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Guinier analysis for homogeneous dielectric spheres of arbitrary size

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Abstract

We show that Guinier analysis of the scattered light intensity from a sphere of radius R and refractive index m yields a radius of gyration that is in general larger than the true, geometric value. Moreover, the ratio of these two quantities is a roughly universal function of the phase shift parameter $\rho = 2kR|m-1|$ where $k = 2\pi/\lambda$, with λ being the optical wavelength. These universal curves are oscillatory and very similar to, but 180° out of phase with, the behavior of the total scattering efficiency. Reasons for these behaviors are proposed and their significance for optical particle sizing are discussed.

1. Introduction

Guinier analysis of scattering data allows for the determination of the radius of gyration R_g of an arbitrarily shaped particle [1]. This combined with the simplicity of the analysis has led to its widespread use in X-ray [2], neutron [3], and light scattering applications [4]. For light scattering a particularly attractive feature of the Guinier analysis is that sizing of particulates can be achieved without knowledge of the particle refractive index.

The Guinier formula is based on a second-order expansion of the structure factor of the particle. The structure factor is the square of the Fourier transform of the density distribution of the particle, hence application of the Guinier analysis implicitly assumes that the particle is uniformly illuminated throughout its volume. According to Mie theory this latter condition is known not to hold for spheres of appreciable size or refractive index [5]. This, and the fact that analysis of light scattering from spheres is useful in many applications, brings us to the purpose of this paper, which is to ask: what is the range of validity for the Guinier analysis for light scattering from spheres; and in what manner, if at all, does it break down?

2. The Guinier equation

If $\rho(\vec{r})$ is the density distribution of the particle, then the first approximation that is made on the path to the Guinier equation is that each differential element of the particle experiences the same total incident field i.e., the particle is uniformly illuminated. Then the scattering amplitude at the detector is the sum of waves, represented by $e^{i\vec{q}\cdot\vec{r}}$, with amplitude proportional to $\rho(\vec{r})$, for each differential unit of the

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distribution. The scattered intensity is the square of the total amplitude, thus

$$I(\vec{q}) = c\left|\int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}\right|^2. \quad (1)$$

In Eq. (1) c is a constant related to the refractive index and incident wavelength and $\vec{q}$ is the scattering wave vector with magnitude given by

$$q = 2k\sin(\theta/2). \quad (2)$$

In Eq. (2) $k = 2\pi/\lambda$, where λ is the wavelength, and θ is the scattering angle. Eq. (1) occurs in the weak scattering limit where intraparticle multiple scattering is insignificant.

The next approximation involved in the Guinier equation is that the density distribution $\rho(\vec{r})$ is isotropic. This is satisfied by a uniform sphere but not for irregular particles. However, scattering from an ensemble of irregular but randomly oriented particles can be analyzed as if each particle was orientationally averaged to achieve isotropy. With isotropy, the solid angle of $d\vec{r}$ can be integrated in Eq. (1) to obtain

$$I(q) = 16\pi^2 c\left|q^{-1}\int \rho(r) r \sin qr \, dr\right|^2. \quad (3)$$

The third approximation involves confining the observation of the scattered intensity to small q. Then the sin qr term can be expanded to two terms. Doing this and normalizing by $I(0)$ yields

$$I(q)/I(0) = 1 - q^2R_g^2/3. \quad (4)$$

This is one form of the Guinier equation. To achieve Eq. (4) from Eq. (3) use was made of isotropy and the definition of the radius of gyration of the particle or aggregate

$$R_g^2 = \int \rho(\vec{r}) r^2 d\vec{r} / \int \rho(\vec{r}) d\vec{r}. \quad (5)$$

The Guinier analysis involves inverting Eq. (4) which yields with $qR_g < 1$

$$I(0)/I(q) = 1 + q^2R_g^2/3. \quad (6)$$

3. Calculational results

We used the BHMIE program of Bohren and Huffman [6] to create scattered intensities from homogeneous, dielectric spheres. These calculations were performed for the common experimental arrangement of incident and scattered light polarization perpendicular to the scattering plane defined by the incident and scattered wave vectors. Inputs to the algorithm are the size parameter, which we shall write as kR, where $k = 2\pi/\lambda$ is the magnitude of the wavevector for light of wavelength λ, and R is the radius of the sphere; m, the refractive index of the sphere divided by the refractive index of the medium; and θ, the scattering angle.

The calculated scattered light is considered to be not a function of θ, but rather a function of the scattering wavevector q. This parameter has significant physical meaning because its inverse is essentially the 'probe length' of the scattering experiment [4,7]. Recently we have shown its significance for Mie scattering from spheres in that is uncovers useful patterns and functionalities heretofore undescribed [8].

The Guinier analysis proceeds by plotting the inverse, normalized intensity versus q^2 to create a Guinier plot, which according to the Guinier equation in the form of Eq. (6), should be a straight line with slope equal to $R_g^2/3$ when $qR_g < 1$. Using the Mie results of BHMIE we find such plots to have a slight upward curvature, the degree of which is dependent upon kR and m. This causes us to measure the slope in the limit of $qR_g \to 0$.

Fig. 1 shows a Guinier plot for a size parameter of $kR = 50$ with different refractive indices m. The slopes of the plots increase with m indicating that

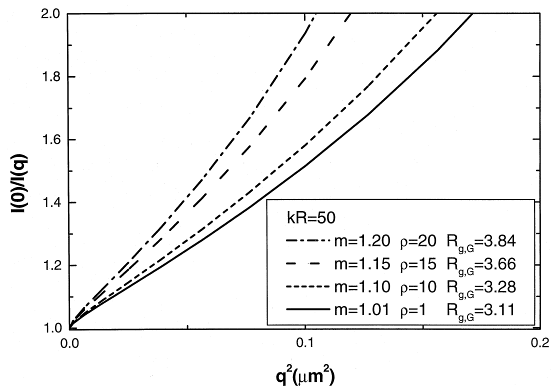

Fig. 1. Guinier plot of calculated Mie scattering data for spheres with size parameter $kR = 50$ and different refractive indices m. To give the plot some physical relevance we assume $\lambda = 0.5$ μm, thus $R = 3.98$ μm and $R_g = 3.08$ μm.

the R_g values inferred from these plots is increasing. Of course, the size of the sphere is not changing with m, so the apparent change must be an artifact of the Guinier analysis applied to the sphere in a regime where the assumptions behind the analysis are breaking down. Despite this obvious breakdown, the R_g inferred from the Guinier plots might still be useful for sizing spheres with light scattering if some pattern in their behavior can be found.

Such a pattern exists when the behavior of the Guinier inferred radius of gyration, which we will designate as $R_{g,G}$, is normalized by the true radius of gyration of the sphere, $R_g = \sqrt{3/5}\,R$, and is plotted as a function of the phase shift parameter ρ as shown in Figs. 2 and 3. This parameter is defined by the equation

$$\rho = 2kR|m-1|, \tag{7}$$

and represents the difference in phase between a wave that travels a distance equal to the diameter of the particle in the medium and a wave that travels the same distance through the particle. We are finding with this and past work that ρ is quite an illustrious parameter. It is also the parameter that determines the range of validity for Rayleigh–Debye–Gans theory for scattering from a sphere, valid for $\rho < 1$, and when the full Mie theory is required, necessary when $\rho \gtrsim 1$ [6]. In recent work [8] we have found that the Mie differential scattering curves

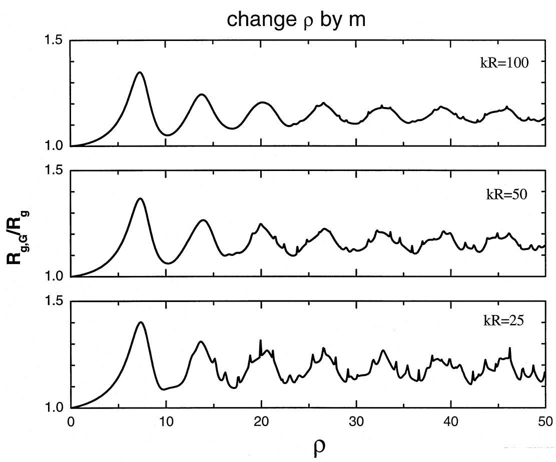

Fig. 2. The ratio of the Guinier inferred to real radius of gyration, $R_{g,G}/R_g$ versus phase shift parameter ρ for spheres with three different size parameters. The refractive index m was varied to vary ρ.

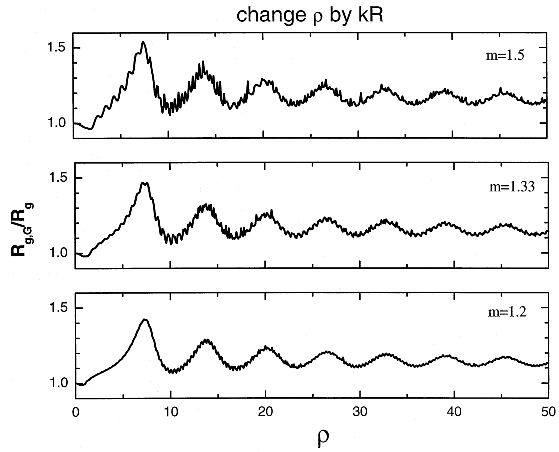

Fig. 3. The ratio of the Guinier inferred to real radius of gyration, $R_{g,G}/R_g$, versus phase shift parameter ρ for spheres with three different refractive indices. The size parameter kR was varied to vary ρ.

plotted as a function of q showed a quasi-universal behavior when parameterized by ρ. Now we find, as illustrated in Figs. 2 and 3, that $R_{g,G}/R_g$ plotted as a function of ρ again yields quasi-universal behavior. By ‘quasi-universal’ we mean that regardless of the values of the size parameter kR and the relative refractive index m, nearly the same functionality with ρ is seen. Close inspection of Figs. 2 and 3 shows that the universality is not perfect in that the details of $R_{g,G}/R_g$ vs. ρ vary with kR and m. The general trends, however, are the same regardless of kR and m; hence a pattern has presented itself, which we now explore.

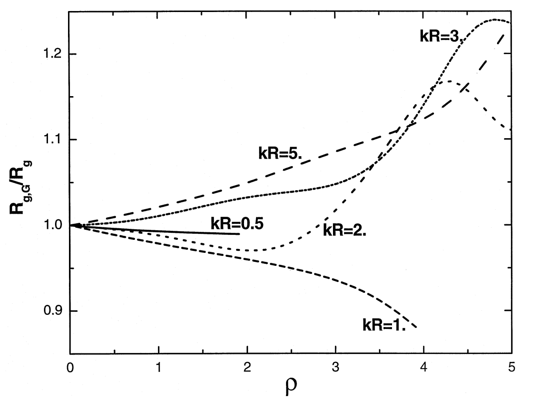

Fig. 4. Detailed behavior of $R_{g,G}/R_g$ at small size parameter kR and phase shift parameter ρ.

Figs. 2 and 3 show that $R_{g,G}/R_g$ is oscillatory with its first peak near $\rho = 7$ and a period of approximately 6.6. The oscillation is slowly damped at large ρ and slowly approaches an asymptotic value of about $R_{g,G}/R_g \simeq 1.12$ as $\rho \to \infty$. As $\rho \to 0$, $R_{g,G} \to R_g$ as expected since this is the weak scattering limit and there none of the assumptions leading to the Guinier equation are violated by the dielectric sphere. Remarkably, values of $R_{g,G}/R_g > \sqrt{5/3} = 1.29\ldots$ exist to imply $R_{g,G} > R$.

The behavior of $R_{g,G}/R_g$ at small ρ is not universal especially for $kR \simeq 1$ as shown in Fig. 4. As $kR \to 0$, $R_{g,G}/R_g \simeq 1.00$ at small ρ, but as kR increases $R_{g,G}/R_g$ vs. ρ develops first a negative slope which maximizes at $kR \simeq 1.2$, then this slope swings back to zero for $kR \simeq 2.5$ and continues to increase to a positive slope for all $kR > 2.5$. This accounts for the difference at small ρ between Figs. 2 and 3. Fig. 3, where kR is varied and m held constant, shows an initial decrease in $R_{g,G}/R_g$ with increasing ρ, whereas Fig. 2, in which m is varied and kR held constant, does not. The minimum in Fig. 3 at small ρ occurs near $kR \simeq 1$.

The patterns of Figs. 2 and 3 are quite similar to the behavior of the scattering efficiency plotted versus ρ. The scattering efficiency Q is the total scattering cross section σ divided by the geometric cross section of the sphere, πR^2, thus $Q = \sigma/\pi R^2$. Plots of Q vs. ρ are also quasi-universal. In Fig. 5 we compare Q and $R_{g,G}/R_g$ for $m = 1.33$ and 1.5 spheres and see that the damped oscillatory behaviors versus ρ of each are 180° out of phase.

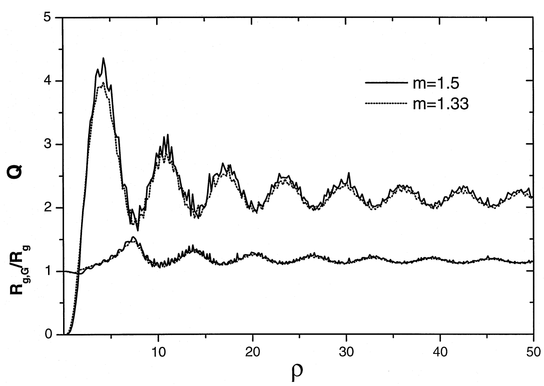

Fig. 5. Comparison of the behaviors of $R_{g,G}/R_g$ and the total scattering efficiency Q.

The large ρ limit of $R_{g,G}/R_g$ should represent the geometric limit. In this limit the large sphere acts as a circular obstacle and Fraunhofer diffraction occurs. Then, the diffraction intensity is given by [9]

$$I(q) = I(0)\left[\frac{J_1(qR)}{qR}\right]^2 \qquad (8)$$

where $J_1(x)$ is the first Bessel function. Expansion of Eq. (8) for small qR [10], the forward scattering limit, yields

$$I(q) = I(0)\left(1 - \frac{1}{4}q^2R^2\right). \qquad (9)$$

For a uniform sphere, Eq. (5) yields $R^2 = (5/3)R_g^2$. Then the Guinier analysis, Eq. (4), applied to Eq. (9) yields

$$R_{g,G}/R_g \simeq 1.12. \qquad (10)$$

This is in agreement with the calculational results of Figs. 2 and 3 as ρ grows large.

4. Discussion

We ask why the Guinier analysis of Mie scattering yields radii of gyration different and, for the most part, bigger than the true, geometric radii of gyration of the spherical particles? The general answer lies in the assumptions that go into the derivation of the Guinier regime, discussed above and summarized here as: (1) the volume of the sphere is uniformly illuminated; (2) the particle is isotropic; and (3) only the small $(qR_g < 1)$ regime is considered.

Of these assumptions the most glaring weakness for spherical particles is the first. It is well known that as the sphere increases in either size, refractive index or both, as parameterized by ρ, the interior distribution of the electromagnetic field becomes nonuniform [5]. This occurs when the regime of the Rayleigh–Debye–Gans (RDG) theory, for which Eq. (1) is valid, is left, i.e., when $\rho \gtrsim 1$. This nonuniformity can be thought of as a result of the electromagnetic boundary conditions or, more intuitively, as due to intrasphere multiple scattering between different differential elements of the sphere. Regardless of the physical origin of the nonuniformity, the nonuniform interior illumination means that each differential unit of the sphere does not contribute equally to the scattered field; hence Eq. (1), the beginning equation to the Guinier result, cannot hold.

The redistribution of the interior field away from uniform as ρ increases can be qualitatively described as an enhancement near the inner surface of the sphere. Given this, it is reasonable to propose that the edges of the scattering sphere are more heavily weighted by the field than the interior hence the 'interior-field-weighted' radius of gyration is larger than the geometric radius of gyration. It could be that it is this interior-field-weighted radius of gyration that is seen in the Guinier regime and responsible for $R_{g,G} > R_g$.

This argument may be made quantitative by including interior field weighting in Eq. (1). For simplicity we assume $\rho(\vec{r}) = 1$ everywhere within the sphere and ignore the proportionality constant. We embody the interior field weighting by including it within the integral. Thus, if $E_{int}(\vec{r})$ is the interior field,

$$I(\vec{q}) = \left| \int E_{int}(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \right|^2. \quad (11)$$

Eq. (11) generalizes the RDG notion that the scattering is the Fourier transform of the sphere, to the concept that the scattering is the Fourier transform of the interior field of the sphere. Given Eq. (11) the Guinier analysis can proceed as for Eq. (1) through (6) to yield

$$R_{g,E}^2 = \int E_{int}(r) r^2 dr \Big/ \int E_{int}(r) dr. \quad (12)$$

In Eq. (12) we use $R_{g,E}$ to designate the radius of gyration of the interior-field-weighted sphere.

As for the derivation of the Guinier equation, derivation of Eq. (12) also assumed isotropy, not only of $\rho(\vec{r})$, but now also of $E_{int}(\vec{r})$. Our Mie calculations show that $E_{int}(\vec{r})$ is very anisotropic so our optimism for Eq. (12) must be guarded. Indeed, calculation of $R_{g,E}$ with Eq. (12) as a function of ρ does not compare well to $R_{g,E}$ from the Guinier analysis; the only favorable quality being that $R_{g,E}$ increases with ρ.

The above analyses imply that $R_{g,G}$ is larger than R_g at least in part due to the redistribution of the interior field toward the inner surface of the sphere, but the anisotropy of this redistribution (not to mention its complexity) has thwarted our attempt to find a straightforward physical interpretation.

5. Particle sizing

These results have significance for particle sizing with light scattering. For example, if one were to apply the Guinier analysis to light scattering data from particles with a size parameter of $kR = 12$ and a relative refractive index of $m = 1.33$, an R_g value approximately 40% larger than the true R_g would be measured. This is seen by the result in Fig. 3 for $m = 1.33$ and the calculated value of $\rho = 8$.

Obviously curves such as those in Figs. 2–4 can be used with Guinier measurements to yield accurate values of the spherical particle radius. A good procedure would be to use the Guinier analysis to determine an $R_{g,G}$. Then calculate ρ. (Note this requires some low precision knowledge of the refractive index.) With ρ use plots like Figs. 2–4 to determine the ratio $R_{g,G}/R_g$. Then use this ratio and the measured $R_{g,G}$ to determine the true R_g. We have used this procedure with success, and have never found a second iteration necessary since the improvement for a second iteration is usually less than a few percent, within typical experimental error.

6. Conclusions

Guinier analysis of scattered light from spherical particles is valid only in the limit of the phase shift parameter $\rho \lesssim 1$. This analysis breaks down for $\rho > 1$ since then the interior of the sphere is no longer uniformly illuminated.

Fitting of the Guinier equation to Mie scattering intensities for homogeneous spheres with $\rho > 1$ yields radii of gyration larger than the true, geometric radius of gyration. The ratio of these two quantities, $R_{g,G}/R_g$, is a quasi-universal function of ρ. The functionality is oscillatory with $R_{g,G}/R_g = 1$ as $\rho \to 0$ and $R_{g,G}/R_g \simeq 1.12$ as $\rho \to \infty$, the Fraunhofer diffraction limit. Plots of $R_{g,G}/R_g$ vs. ρ are very similar to Q vs. ρ where Q is the total scattering efficiency, but the oscillatory behaviors are 180° out of phase. Experimental sizing of spherical particles using the Guinier analysis of scattered light must account for these effects when ρ is in the range of $\rho \gtrsim 1$.

Acknowledgements

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References

[1] A. Guinier, Ann. Phys. 12 (1939) 161.
[2] A. Guinier, G. Fournet, C.B. Walker, K.L. Yudowitch, Small Angle Scattering of X-Rays, Wiley, New York, 1955.
[3] S.W. Lovesey, Theory of Neutron Scattering from Condensed Matter, Clarendon Press, Oxford, 1994.
[4] C.M. Sorensen, Aerosol Sci. Tech., to be published.
[5] P.W. Barber, S.C. Hull, Light Scattering by Particles: Computational Methods, World Scientific, Singapore, 1990.
[6] C.F. Bohren, D.R. Huffman, Absorption and Scattering of Light by Small Particles, Wiley, New York, 1983.
[7] C. Oh, C.M. Sorensen, J. Nanoparticle Res. 1 (2000) 369–377.
[8] C.M. Sorensen, D.F. Fischbach, Opt. Commun 173 (2000) 145–153.
[9] E. Hecht, Optics, Addison-Wesley, Reading, 1998.
[10] M. Abramowitz, I.A. Stegun, Handbook of Mathematical Functions, Dover, New York, 1972.