Comment on “Theory of electron energy loss in a random system of spheres”

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Abstract

In a recent paper, Barrera and Fuchs [Phys. Rev. B 52, 3256 (1995)] provide a theory of electron energy loss in a random system of spheres. In this comment, we point out that the approach of Barrera and Fuchs (A) completely ignores magnetic excitations and retardation, which is inconsistent with the data of energy loss of fast electrons, (B) does not yield the correct $k \to 0$ limit, hence, does not recover correctly the Maxwell-Garnett formula, and (C) does not use the correct screened potential at any $k$.

61.80.Mk, 77.22.-d, 77.84.Lf
A major point of a recent paper by Barrera and Fuchs on the electron energy loss in a composite medium with randomly distributed spheres is to determine the effective dielectric function of the composite with a mean-field theory that includes all multipoles and the two-particle distribution. This has already been done in the quasistatic case, \( k = 0 \). Barrera and Fuchs attempt a generalization of that to finite \( k \). They retain the quasistatic multipolar expansion, the corresponding re-expansion formula, and the mean-field average procedure already developed and simply replace the external potential \(-E_0z\) with \( V_0 e^{ikz} \). Then, they claim that, in the limit \( k \to 0 \), they recover the Maxwell-Garnett formula (MGF), which was demonstrated in the quasistatic case.

However, for the energy loss of fast electrons, with incident energies of order 100 KeV, the magnetic excitations and the retardation are not negligible. So, the treatment of Ref. is more limited than a previous approach based on the Poynting vector, in which magnetic excitations essentially contribute to the energy loss. The complete \( k \neq 0 \) problem, including both electric and magnetic excitations, is governed by Helmholtz equation: a full treatment of wave propagation for periodic lattices of spheres has been provided in Ref. and in Ref. with electric excitations only.

Furthermore, the mean-field average of Ref. is incorrect, and does not lead to the MGF for \( k \to 0 \). We can show that by demonstrating first what should be the correct mean-field average and the correct derivation of the MGF for \( k \to 0 \).

Starting from the central multipolar Eq. (16) of Ref. since we are only interested in the induced dipole moment in the \( k \to 0 \) limit, we take \( l = 1 \) and expand \( q_{10}^0 \) for small \( k \). We then perform the mean-field average, which yields

\[
\langle q_{10} \rangle = -ikV_0 \sqrt{\frac{3}{4\pi}} \alpha_1 \delta_l - \frac{(2l + 1)}{4\pi} \alpha_1 \sum_{l'} \langle \sum_j B_{10}^{l'0j} \rangle \langle q_{l0} \rangle. \tag{1}
\]

These equations are basically those developed in Ref. with the replacement \( E_0 = -ikV_0 \) for the applied field (which is exactly the external field of Barrera and Fuchs, for small \( k \)). Both the average coupling \( \langle \sum_j B_{10}^{l'0j} \rangle \) and the average field depend on the system configuration, and must be done consistently to obtain the correct effective dielectric function. In Ref.,
a parallel-plate configuration was introduced, which correctly yields the MGF for isotropic two-particle distributions. One of the advantages of the parallel-plate configuration is that the macroscopic average field is simply the potential difference between the electrode plates, divided by their separation. On the other hand, Ref. [1] effectively adopts a large spherical configuration, with a hard-sphere two-particle distribution. All the volume integrals therein are indeed performed over such large sphere. For such system, the correct average must be

$$
\langle \sum_j B_{10i}^{l'0j} \rangle = \gamma_{ll'} \int \rho^{(2)}(r) Y_{l'+1,0}(\theta) r^{-(l'+2)} d^3r
$$

$$
= \gamma_{ll'} \int_0^{\infty} \frac{\rho^{(2)}(r)}{r^{l'}} dr \int Y_{l'+1,0}(\theta) d\Omega = 0,
$$

where $\gamma_{ll'}$ are given in Eq. (D8) of Ref. [1]. Although the upper limit of the integral over $r$ is taken to infinity, one must keep in mind that the system, no matter how large, must be finite. So, the proper procedure must be that of doing the angular integrations first. Now, in the last term of Eq. (1), $-\sqrt{3/4\pi} \langle \sum_j B_{10i}^{l'0j} \rangle \langle q_{l'0j} \rangle$ represents the uniform part of the average field produced by the $l'$-order multipoles of the surrounding particles onto the given central particle. That induces a dipole moment on the central particle, as does the applied field, represented by the first term in the right-hand side of Eq. (1). So, our result (2) implies that a spherical shell of uniformly distributed multipoles produces zero field inside. That is indeed the physically correct result, consistent with the well known elementary example of a uniformly charged spherical shell ($l' = 0$), or that of a uniformly polarized spherical shell ($l' = 1$).

Substituting Eq. (2) into Eq. (1), one obtains the average polarization

$$
\langle P \rangle = \sqrt{\frac{4\pi}{3} n \langle q_{10} \rangle} = -ikV_0 n \tilde{\alpha}_1 a^3,
$$

where $\tilde{\alpha}_1 = \alpha_1 / a^3$. Correspondingly, the macroscopic average field for such a spherical system can be obtained by solving the boundary-value problem of a homogeneous sphere with a dielectric function $\epsilon_e$ in the applied field $-ikV_0$, as done correctly in Eq. (8.3) of Ref. [3], for example, yielding
\( \langle E \rangle = -ikV_0 \frac{3}{\epsilon_e + 2}. \)  

(4)

Then, from the standard definition of the effective dielectric function (for a vacuum host)

\[ \epsilon_e = 1 + 4\pi \langle P \rangle / \langle E \rangle, \]

(5)

one obtains

\[ \epsilon_e = \frac{1 + 2f \tilde{\alpha}_1}{1 - f \tilde{\alpha}_1}, \]

(6)

where \( f = 4\pi n a^3 / 3 \) is the volume fraction of the particles. This is exactly the MGF. We emphasize again that in order to obtain this result (MGF) correctly, both steps (2) and (4) must be done consistently with the selected (spherical) system configuration.

Now, according to the Eqs. (D11)-(D14) of Ref. [1], the mean-field-average coupling for the hard-sphere two-particle distribution \[ d\rho^{(2)}(r) / dr = n\delta(r - 2a) \] for arbitrary \( k \) is

\[ \langle \sum_j B_{10i}^{l'0j} e^{ik(z_j - z_i)} \rangle = (-i)^{l' - 1} \langle \sum_j B_{10i}^{l'0j} e^{ik(z_j - z_i)} \rangle = (-i)^{l' - 1} (4\pi)^2 (l' + 1)! n j_{l'v}(k2a) \sqrt{3(2l' + 1)l'! k} (2a)^{l'}. \]

(7)

If the theory of Barrera and Fuchs were correct and reproduced the MGF in the \( k \to 0 \) limit, as they claim, Eq. (7) should vanish in such limit, as shown in Eq. (2). However, when the limit \( k \to 0 \) is taken, Eq. (7) yields instead

\[ \langle \sum_j B_{10i}^{l'0j} \rangle' = (-i)^{l' - 1} \begin{cases} \infty, & (l' = 0) \\ 2n(4\pi/3)^2, & (l' = 1) \\ 0, & (l' > 1). \end{cases} \]

(8)

Here, we have used a prime to distinguish this incorrect result of Ref. [1] from our correct Eq. (2). The incorrect result (8) would imply that a uniformly charged spherical shell, with a finite and real charge density, would produces inside an infinite and imaginary field, which is obviously wrong. Likewise, a uniformly polarized spherical shell would produce inside a field in the opposite direction to the polarization, which is also clearly incorrect. Furthermore, if the shape of the system is not spherical, or the two-particle distribution is not spherical, the higher multipoles \( (l' > 1) \) of the surrounding particles will contribute.

In that case, the
incorrect \( \langle \sum_j B_{ij}^{(0)} \rangle' \) would be imaginary or complex for some \( l' \). Then, real higher multipoles would also produce complex fields on the central particle, which is definitely incorrect.

There is another basic and independent error in the derivations of Ref. 1: namely, no distinction is made between the fields screened and unscreened by the spherical system. This in itself is enough to prevent a correct result for both finite and vanishing \( k \). Combining that with the error in obtaining the mean-field averages, one cannot expect to recover correctly the MGF. Indeed, using the incorrect result (8), one obtains for the average polarization

\[
\langle P \rangle' = -ikV_0n\frac{\bar{\alpha}_1a^3}{1 + 2f\bar{\alpha}_1}.
\]  

Then, it is easily verified that the incorrect result (8) leads to

\[
\epsilon'_e = \frac{1 + 4f\bar{\alpha}_1}{1 + f\bar{\alpha}_1},
\]  

if the screened field (4) is used, and to

\[
\epsilon'_e = \frac{1 + 5f\bar{\alpha}_1}{1 + 2f\bar{\alpha}_1},
\]  

if the unscreened field is used. Evidently, neither of these results (10) and (11) represents the correct MGF. Nonetheless, Barrera and Fuchs claim that they obtain that.

It may be worth noticing that, although Eq. (9) of Ref. 1 defines the effective dielectric function through potentials, rather than electric fields, that has no effect on the mean-field averages. Nor does it avoid the screening requirement on the potential, otherwise there would be no justification to use any particular geometry, and the result would be completely arbitrary.

In summary, we have shown that the mean-field average of Ref. 1 is incorrect, does not reproduce the Maxwell-Garnett formula in the \( k \rightarrow 0 \) limit, and does not use the correct screened potential. Combined with the limitations of ignoring magnetic excitations and retardation in the response, that leads to the conclusion that the relatively good fitting of experimental data obtained in Ref. 1 is at best fortuitous, and simply reflects an arbitrary adjustment of parameters, such as the volume fractions and the particle radii.
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