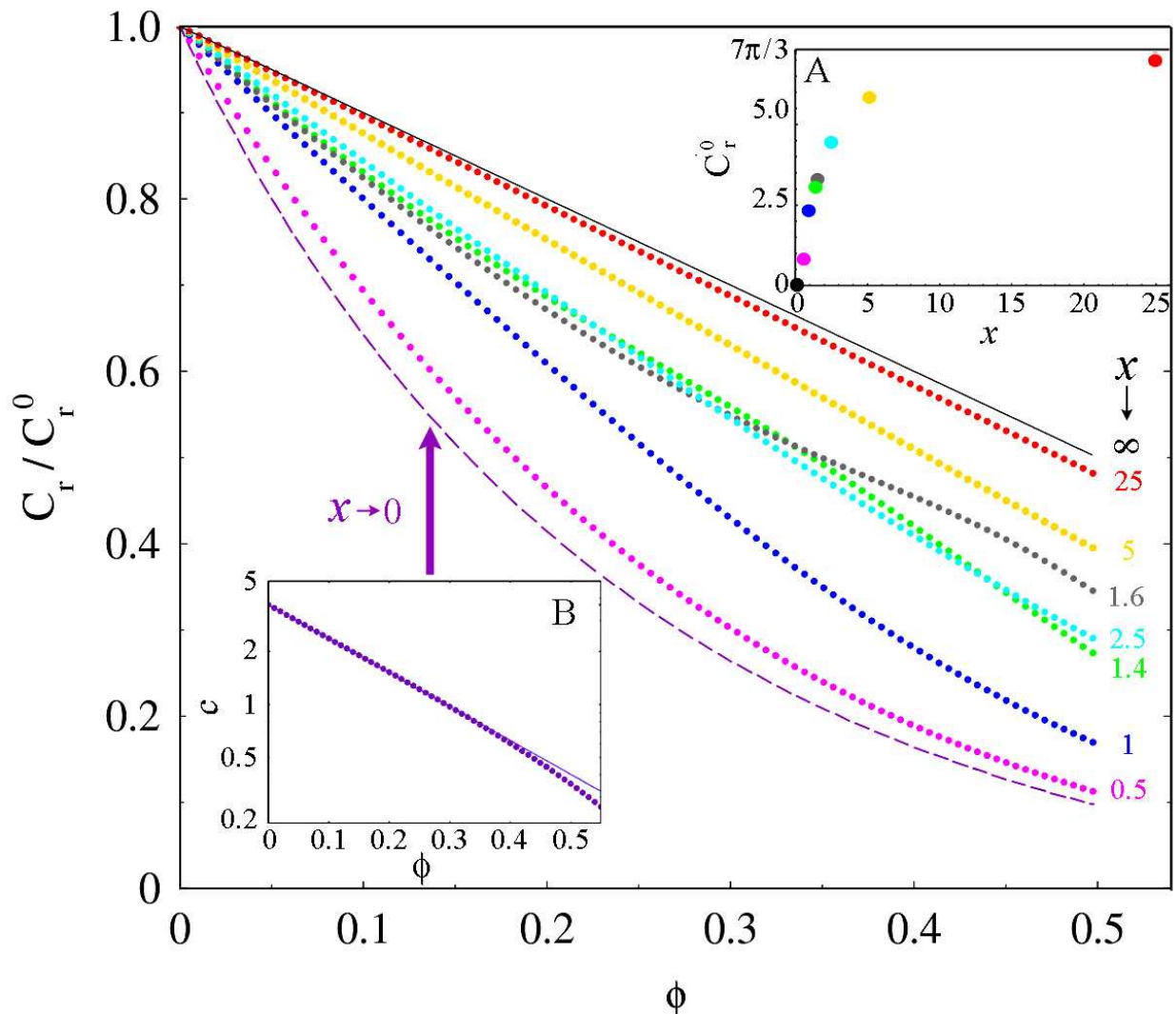
FIG. 2: Inset A: Single-particle (Mie) limit of the real part C_r^0 of the correlation factor of hard spheres for several values of $x = ka$. Body: Full correlation contribution C_r, scaled to C_r^0 and plotted as a function of ϕ for the same values of x. The full and dotted line respectively show the limiting behavior for $x \to \infty$ and $x \to 0$. Inset B: Slope of C_r versus x^2 in the limit $x \to 0$, plotted on a semi-log scale and fitted with a single exponential.

These distinctive structural effects are better investigated by considering a specific case, which also allows to inquire how consistent and experimentally detectable are correlation contributions to the refractive index. As a colloidal system of practical relevance, we focus on suspensions of monodisperse polystyrene (PS) latex particles ($n_p \simeq 1.59$) in water ($n_s \simeq$ 1.33). For this colloid, despite a substantial refractive index mismatch between particle and solvent, the terms we neglect should not be larger than 20% of the 2nd order term
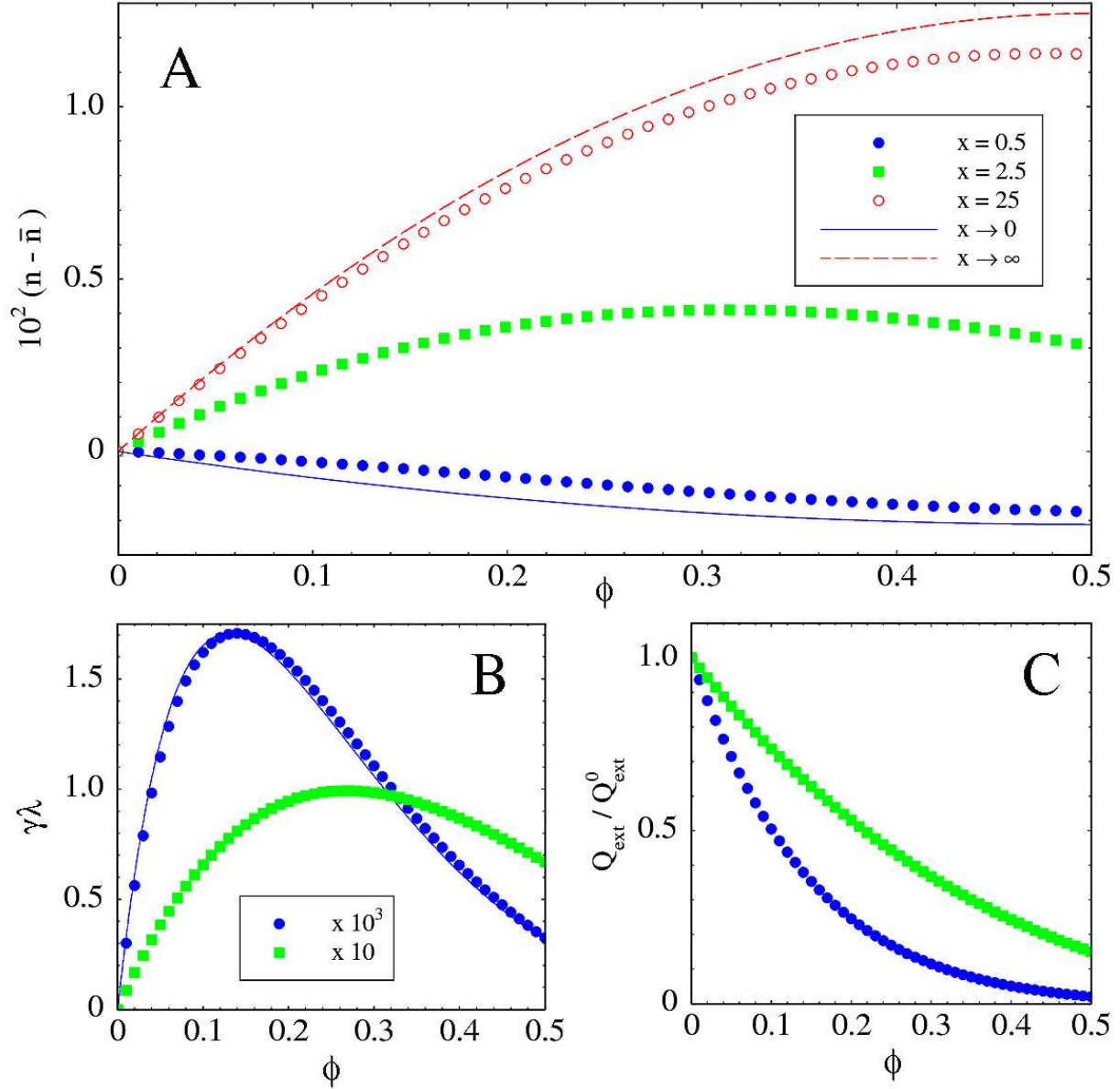
FIG. 3: Panel A: Excess correlation contribution $n - \overline{n}$, where $\overline{n} = n_s + \Delta n_{ps}\phi$, to the real part of the refractive index for suspensions of polystyrene particles ($n_p = 1.59$) in water ($n_s = 1.33$), corresponding to the values of x in the legend. The full and dashed lines respectively correspond to the limits $x \to 0$ in Eq. (65) and $x \to \infty$ in Eq. (66). The dependence on volume fraction of the dimensionless extinction coefficient, $\gamma\lambda$, and of the scattering efficiency scaled to the Mie value, Q_{ext}/Q_{ext}^0, are shown in Inset B and C, respectively.

in $\Delta n_{ps}/n_s$. Panel A in Fig. 3 shows that, for $x = 0.5$ ($a \simeq 0.06\lambda$), the difference $n - \bar{n}$ between the suspension refractive index and the value obtained by simply averaging over

volume fractions, $\bar{n} = n_s + \Delta n_{ps}\phi$, is pretty close to the quadratic term in Eq. (65), whereas for $x = 25$ ($a \simeq 3\lambda$) it already approaches the limiting expression given by Eq. (66). Panel A also shows that for $x = 2.5$ ($a \simeq 0.3\lambda$), a value sufficiently large for C_r/C_r^0 to show a linear trend in ϕ (see Fig. 2), $n - \bar{n}$ is a quadratic function of ϕ, as expected from Eq. (64).

For what concerns extinction, the value $x = 25$ ($\delta \simeq 10$) is far too large to be discussed within our approximation. Fig. 1 shows however, that this is still reasonably feasible for $x = 2.5$ ($\delta \simeq 1$), which can then be compared to the behavior for $x = 0.5$ ($\delta \simeq 0.2$), corresponding to particles which are much smaller than the wavelength. For particles of this size, the scattered intensity is basically independent from the scattering wave-vector q, and proportional to the product of the volume fraction times the osmotic compressibility of the suspension. Using the Carnahan-Starling equation of state for hard spheres,[22] both σ_{ext} and γ should then be proportional to

$$\phi \left(\frac{\partial \Pi}{\partial \phi} \right)^{-1} = \phi + \frac{2\phi^2(4 - \phi)}{(1 - \phi)^4} \tag{70}$$

Panel B in Fig. 3, where this functional behavior is compared to the dimensionless quantity $\gamma\lambda$, shows that this is indeed the case, to a good degree of approximation. Notice in particular that the extinction coefficient displays a strong maximum for a particle volume fraction which is very close to the known value $\phi \simeq 0.13$ where the scattering from small hard-spheres peaks. A similar non-monotonic trend is observed for $x = 2.5$ too, but the value where γ peaks is shifted to the consistently higher value $\phi \simeq 0.27$. As we shall shortly investigate in more detail, γ is eventually determined by the that part of the structure factor that is detected within the experimentally accessible q-range, and this strongly depends on particle size. The strong effect of interparticle interactions on extinction is better appreciated in Panel C, where we plot the volume fraction dependence of the ratio of the scattering efficiency Q_{ext} obtained form Eq. (51) to its value Q_{ext}^0 in the absence of inter-particle correlations. For both values of x, Q_{ext} strongly decreases with ϕ, reaching a value at $\phi = 0.5$ that is about seven times smaller than Q_{ext}^0 for $x = 2.5$, and as much as *fifty* times smaller for $x = 0.5$.

To highlight distinctive correlation effects, it is particularly useful to investigate the behavior of the refractive index for $\phi = 0.5$, which is the limiting volume fraction of a hard spheres fluid, as a function of the scaled particle size x. In Panel A of Fig. 4, the difference Δn between the refractive index n and its volume-average approximation $\bar{n} = n_s + \Delta n_{ps}$ is contrasted to the single-particle Mie limit $\Delta n = n^0 - \bar{n}$. For comparison,
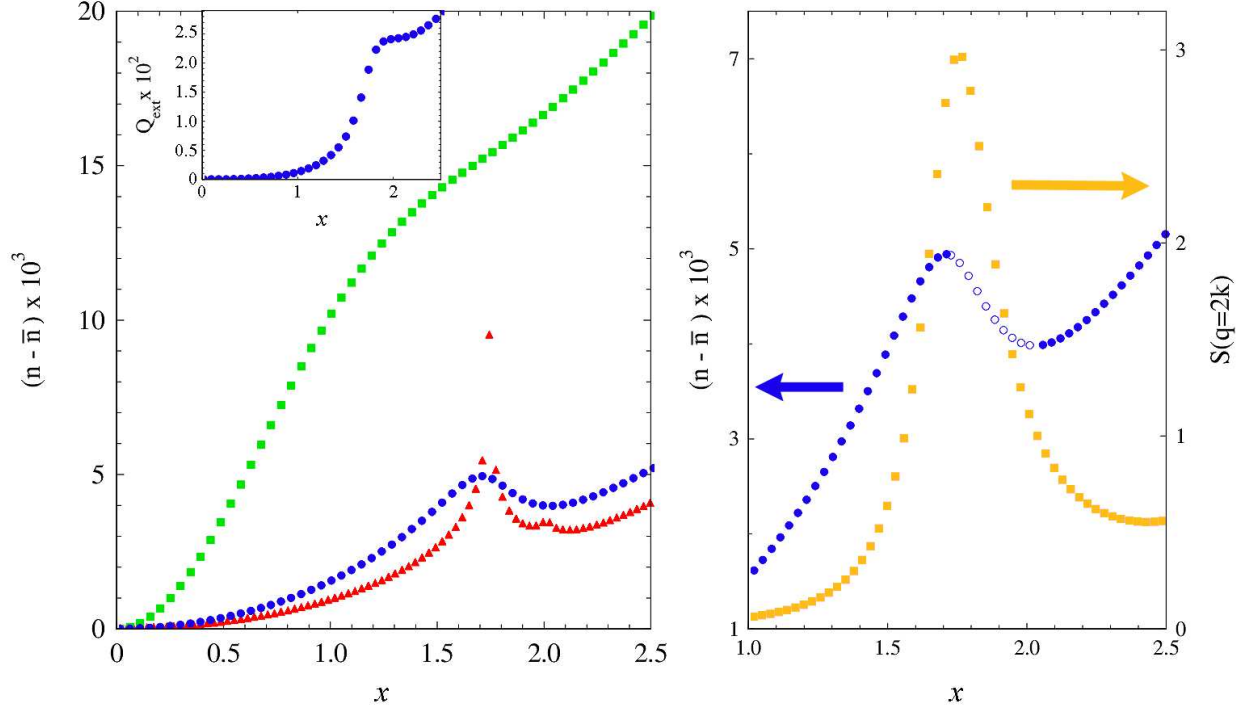
FIG. 4: Panel A: Refractive index increment $\Delta n = n - \bar{n}$ for a suspension of polystyrene particles at $\phi = 0.50$ (fluid phase, dots) and at $\phi = 0.55$ (FCC colloidal crystal, triangles), compared to the the values $\Delta n = n^0 - \bar{n}$ obtained by neglecting inter-particle structural correlation (Mie limit, squares). The scattering efficiency Q_{ext} is shown in the Inset. Panel B: Detailed behavior of Δn in the region $1 \leq x \leq 2.5$, compared to the behavior of the structure factor of the HS fluid, calculated using the Verlet–Weis approximation[18] and evaluated at the maximum experimentally detectable wave-vector $q = 2x/a = 4\pi n_s/\lambda$ (see text).

we also include the corresponding data for the face-centered-cubic crystal at $\phi = 0.55$ in equilibrium with the fluid phase. It is important to point out that the latter assumes orientation symmetry, and therefore corresponds to the data that would be obtained for a randomly-oriented polycrystalline sample. Several features of the plot are worth be pointed out. First, $n - \bar{n}$ is *substantially* smaller for both the fluid and colloidal crystal phase than in the non-interacting approximation. In particular, the quadratic increase of Δn_p at small x, expected from the discussion of C_r in Fig. 2, is more than one order of magnitude weaker than in the Mie case. The effect of repulsive HS interactions is even more dramatic on extinction: the Inset in Panel B shows indeed that, in the fluid phase (extinction in the crystal vanished, since it is assumed as ideal), the scattering efficiency is extremely small for

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$x \lesssim 1$, rising for $x \gtrsim 2$ to values which are still several times smaller than in the Mie theory. A very peculiar feature is finally the presence of a strong peak for the crystal phase, and of a less pronounced "bump" for the fluid phase, occurring in the region $1.5 \lesssim x \lesssim 2$ where we already pointed out a peculiar behavior of C_r (see Fig. 2). The origin of this rather surprising effect can be grasped by considering Panel B . There, together with an expanded view of the "bump" region, we plot the structure factor $S(q)$ for a HS fluid at $\phi = 0.50$, calculated at the wave-vector $q = 2k = 4\pi n_s/\lambda$ corresponding to the *backscattering* condition $\theta = \pi$. In other words, for a given experimental value x^*, fixed by both the particle size and the incident wavelength, only those wave-vectors q of the structure factor with $q \leq 2x^*/a$ fall within the detectable range and contribute to the scattering cross section. ¿From the plot, we clearly see that the refractive index increase is associated with (and actually slightly anticipates) the progressive "entrance" of the first peak of $S(q)$ in the detectable range. A further interesting observation comes from noticing that, for a fixed particle size, the curve is basically a plot of the refractive index versus the inverse of the incident wavelength. Then, the trailing part of the peak which follows the maximum, shown with open dots in Panel B, corresponds to a region where the refractive index increases with increasing λ, which is the hallmark of an *anomalous dispersion* region.[41] As a matter of fact, the overall trend strongly resembles the behavior of the refractive index $n(\omega)$ of a Lorentz oscillator close to its natural resonance frequency ω_0: n already shows an increase for $\omega < \omega_0$, followed by an anomalous dispersion region where $n(\omega)$ is a decreasing function of ω, and by a final recovery. No true absorption is however present in the problem we are considering. This finding seems to suggest that, besides in resonant absorption, anomalous dispersion may take place in the presence of any process in the medium, such as scattering, that lead to extinction of the incident field.

F.   Feasibility of the experimental determination of correlation effects

It is useful to inquire whether and how correlation effects on the refractive index can be experimentally investigated. In Panel A of Fig. 3 the correlation contribution to n reaches, for $x = 2.5$ and $\phi \gtrsim 0.3$, a value of about 4×10^{-3}, which is well within the accuracy of a good refractometer. However, Panel B shows that in these conditions extinction is quite large, giving an extinction length $\gamma^{-1} \simeq 10\lambda \simeq 30a$: investigations should then be

performed using method exploiting a low penetration depth (see below). Given the low extinction, correlation effects are arguably much easier to be detected in the very large ϕ limit discussed in Fig. 4, . For instance, for $x = 1$, where in fluid phase $Q_{ext} \simeq 10^{-3}$, corresponding to an extinction length still as large as about 300λ, the refractive indexes of both the fluid and the crystal phase already differ from the Mie prediction by about 10^{-2}, and of 6×10^{-4} between themselves.

Unfortunately, accurate data on the refractive index of dense colloids are scarse, and not very recent.[23, 24] Moreover, as common in light scattering practice, experiments mostly focused on measuring the refractive index increment $\mathrm{d}n/\mathrm{d}\phi$ (or, more usually $\mathrm{d}n/\mathrm{d}c$, where c is the concentration in mass/volume), which amounts to implicitly assume that n is linear in ϕ. However, at first order in ϕ, the correlation factor C_r reduces to the Mie limit C_r^0, and inter-particle correlations show up only at order ϕ^2. It is however worth mentioning a rather surprising result obtained long ago by Okubo,[25] which may be related to the results we discussed in Fig. 4. By measuring the refractive index of strongly deionized charged PS suspensions, Okubo observed indeed a substantial peak in the refractive index, located very close the transition between the fluid and the colloidal crystal phase. Unfortunately, this early investigation has not been further pursued, at least to our knowledge.

Modern approaches based on fiber optic sensing[26], or made in a total internal reflection configuration[27], should provide a sufficient accuracy to detect correlation effects even for strongly turbid samples. Yet, when using methods relying on so small penetration depths, care should be taken to avoid probing correlation effects on the particle distribution at the interface between the solution and the sensor wall, rather than bulk structural properties. An interesting alternative would be using a novel optical correlation method recently introduced by Potenza *et al.*,[28] which consists in measuring the 2-dimensional power spectrum $P(q_x, q_y)$ of the transmitted beam intensity distribution on a plane placed at close distance z from the sample. By means of the optical theorem, one finds for N identical scatterers:

$$P(q_x, q_y) = \frac{4\pi^2}{k^2}|Ns(0)|^2 \sin^2\left(\frac{q^2 z}{2k} - \varphi\right) \tag{71}$$

where $q^2 = q_x^2 + q_y^2$ and (in our notation) $\varphi = \arg[s(0)]$. Eq. (71) describes a fringe-like pattern characterized by a phase shift φ which is directly related to the ratio between the imaginary and the real part of the scattering amplitude. One of the major advantages of the method is that it can be applied to very turbid samples too, since multiple scattering

yields only a constant background that can be easily subtracted out. The technique has successfully been applied to investigate dilute colloidal suspension.[28] At sufficiently high ϕ, however, inter-particle correlation effects should yield noticeable deviations with respect to the Mie expression used to evaluate the fringe pattern.

V. CONCLUSIONS

In this article we have presented a general microscopic theory for the attenuation and the phase delay suffered by an optical plane wave that crosses a system of interacting colloidal particles, deriving an expression for the forward scattered wave, exact at second order in the molecular polarizability, which explicitly takes into account the interactions among all induced dipoles. Whereas previously available treatments have separately discussed either attenuation (neglecting corrections due to radiation reaction) or refractive index (using some variant of the Lorentz-Lorenz formula and ignoring interparticle correlations), our approach treats on an equal basis the real and the imaginary part of the refractive index. In detail:

- We have investigated the role of radiation reaction on light extinction, showing that the structural features of the suspension are encoded into the forward scattered field by multiple scattering effects, whose contribution is essential for the so-called "optical theorem" to hold in the presence of interparticle interactions. The local field acting on a specific dipole is the sum of the external field plus all the fields due to the presence of all the other oscillating dipoles within the scattering volume. Our treatment considers the average local field, which is polarized as the external field, while the fluctuations of the local field, not discussed here, give rise to what is usually called multiple scattering;

- In the case of negligible interparticle interactions, our results are found to be consistent, at second order in the polarizability, with the exact Mie theory for spherical particles;

- We have discussed our results in the framework of effective medium theories, presenting a general result for the effective refractive index valid, whatever the structural properties of the suspension, in the limit of a particle size much larger than the wavelength;

- In the case of correlated particles we found that significant corrections to the value of

the refractive index exist when the x parameter is of the order of one, that is, when the particle size is comparable to the wavelength of light;

- By treating concentrated hard-sphere suspensions, we have unraveled subtle anomalous dispersion effects for the suspension refractive index and we have discussed the feasibility of an experimental test of our calculations.

It is finally useful to point out that the general approach we have followed can in principle be extended to investigate other interesting physical problems. Strong analogies exist for instance between the scattering of (vector) electromagnetic and (scalar) ultrasonic waves from a particle dispersion. Although in the case of ultrasonic scattering no analogous of point-like dipoles exists, an approach formally identical to the Mie scattering theory can be developed, once the whole colloidal particle is assumed to be an elementary scatterer, responding to the incident acoustic field via its density and compressibility difference with the solvent.[29] An extension of the approach we developed for the refractive index might then provide an explicit expression for the dispersion of the sound speed in a correlated suspension. It is however worth pointing out that, in acoustic scattering, absorption effect are usually far from being negligible.

Similarly, finding the thermal conductivity of a suspension within an effective medium approach is formally analogous to evaluate its dielectric constant in the long-wavelength limit. In Section IV D we have shown that, for a weakly inhomogeneous medium, the static dielectric constant is not affected by correlation, and is always given by Eq. (69): the same result should then hold for the thermal conductivity. However, the case of a dispersion of correlated particles with a thermal conductivity much higher than the base fluid (metal nanoparticles, for instance) could still be investigated by a suitable extension of the general equations (27, 29), at least numerically. This may shed light on the highly debated problem of the so-called "anomalous" enhancement of thermal conductivity in nanofluids. [30]

Appendix A

For a homogeneous, uncorrelated mixture of point-like particles with polarizabilities α_1, α_2 and number densities ρ_1, ρ_2, a straightforward generalization of Eq. (16), applied to a

slab geometry for an incident field of the form (10), yields, at 2nd order in the polarizability:

$$n^d = 1 + 2\pi(\alpha_1 \rho_1 + \alpha_2 \rho_2) + \frac{2}{3}\pi^2(\alpha_1 \rho_1 + \alpha_2 \rho_2)^2, \tag{A1}$$

where the superscript "*d*" is to remind that Eq. (A1), which just states that in the absence of correlation the polarizability per unit volume of the mixture is additive, applies only to point-like dipoles. Let us now identify species 2 with molecules constituting the colloidal particle. When correlations are included, by generalizing the procedure discussed in Section IV, we obtain a general expression of the complex refractive index of colloidal particles embedded in a correlated fluid:

$$\begin{aligned}
\tilde{n} = 1 \ + \ & 2\pi(\alpha_1 \rho_1 + \alpha_p \phi) + \frac{2}{3}\pi^2(\alpha_1 \rho_1 + \alpha_p \phi)^2 \\
+ \ & 2\pi \left\{ \alpha_1^2 \rho_1^2 \, C[h_{11}(q)] + \alpha_p^2 \, \phi v C[F^2(q) S_{pp}(q)] + 2\alpha_1 \alpha_p \, \rho_1 \phi \, C[F(q) h_{1p}(q)] \right\}
\end{aligned} \tag{A2}$$

where we have defined a correlation functional $C[f(q)]$ that generalizes expression (29) to:

$$C[f(q)] = \frac{1}{4\pi^2 k^2} \int d\mathbf{q} \left[\frac{k^4 + (\mathbf{k} \cdot \mathbf{q})^2}{q^2 - k^2 + i\eta} - \frac{k^2}{3} \right] f(|\mathbf{k} - \mathbf{q}|) \tag{A3}$$

In the special limit where we identify type-1 particles with the molecules of the solvent, considered as an incompressible continuum, the number density of the solvent ρ_s in the *free* volume $V(1 - \phi)$ is related to ρ_1 by

$$\rho_s = \frac{\rho_1}{1 - \phi} \tag{A4}$$

and the correlation functions $h_{11}(q)$, and $h_{1p}(q)$ can be related to that of the colloidal particle $h_{pp}(q) \equiv h(q)$:

$$h_{11}(q) = \frac{\rho_p v^2}{(1 - \phi)^2} \, F^2(q)[1 + \rho_p \, h(q)] \tag{A5}$$

$$h_{1p}(q) = -\frac{v}{1 - \phi} \, F(q)[1 + \rho_p \, h(q)] \tag{A6}$$

When these expressions are inserted into Eq. (A2) we find

$$n = 1 + 2\pi \left[\alpha_s \rho_s(1 - \phi) + \alpha_p \, \phi\right] + \frac{2}{3} \pi^2 \left[\alpha_s \rho_s(1 - \phi) + \alpha_p \, \phi\right]^2. \tag{A7}$$

It is easy to show that this form is in fact fully equivalent to Eq. (64), when the latter is expanded to second order in $n_s - 1$ and $n_p - 1$.

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[32] The factor $k = 2\pi/\lambda$ introduced the denominator of Eq. (1) makes $S(\mathbf{k}_i, \mathbf{k}_s)$ dimensionless. By factoring out an imaginary unit, which is related to the Gouy phase shift accumulated in far-field between a spherical and a plane wave, the amplitude function coincides in the short-wavelength limit (aside from polarization effect) with a standard normalized diffraction pattern [13]. Note that in terms of the vector scattering amplitude $\mathbf{f} = i(S/k)\mathbf{n}_s$ commonly used in particle scattering, the optical theorem reads $\sigma_{ext} = (4\pi/k^2)\text{Im}[\mathbf{n}_i \cdot \mathbf{f}(\mathbf{k}_s = \mathbf{k}_i)]$.

[33] For optically anisotropic (birefringent) media, the directions of polarization of the incident and scattered field in the forward direction do not coincide, namely, the scattered field contains a "depolarized" component that, being perpendicular to $\mathbf{n}_i$ cannot of course interfere with the incident beam. Nevertheless, Eq. (2) states that the *total* scattering cross section (including that due to depolarized scattering) is still accounted for by the sole polarized component. The reason for this correct, but apparently paradoxical result is discussed in a recent publication[31] concerning light scattering from anisotropic colloidal particles.

[34] Because of the choice we made for the phase of the incident and scattered field, the scattering amplitude we define is the complex conjugate of the one defined by van de Hulst[13]

[35] Formally, ξ can be defined as $\xi = \int d\mathbf{r} r^2 h(r)/\int d\mathbf{r} r h(r)$, which for an exponentially-decaying correlation function coincides with the decay length.

[36] Notice that, as a matter of fact, $F(q)$ is the purely "geometrical" form factor obtained for the scattering from a uniform sphere in the Rayleigh–Gans approximation by assuming that the incident field on each volume element is the *unperturbed* external field

[37] This is known as the "extinction paradox", since a very large particle apparently "casts a shadow" which is the double of its geometrical cross section. Consistency with the "macroscopic" experience is recovered by noticing that half of the scattered light is scattered in an extremely narrow diffraction cone around the forward direction, which could be excluded only using a detector with an acceptance angle $\vartheta \ll \lambda/2a$

[38] Of course, if Δn_p is *identically* equal to 0, Q_{ext}^0 must vanish. What (59) actually means is that $Q_{ext}^0(\delta)$ is discontinuous: $\lim_{\delta \to 0} Q_{ext}^0(\delta) \neq Q_{ext}^0(0)$

[39] Maxwell actually discussed the problem of the electrical conductivity of a matrix containing spherical inclusions. His results were later extended to the optical properties of metal films by James Clerk Maxwell Garnett, who owes his rather curious name to the admiration of his father, William Garnett, for his own friend and mentor J. C. Maxwell.

[40] It is useful to notice that, at 2nd order in $\Delta \epsilon_p$, also the rigorous upper and lower limits for ϵ^* given by the Hashin-Shtrikman bonds coincide.

[41] From Panel A, anomalous dispersion is of course present, and even much more pronounced, for the crystal phase. However, since we simply model the system as an FCC crystal at $T = 0$, neglecting therefore the "rattling" motion of the particles at finite T, we cannot make a realistic correlation with the behavior of $S(q)$. Notice however that, in spite of the fact that in this idealized model the structure factor peaks are discontinuous delta functions, the peak in the refractive index is finite.