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Evaluation of extended Maxwell-Garnett theories

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Abstract

A few versions of effective medium theories that have been suggested as size dependent extensions of the Maxwell-Garnett theory are compared. The degree to which the different theories satisfy a physical consistency criterion is evaluated. The inapplicability of the extended Maxwell-Garnett theories to heating rate calculations is discussed. © 2000 Published by Elsevier Science B.V.

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1. Introduction

The optical properties of heterogeneous materials can be described in terms of effective dielectric constants. Two widely used effective medium theories are the Maxwell-Garnett (MG) theory [1] and the Bruggeman theory [2]. In both theories the effective dielectric constant does not depend explicitly on the size of the grains or inclusions occurring inside the medium. This is because these are quasi-static theories, and their applicability is restricted to grain sizes much smaller than the wavelength of the incident radiation. The relative merits and deficiencies of the MG and Bruggeman theories have been the subject of much discussion, and it appears that the correct choice depends on the topology of the heterogeneous medium. For simplicity we will restrict the discussion to the MG theory. Analogous considerations can be applied to the Bruggeman model. We consider the case of small spherical particles having a complex dielectric constant ε_i, which are embedded, at a volume density f, in a host medium having a real dielectric constant ε_h. Let x be the sphere size parameter, $x = \sqrt{\varepsilon_h}\,\omega a/c$, where a is the sphere radius and ω is the angular frequency of the incident radiation. A necessary condition for the applicability of the MG theory is $x \ll 1$. Recently, various extensions of the MG theory have been suggested, the aim of which was to remove this restriction. These extended MG theories yield the dependence of the effective dielectric constant $\bar{\varepsilon}$ on x, and are typically used for x values up to about 0.5. The MG theory is an *unrestricted* effective medium theory, i.e., the MG dielectric constant can be used in the same way that the dielectric constant of a homogeneous medium is used, to calculate all the optical properties of the medium, as well as energy absorption and heating rates. As shown by Bohren [3], the

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extended MG theories are restricted in their applicability. For example, they *cannot* be used for calculating heating rates in composite media. This point will be further discussed in Section 4. Even when we restrict the application of the extended MG theory to the calculation of the extinction coefficient of the heterogeneous medium, which is the minimal requirement, we find that the various extended MG versions suggested in the literature may yield widely differing results. Hence, it would be useful to provide physical criteria for assessing the various theories. One straightforward consistency criterion can be obtained in the limit of small f, as will be discussed in detail in Section 3, where we also present numerical calculations, in which we check how well the various extended MG theories satisfy this criterion.

Since the small f criterion is based on the Mie theory [4], we recall here the Mie result for the extinction cross section [4,5]

$$Q_t = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)\mathrm{Re}(a_n + b_n). \tag{1}$$

Here, the extinction cross section is given in units of the geometric cross section, and the Mie coefficients a_n and b_n are given by

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)} \tag{2}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)}. \tag{3}$$

Here ψ_n and ξ_n are the Riccati–Bessel functions and m is the ratio of the index of refraction of the sphere material to that of the host medium.

2. MG theory and its extended versions

The MG formula for the effective dielectric constant can be derived in a number of ways [1,6,7]. Here we follow a derivation that can be naturally extended to include size effects. The effective dielectric constant $\bar{\varepsilon}$ of a suspension of small spherical particles of radius a embedded in a host medium of dielectric constant ε_h is given by the Clausius–Mossotti equation

$$\frac{\bar{\varepsilon} - \varepsilon_h}{\bar{\varepsilon} + 2\varepsilon_h} = \frac{f}{a^3}\alpha. \tag{4}$$

Here α is the particle dipole polarizability, $f = (4\pi/3)na^3$ is the volume fraction of the embedded particles, and n is the particle number density. For sphere sizes much smaller than the wavelength of the incident radiation, the electrostatic value of the polarizability can be employed. This is given by [8]

$$\alpha = \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} a^3 \tag{5}$$

where ε_i is the dielectric constant of the sphere material. When substituted into (4), this yields the usual MG formula

$$\frac{\bar{\varepsilon} - \varepsilon_h}{\bar{\varepsilon} + 2\varepsilon_h} = f\frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \tag{6}$$

or, in an explicit form for the effective dielectric constant

$$\bar{\varepsilon} = \varepsilon_h \frac{\varepsilon_i(1+2f) + 2\varepsilon_h(1-f)}{\varepsilon_i(1-f) + \varepsilon_h(2+f)}. \tag{7}$$

This equation, in which the sphere radius a does not appear, is valid only for $a \ll \lambda$, where λ is the wavelength of the incident wave. We now describe three different extensions of the MG theory, which have been proposed so as to account for finite size effects.

2.1. Mie theory based extension (MMG)

Doyle [9] has suggested that a size dependent extension of the MG formula can be obtained by using for α in (4) the electric dipole polarizability which follows from the Mie theory. This polarizability is given, in terms of the Mie coefficient a_1, by

$$\alpha = \mathrm{i}\frac{3a^3}{2x^3}a_1. \tag{8}$$

This yields the following extended MG formula

$$\bar{\varepsilon} = \frac{x^3 + 3\mathrm{i}fa_1}{x^3 - \frac{3}{2}\mathrm{i}fa_1}. \tag{9}$$

Bohren [3] has pointed out that the optical properties of a suspension of small spheres may depend not only on the effective dielectric constant $\bar{\varepsilon}$, but also on the effective relative magnetic permeability $\bar{\mu}$. The latter quantity can be different from unity, even when the inclusion and host materials are non-magnetic. This happens when the Mie coefficient b_1, which represents the magnetic dipole term is not negligible. In analogy with the derivation of (9), the effective permeability can be shown to be given by [10]

$$\bar{\mu} = \frac{x^3 + 3\mathrm{i} f b_1}{x^3 - \frac{3}{2}\mathrm{i} f b_1}. \quad (10)$$

2.2. Integral equation based extension (IMG)

A different type of extension of the MG theory has been suggested by Lakhtakia [11]. He employed an integral equation formalism to obtain a size dependent correction to the polarizability of an electrically small sphere. The derivation is based on an improved calculation of the Green's function which appears in the integral equation. However, it relies on the approximation that the electric field inside the sphere is constant. The size dependent effective dielectric constant obtained by this approach is

$$\bar{\varepsilon} = \varepsilon_{\mathrm{h}} \frac{3\varepsilon_{\mathrm{h}}(1-z) + 2f(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{h}})}{3\varepsilon_{\mathrm{h}}(1-z) - f(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{h}})} \quad (11)$$

where

$$z = \left(\frac{\varepsilon_{\mathrm{i}}}{\varepsilon_{\mathrm{h}}} - 1\right)\left[\frac{2}{3}(1 - \mathrm{i}x)\mathrm{e}^{\mathrm{i}x} - 1\right]. \quad (12)$$

2.3. Dynamical MG model (DMG)

This is another version of an extended MG theory, which was applied to the interpretation of the optical extinction spectra of small metal particles [12,13]. It is based on a calculation of size corrections to the depolarization factor [14], which was carried out up to terms of the order of x^3. This derivation is, however, approximate since it involves the assumption of homogeneous polarization over the volume of the sphere. The resulting effective dielectric constant is

$$\bar{\varepsilon} = \varepsilon_{\mathrm{h}} \frac{\varepsilon_{\mathrm{i}}(1+2f) + 2\varepsilon_{\mathrm{h}}(1-f) + (\varepsilon_{\mathrm{h}} - \varepsilon_{\mathrm{i}})(1-f)\Delta}{\varepsilon_{\mathrm{i}}(1-f) + \varepsilon_{\mathrm{h}}(2+f) + (\varepsilon_{\mathrm{h}} - \varepsilon_{\mathrm{i}})(1-f)\Delta} \quad (13)$$

where $\Delta = x^2 + (2/3)\mathrm{i}x^3$.

3. Low density consistency requirement

Although the question of which physical properties can be deduced from size dependent effective medium theories has been the subject of some debate [3,15], the basic minimal requirement is that they correctly predict the optical extinction coefficient. In the limit of small f this requirement provides a simple consistency test, that can be applied to the various theories. Although this consistency test is well known, it has not been systematically applied in order to check the various extended MG theories.

The energy removed from the incident beam by scattering and absorption can be expressed in terms of an extinction coefficient μ, defined by the relation $I = I_{\mathrm{o}}\mathrm{e}^{-\mu d}$, where I_{o} is the irradiance by the incident beam and I is the irradiance after the beam has traversed a distance d. In the case $f \ll 1$, when the spheres scatter independently, the extinction coefficient is related to the single sphere extinction cross section Q_{t} by [16] $\mu = n\pi a^2 Q_{\mathrm{t}}$. On the other hand, in terms of the effective dielectric constant $\bar{\varepsilon}$, the propagation constant is given by $\bar{k} = (\omega/c)\sqrt{\bar{\varepsilon}}$, which implies that the extinction coefficient is given by $\mu = (2\omega/c)\bar{n}_2$, where $\bar{n}_2$ is the imaginary part of the complex effective refractive index $\bar{n} = \bar{n}_1 + \mathrm{i}\bar{n}_2$, defined by $\bar{n} = \sqrt{\bar{\varepsilon}}$. Comparing the two different expressions for the extinction coefficient, we find that in the limit $f \to 0$, the following consistency requirement must be satisfied

$$\bar{n}_2 = n_2^{\mathrm{M}}. \quad (14)$$

Here, the Mie theory based n_2^{M} is given by

$$n_2^{\mathrm{M}} = \frac{3}{8}\frac{fQ_{\mathrm{t}}}{x} n_{\mathrm{h}} \quad (15)$$

and $n_{\mathrm{h}} = \sqrt{\varepsilon_{\mathrm{h}}}$ is the refractive index of the host material. We note that for effective medium theories which also incorporate an effective permeability, the effective refractive index is defined by $\bar{n} = \sqrt{\bar{\varepsilon}\bar{\mu}}$ .We have calculated the ratio $\eta = \bar{n}_2/n_2^{\mathrm{M}}$, which should tend to unity as $f \to 0$, for the various size dependent MG theories. The curves shown in Fig. 1 were calculated for inclusions having a dielectric constant $\varepsilon_{\mathrm{i}} = 4 + 0.01\mathrm{i}$ and size parameter $x = 0.3$, in a host medium with $\varepsilon_{\mathrm{h}} = 1$. For the MMG theory without a magnetic contribution the ratio comes close to the required value of unity as $f \to 0$, and the agreement improves when the magnetic contribution is included. For the IMG and DMG theories, the deviations from this value are significant.

All the extended theories tend, of course, to the correct MG limit when $x \to 0$, and therefore obey the consistency requirement (14) for $x \ll 1$. However, as the size parameter x increases, large deviations from this criterion occur in some of the theories. We have calculated $\eta = \bar{n}_2/n_2^{\mathrm{M}}$, in the small f limit, for various types of inclusions, as a function of the size parameter, and the results are shown in Figs. 2–5. For a non-absorbing inclusion, Fig. 2, the MMG theories obey the condition (14) quite closely, up to at least $x = 0.5$, while the IMG and the DMG do not. For an absorbing inclusion, Fig. 3, the MMG

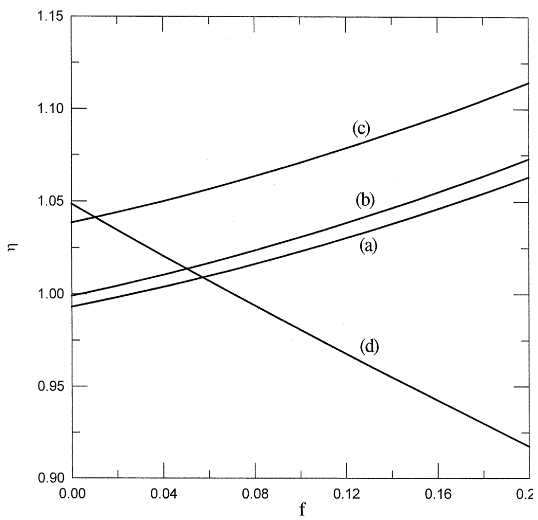

Fig. 1. The dependence of the ratio $\eta = \bar{n}_2 / n_2^{\mathrm{M}}$ on the volume fraction for: (a) MMG theory without magnetic permeability; (b) MMG with magnetic permeability; (c) IMG theory; and (d) DMG theory. The calculations were performed for $x = 0.3$, $\varepsilon_{\mathrm{h}} = 1$ and $\varepsilon_{\mathrm{i}} = 4 + 0.01\mathrm{i}$.

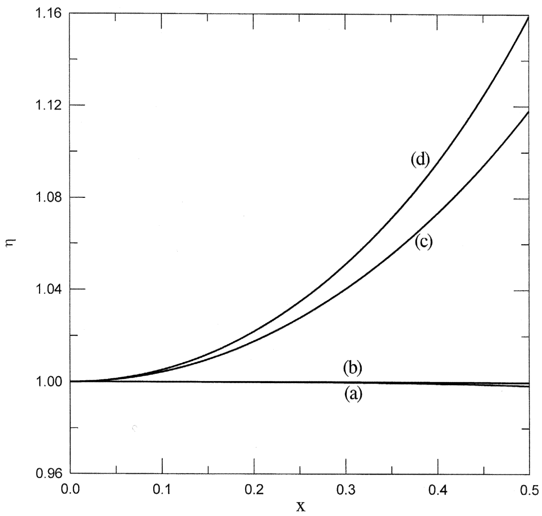

Fig. 2. The dependence of the low density limit of the ratio $\eta = \bar{n}_2 / n_2^{\mathrm{M}}$ on the size parameter for: (a) MMG theory without magnetic permeability; (b) MMG theory with magnetic permeability; (c) IMG theory; and (d) DMG theory. The calculations were performed for $\varepsilon_{\mathrm{h}} = 2$ and $\varepsilon_{\mathrm{i}} = 5$.

theory with the effective permeability contribution, curve (b), obeys the consistency requirement much better than the other theories. The discrepancy between curves (a) and (b) arises when the magnetic contribution, due to the Mie coefficient b_1, becomes significant. The deviation of curve (b) from unity begins only when the contribution of higher order

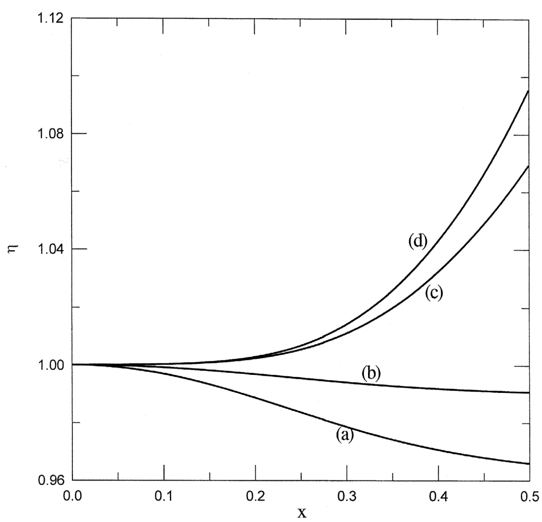

Fig. 3. Same as Fig. 2, but for $\varepsilon_{\mathrm{i}} = 5 + 0.1\mathrm{i}$.

Mie coefficients (such as a_2, b_2) to the extinction cannot be ignored.

An interesting case is that of an inclusion for which the real part of the dielectric constant is negative. This occurs for dispersive materials, e.g., for metals at frequencies lower than the plasma frequency, and for ionic crystals in the Reststrahlen region. The calculated $f \to 0$ limit of η for such a case is shown in Fig. 4. Whereas the IMG and DMG results remain close to the required value of unity only for an extremely small range of x, the MMG curves (with and without the magnetic contribution) exhibit practically no deviation up to $x = 0.5$. This indicates that the electric dipole contribution, due to the Mie coefficient a_1, is dominant, and justifies Doyle's use of (9), without invoking $\bar{\mu}$, in his treatment of the optical properties of a suspension of metal spheres [9].

Another case, for which an extended MG theory has been applied, is that of fine metal particles dispersed in composite adhesives, and irradiated by microwaves. At microwave frequencies, the perfect conductor limit can be used, and Eqs. (11)–(13) can be simplified by taking the limit $\varepsilon_i \to \infty$. The Mie coefficients also become simpler in this limit [17]. The small f limit of the ratio η, calculated for this case, is shown in Fig. 5. For the dielectric constant of the host material the value $\varepsilon_h = 2.5$ has been employed. It can be seen that the magnetic contribution cannot be ignored, even in the small size limit. In fact, in the limit of small f and small x, and using the perfect metal assumption, it is easily found from (9), (11) and (13) that $\bar{n}_2 = n_h f x^3$ for the MMG, IMG and DMG theories. However, if the effective permeability is included, the result $\bar{n}_2 = (5/4) n_h f x^3$ is obtained in the same limiting case. Therefore, in the dilute, small size limit, the correct theory, which includes the magnetic contribution, yields an extinction coefficient that is larger than that obtained from all the other theories by a factor of $5/4$.

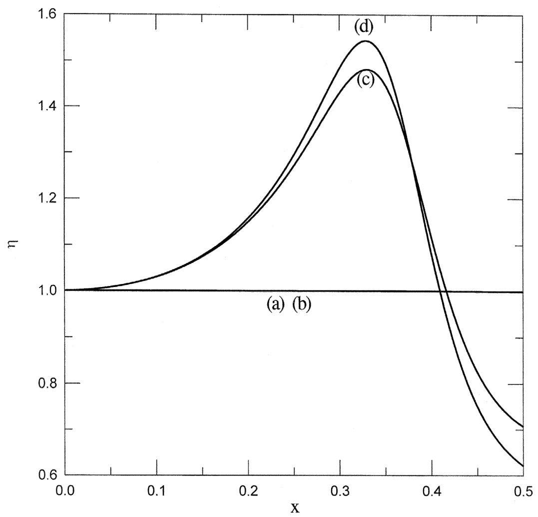

Fig. 4. Same as Fig. 2, but for $\varepsilon_i = -5 + 0.3i$.

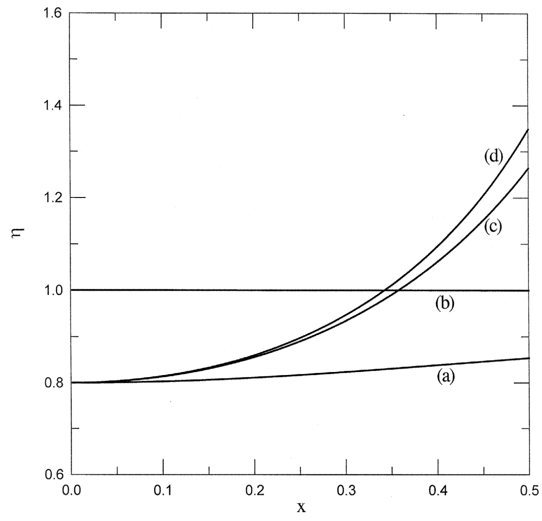

Fig. 5. Same as Fig. 2, but for $\varepsilon_i = \infty$ and $\varepsilon_h = 2.5$.

4. Inapplicability of extended MG theories to heating rate calculations

For a homogeneous material, the fact that the dielectric constant has a nonzero imaginary part implies that the material will partly absorb the electromagnetic wave passing through it. This inevitably leads to heating, the rate of which can be calculated in terms of the complex dielectric constant. However, these statements are not applicable to the effective dielectric constant obtained from extended MG theories. As has been discussed by Bohren [3], the effective dielectric constant obtained from an extended MG theory cannot be used for calculating heating rates. In fact, for non-absorbing spheres embedded in a non-absorbing medium, the effective dielectric constant obtained from any type of extended MG theory will have an imaginary part that increases with the sphere size. However, this is due to the increase of the scattering, and not due to absorption. Here, again, in the small f region we can perform explicit calculations that demonstrate this quantitatively. From (14) and (15) we find that, in the small f limit, $\bar{n}_2$ (the imaginary part of the effective refractive index) is proportional to the extinction cross section Q_t. Since Q_t is the sum of the absorption and the scattering cross sections, we can also decompose $\bar{n}_2$ into absorption and scattering contributions, in the form

$$\bar{n} = \bar{n}_2^{a} + \bar{n}_2^{s}. \tag{16}$$

We have calculated these quantities for the case of spheres having a dielectric constant $\varepsilon_i = 5 + 0.1i$ embedded in a host medium with $\varepsilon_h = 2$, at a density $f = 0.001$, and the results are shown in Fig. 6. It can be seen that the increase of $\bar{n}_2$ with particle size is mainly due to the increase of the scattering, while the absorption increases only very slightly. This demonstrates that the imaginary part of the effective refractive index obtained from extended MG theories cannot be used to evaluate the absorption, or the heating rate. Although the decomposition shown here can be performed explicitly only for very small f, the conclusion that the increase of the extinction coefficient with increasing particle size is mainly due to increased scattering, rather than absorption, should remain valid even when f is not very small.

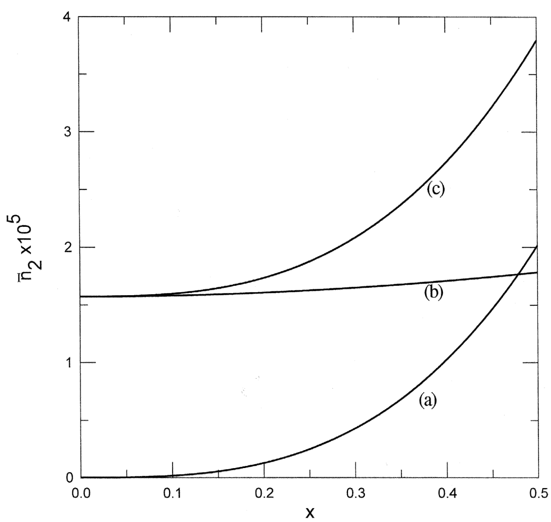

Fig. 6. Decomposition of the imaginary part of the effective refractive index, curve (c), into absorption (curve (b)) and scattering (curve (a)) contributions. The calculation was performed for $f = 0.001$, $\varepsilon_h = 2$, $\varepsilon_i = 5 + 0.1i$.

Recently, it has been suggested that the dielectric loss and the microwave absorption capacity of organic composites may be enhanced by doping them with fine metallic particles [18]. This idea was explored with the help of calculations based on the IMG, and it was shown that the imaginary part of the effective dielectric constant increases strongly with particle size (at a fixed volume fraction f) [18]. However, as discussed above, this increase does not imply a corresponding increase of the absorption capacity of the composite.

5. Discussion

A consistency requirement based on simple physical considerations has been applied to a number of extended MG theories. The extended MG theory which is based on the Mie theory (MMG) naturally satisfies the consistency requirement, as long as the particles are small enough, so that the Mie coefficients a_n and b_n with $n > 1$ can be neglected. In this case, the MMG without an effective magnetic permeability is applicable whenever the Mie coefficient b_1 can be neglected. The other two extended MG theories, that have been tested, obey the consistency requirement only over an extremely limited range of sphere sizes. This is not surprising, since these theories have been derived using the approximation that the electric field (or the polarization) is constant over the sphere volume. Since the MMG is derived by using the exact electric field, including its deviation from uniformity, it yields better results than theories in which this deviation is neglected. Even as regards simplicity, the MMG formulae (9) and (10) are rather easy to use. The coefficients a_1 and b_1 involve only the simple functions $\psi_1(\rho) = (\sin\rho/\rho) - \cos\rho$ and $\xi_1(\rho) = -e^{i\rho}(1 + (i/\rho))$.

We have also shown that, in the small f limit, the applicability of the effective dielectric constant for obtaining heating rates [18] can be checked quantitatively. These calculations support the conclusion of

Bohren [3], that the effective dielectric constant obtained from extended MG theories cannot be used for calculating heating rates.

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