Journal of Nanoparticle Research **1:** 369–377, 1999.

Scaling approach for the structure factor of a generalized system of scatterers

C. Oh and C.M. Sorensen
Department of Physics and Program for Complex Fluid Flows, Kansas State University, Manhattan, KS 66506-2601, USA

Received 7 June 1998; accepted in revised form 3 February 1999

Key words: light scattering, structure factor, nanoscale systems, aerosol, colloids, gels

Abstract

A scaling approach for understanding the broad, general features of scattering of waves from nanoscale systems is presented. The approach uses the concept of a system of scatterers with arbitrary length scales, mass and surface fractal dimensions, and correlations between scatterers. It is based on comparing q^{-1}, where q is the magnitude of the scattering wave vector, to the various length scales of the system of scatterers to determine whether the waves are scattered in phase or not. This comparison along with the fact that only fluctuations in the density of the scatterers scatter waves, yields power laws and cross over points which make up the structure factor. The system of scatterers can represent single spheres, fractal aggregates, or ensembles of such entities in a scattering volume. Hence a large range of experimental situations can be described and are unified under this comprehensive description.

Introduction

The scattering of waves, e.g., light, X-rays, and neutrons, is an important method for determining the structure of nanophase materials (Guinier et al., 1955; Glatter & Kratky, 1982; Martin & Hurd, 1987; Vacher et al., 1988; Schaefer et al., 1986; Freltoft et al., 1986; Schmidt, 1995; Beaucage, 1996; Sorensen, 1997; Bianco, 1998). In particular, the structure of clusters of spheres and ensembles of these clusters is important in a variety of areas including aerosols, colloids and gels. Thus it is important to have an accurate understanding of how to interpret scattering from these systems. This can be difficult, however, given the wide range of length scales involved in complex systems and the great variety of structures.

Much previous work in this area has endeavored to use scattering data to determine the spatial, density–density autocorrelation function for the system. This autocorrelation function and the structure factor, $S(q)$, which describes the scattered intensity as a function of $\vec{q}$, the scattering wave vector, are Fourier transform pairs. Such methods have been applied to the problem of scattering by individual fractal aggregates and systems of aggregates, either dilute or as the gel is approached. The autocorrelation function gives a complete description of the structure of the system, but its accurate determination from the structure factor is limited by uncertainty in the scattering data and the data's limited range in q, both of which are further complicated by the Fourier inversion. Given this, an analysis is considered successful if key length scales and concepts of structural arrangements or shapes can be determined, and this can often be obtained by direct analysis of the structure factor itself. In recent work (Sorensen et al., 1998) we have avoided the density autocorrelation function and considered the structure factor directly for systems of aggregates. Such an approach is not uncommon and has been used frequently for interpretation of scattering from fractal aggregates (Dobbins & Megaridis, 1991; Gangopadhyay et al., 1991; Charalampopoulos, 1992; Sorensen et al., 1992; Koylu et al., 1995). We believe this simple economization allows one to interpret more clearly difficult

features in the structure factor of more complex systems such as the peak that occurs in colloids near the gel point and spinodally decomposing systems and the low q behavior in composite systems.

With this direct view of the structure factor in mind, in this paper we present a scaling description for scattering based on comparison of the scattering length scale, q^{-1}, and the various length scales of the system. Our results are valid under the assumption of single scattering, which for light scattering is good for systems of density low enough so that the effective index of refraction is low, for instance fractal aggregates. For small angle X-ray and neutron scattering a low effective index of refraction is prevalent. Positive features of our scaling theory or approach are that its conceptual simplicity leads to physical understanding and insight for the scattering process and the interpretation of the scattered intensity. Another important feature is that the scaling approach unifies many possible experimental systems such as dense spheres, fractal aggregates of spheres, and ensembles of aggregates in a scattering volume, under the same concept of a 'System of Scatterers' that can describe all situations. The approach can predict correct power law dependencies for $S(q)$ on q and crossover points between two such regions, but it can not completely describe the coefficients of these power laws. It also does not predict the functional details of the crossovers nor interference ripples (Kerker, 1969) that might underlie the power laws. The theory, however, is still of great utility because rarely is the system defined well enough (e.g. precisely monodisperse) that these details are warranted.

The scaling approach

Consider a system of N identical point scatterers, i.e., a system of scatterers. The information about the structure of the system is in the structure factor, which is given by

$$S(\vec{\mathrm{q}}) = \sum_{i,j}^{N} \mathrm{e}^{\mathrm{i}\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_i - \vec{\mathrm{r}}_j)} \tag{1}$$

where $\vec{\mathrm{r}}_i$ and $\vec{\mathrm{r}}_j$ represent the positions of i- and j-th scatterers and $\vec{\mathrm{q}} = \vec{\mathrm{k}}_\mathrm{s} - \vec{\mathrm{k}}_0$ is the scattering wave vector representing the momentum change between the incident ($\vec{\mathrm{k}}_0$) and the scattered ($\vec{\mathrm{k}}_\mathrm{s}$) field momenta. We remark that the structure factor is often defined as the double sum in Eq. (1) but divided by either N or N^2. These different normalizations have their different utilities. We chose the form (1) here because the N dependency is the most explicit in this form. We assume that the system has spherical symmetry, i.e., $S(\vec{\mathrm{q}}) = S(q)$. This assumption is applicable, for example, to the case of scattering from an ensemble of asymmetric clusters with random orientations. We will also ignore polarization effects and hence treat the waves as scalars. This is applicable to the common experimental situation in which the incident polarization is perpendicular to the scattering plane defined by $\vec{\mathrm{k}}_0$ and $\vec{\mathrm{k}}_\mathrm{s}$ and when multiple scattering is not significant.

The inherent length scale for a scattering experiment involving waves of any kind is the inverse of the magnitude of the scattering wave vector, which is given by

$$q = 4\pi\lambda^{-1}\sin(\theta/2). \tag{2}$$

In (2) λ is the wavelength and θ is the experimental scattering angle.

The scaling approach is based on the inherent length scale of the scattering, q^{-1}, and the possible in phase or random addition of waves. For a system of N scatterers there are two limiting situations:

1. If the N scatterers are within q^{-1} of each other, the phases of the N scattered waves will be essentially the same, hence the waves will be in phase and add constructively. Then the total scattered amplitude will be proportional to N, thus the total scattered intensity will be proportional to N^2. From the point of view of Eq. (1), this is when $\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_i - \vec{\mathrm{r}}_j) < 1$, hence the double sum equals N^2.
2. If the N scatterers have all pairs separated by distances greater than q^{-1}, the phases of the N scattered waves will be random, hence the waves will add randomly. Then the total scattered amplitude will be proportional to $\sqrt{N}$, thus the total scattered intensity will be proportional to N. From the point of view of Eq. (1), this is when $\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_i - \vec{\mathrm{r}}_j) > 1$, then the N^2 terms in the sum can be represented as a random walk of N^2 unit steps with an average sum proportional to the square root of the number of steps, i.e., N.

In addition, we remember that:

3. Only fluctuations in density scatter waves in the nonzero scattering angle direction. This is a consequence of the Ewald–Oseen extinction theorem (Hecht, 1998).

Comparison of the scattering length scale, q^{-1}, which is controlled via Eq. (2) in the experiment, to the

length scales of the system of scatterers combined with the three concepts above is the scaling approach.

Applications of the scaling approach

Uniform systems

Consider a system of scatterers in a d-dimensional, spherical region of radius R. Make the density of the scatterers uniform by placing them on a regular lattice with $2a$ the nearest neighbor separation, as drawn in the upper left of Figure 1. Then the only fluctuation in density is on the surface of the system in the form of a discontinuity. We now use the scaling approach to understand how waves are scattered by the system. Envision a situation where the system is covered throughout its volume by smaller imaginary regions of size q^{-1}, thus, $q > R^{-1}$. For all the scatterers in the same imaginary region, the phase factor in Eq. (1) is $\vec{q} \cdot (\vec{r}_1 - \vec{r}_j) \lesssim 1$. Thus they scatter with the same phase (situation 1, above) so that

$$S(q) \propto N_q^2 \tag{3}$$

where N_q is the number of scatterers in the small, imaginary region of size q^{-1}. There are many such regions in the system of radius R, but only those on the surface of the system contribute to the scattering because it is only on the surface of this uniform system that there is a fluctuation in density (condition 3, above). Let n_q be the number of regions of size q^{-1} needed to cover the surface of the system. Because of their size, they must all be separated by distances greater than q^{-1}, thus their scattered waves add randomly (situation 2, above) to yield

$$S(q) \propto n_q. \tag{4}$$

Combining Eqs. (3) and (4), we have

$$S(q) \propto n_q N_q^2. \tag{5}$$

By generalizing Eq. (5) to arbitrary q, we can obtain the characteristic behavior of $S(q)$ for a system of scatterers which has only two length scales, namely, the overall size R and the nearest neighbor separation $2a$. Here we will use a instead of $2a$ as the lower length because for $q^{-1} \leq a$ the imaginary region contains only one or zero point scatterers while for $a \leq q^{-1} \leq 2a$, the imaginary region might contain two or more point scatterers. Since we want no more than one scatterer in the imaginary q^{-1}-region at the smallest length scale, a is the proper choice for that scale. Now consider Eq. (5) for arbitrary q.

(i) $q < R^{-1}$. In this case $n_q \simeq 1$ and $N_q \simeq N$ then Eq. (5) yields

$$S(q) \propto N^2. \tag{6}$$

This result is also obtained from the argument that when $q^{-1} > R$, all N scatterers of the system scatter in phase.

(ii) $R^{-1} < q < a^{-1}$. The most general approach allows for arbitrary mass and surface dimensions, D_m and D_s, respectively. Then in this regime $N_q \sim N(q^{-1}/R)^{D_\mathrm{m}}$ and $n_q \sim R^{D_\mathrm{s}}/(q^{-1})^{D_\mathrm{s}}$, which when applied to Eq. (5) yields

$$S(q) \propto N^2 (qR)^{-2D_\mathrm{m}+D_\mathrm{s}}. \tag{7}$$

The size of the system is represented by both N and R. To eliminate one for the other in Eq. (7) define

$$N = k_\mathrm{m}(R/a)^{D_\mathrm{m}}, \tag{8}$$

$$N_\mathrm{s} = k_\mathrm{s}(R/a)^{D_\mathrm{s}}, \tag{9}$$

where N_s is the number of scatterers on the surface and k_m and k_s are constants of order unity

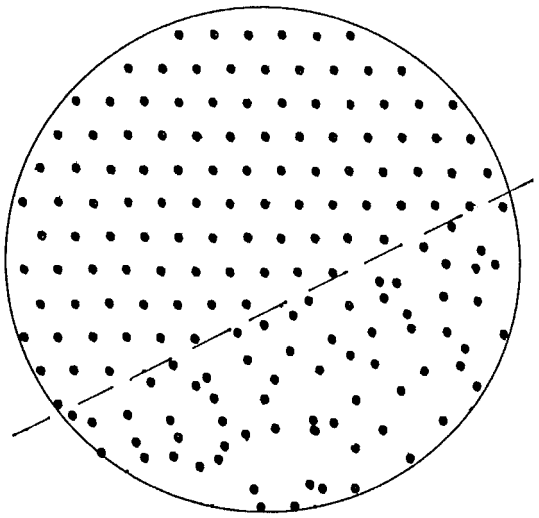

Figure 1. Drawing of a system of point scatterers in a spherical region. In the upper left the scatterers are on a uniform lattice and therefore have no fluctuations in their density within the volume of the sphere. In the lower right the scatterers are displaced randomly from their uniform lattice positions and thus the system has volume fluctuations.

dependent upon the monomer lattice. Then one obtains

$$S(q) \propto k_0 N_s (qa)^{-2D_m+D_s}, \tag{10}$$

where $k_0 = k_m^2/k_s$.

(iii) $q > a^{-1}$. In this regime all scatterers scatter randomly, but only those on the surface contribute to the scattering. Thus $S(q) \propto N_s$. Connection to Eq. (10) at $q = a^{-1}$ implies

$$S(q) \propto k_0 N_s. \tag{11}$$

In summary

$$S(q) \propto \begin{cases} N^2 & \text{for } q < R^{-1}, \\ k_0 N_s (qa)^{-2D_m+D_s} & \text{for } R^{-1} < q < a^{-1}, \\ k_0 N_s & \text{for } q > a^{-1}. \end{cases} \tag{12}$$

Figure 2 shows the generic behavior of Eq. (12). These equations also show how the different q regimes of the structure factor scale with size. When $q < R^{-1}$, the scattering is proportional to the square of the total amount of material; when $q > R^{-1}$ the scattering is proportional to the amount of material on the surface. Thus we call $q < R^{-1}$ the volume region and $q > R^{-1}$ the surface region of the scattering. In the surface region the scattering is also proportional to $k_0 = k_m^2/k_s$ which is dependent upon the lattice arrangement of the monomers. For example, for $d = 2$ one can show $k_0 = (1/3)\pi/\sqrt{2}$, $(1/4)\pi/\sqrt{2}$, and $(4/27)\pi/\sqrt{2}$ for hexagonal, square, and triangular lattices, respectively. However, the product $k_0 N_s$ is not lattice dependent which can be seen by normalization of $S(q)$ by N^2. With the help of Eqs. (8) and (9), this normalization yields

$$N^{-2} S(q) \propto \begin{cases} 1 & \text{for } q < R^{-1}, \\ (qR)^{-2D_m+D_s} & \text{for } R^{-1} < q < a^{-1}, \\ (R/a)^{-2D_m+D_s} & \text{for } q > a^{-1}. \end{cases} \tag{13}$$

This form of our result shows that a graph of $N^{-2}S(q)$ vs. qR would be universal, independent of the lattice, for all sizes when $q < a^{-1}$. This fact and the simplicity of Eq. (13) are an advantage over Eq. (12). However, Eq. (12) explicitly shows the volume and surface regimes and is more facile for considering complex examples.

The result of Eq. (12) displayed in Figure 2 is general and can be applied to a number of physical situations. We give two examples:

(a) *A solid sphere*. Let $a \to 0$ and $D_m = d$, $D_s = d - 1$ where d is the spatial dimension. Then $S(q) \sim q^{-(d+1)}$ when $q > R^{-1}$, a result known as Porod's Law (Porod, 1951; Guinier et al., 1955). If the solid sphere has a fractally rough surface, $d > D_s > d - 1$ and $S(q) \sim q^{6-D_s}$, a well known result (Martin & Hurd, 1987).

(b) *A fractal aggregate*. In a fractal all the monomeric particles are on the surface. Thus $D_m = D_s < d$, then $S(q) \propto q^{-D_m}$ for $q > R^{-1}$, another well known result (Martin & Hurd, 1987; Sorensen, 1998). An aggregate of dense spherical particles with smooth surfaces would apply Eq. (12) twice, once for the fractal and once for the sphere, to yield a total structure factor which is the product

$$S_{TOT}(q) = S_{FA}(q) S_{sphere}(q). \tag{14}$$

This product is depicted in Figure 3 and is consistent with experiment. This was well described by Hasmy et al. (1993).

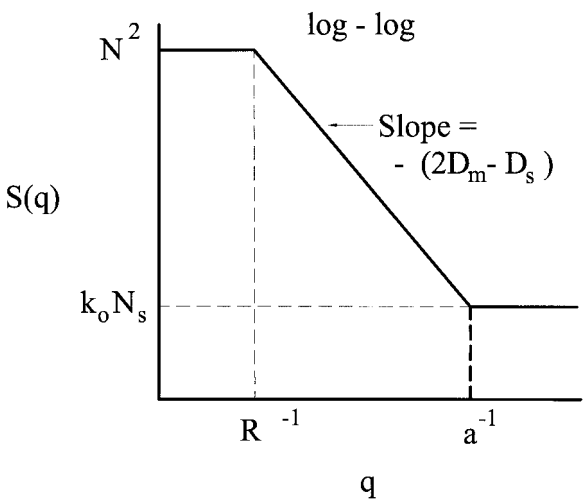

Figure 2. A graphical demonstration of Eq. (12) showing the structure factor for a uniform system of N point scatterers contained in a region of radius R with nearest neighbor separation $2a$. D_m and D_s are the mass and surface fractal dimensions of the system, respectively, N_s is the number of scatterers on the surface, and k_0 is a constant related to the lattice on which the scatterers reside.

Systems with volume fluctuations

So far we have considered scattering only due to fluctuations in density at the surface of the system of scatterers. This is the only possible situation for a fractal aggregate because it is entirely surface, i.e.,

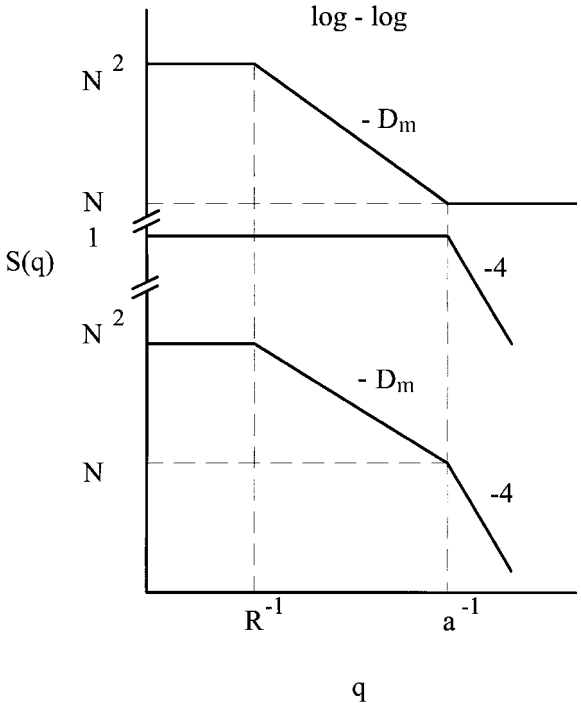

Figure 3. Demonstration of how Eq. (12) can be used to describe the structure factor for a fractal aggregate of radius R composed of N solid spherical monomers of radius a. The aggregate mass fractal dimension is D_m. Upper curve is the fractal aggregate structure factor for point monomers; the middle curve is the solid sphere structure factor, both obtained from Eq. (12). Their product (Eq. (14)) is the total structure factor, the lower curve.

every monomer in the volume of the aggregate is also on the surface of the aggregate. A compact sphere, however, has material not on the surface (which for scattering means not within a distance q^{-1} of the geometric surface) hence within the volume of the sphere which may or may not contribute to the nonzero angle scattering. Above, we assumed there were no fluctuations in density within the volume of the system of scatterers. Here we include 'volume fluctuations' and consider their effect on the structure factor of the system.

Consider again a spherical region of radius R composed of N point scatterers on a regular lattice, as above. To include volume fluctuations displace each monomer randomly relative to its lattice position as drawn on the lower right portion of Figure 2. Doing this not only creates fluctuations in the density of the scatterers throughout the volume, but it also introduces another length scale, the average displacement from the uniform positions. This new length scale should appear in the structure factor and should be describable with our scaling approach.

Let εa, where ε is a multiplicative constant greater than zero, be the average random displacement of the point scatterers from their regular lattice positions. Consider the region $q > a^{-1}$ where, if $\varepsilon = 0$, $S(q) \sim N_s$, i.e., there is only scattering from the surface. Now include volume fluctuation by increasing ε slightly above zero. As long as the inherent length scale of the scattering, q^{-1}, is bigger than εa, i.e., $q < (\varepsilon a)^{-1}$, the volume fluctuations will be invisible to the scattering and then $S(q) \sim N_s$. However, once $q^{-1} \leq \varepsilon a$, i.e., $q \geq (\varepsilon a)^{-1}$, the scattering can 'see' the length εa and then the volume fluctuations contribute to the scattering with each scatterer in the entire sphere contributing equally to the scattering. Also, since $q > a^{-1}$, each scatterer contributes with random phase, so the total scattering is proportional to N. Thus for a system of scatterers with randomized point scatterers, Eq. (12) modifies to

$$S(q) \propto \begin{cases} N^2 & \text{for } q < R^{-1} \\ k_0 N_s (qa)^{-2D_m - D_s} & \text{for } R^{-1} < q < a^{-1} \\ k_0 N_s & \text{for } a^{-1} < q \leq (\varepsilon a)^{-1} \\ N & \text{for } (\varepsilon a)^{-1} < q. \end{cases} \quad (15)$$

This is the most general result in this paper, and it replaces Eq. (12). Figure 4 shows a diagram of this behavior. The transition regime from $k_0 N_s$ to N has a slope of 2, hence a q^2 dependence. This can be understood by expanding the integral form of the structure

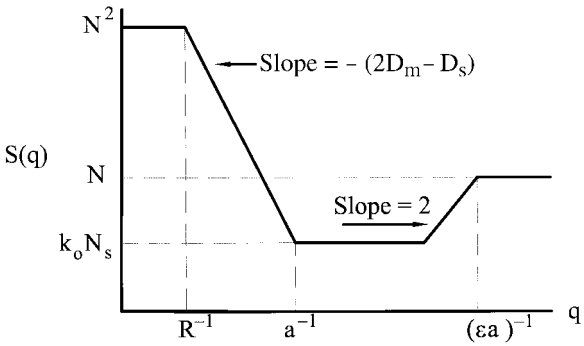

Figure 4. A graphical demonstration of Eq. (15) showing the structure factor for a system of N point scatterers contained in a region of radius R with nearest neighbor separation $2a$.D_m and D_s are the mass and surface fractal dimensions of the system, respectively, N_s is the number of scatterers on the surface, and k_0 is a constant related to the lattice on which the scatterers reside when $\varepsilon = 0$. Finite ε causes volume fluctuations to occur leading to enhanced scattering for $q > (\varepsilon a)^{-1}$.

factor in Eq. (1) at low q as described by Hasmy et al. (1994). Finally, note that as $\varepsilon \to 0$ the fourth regime disappears.

To test the prediction of Eq. (15) a $2d$ circular cluster of point scatterers was created with radius $R = 300a$ on a square lattice. Then the positions of the scatterers were randomized by moving them away from their lattice positions according to

$$\delta x = 2\varepsilon a r, \tag{16}$$

$$\delta y = 3\varepsilon a r. \tag{17}$$

In (16) and (17) δx and δy are the random displacements of a given scatterer along the x and y directions, respectively, and r is a random number bounded as $-1 \leq r \leq 1$. Each scatterer used the same ε but had its own random number r. This cluster was created for various values of ε, and the structure factors were computed using Eq. (1). The results, given in Figure 5 for a variety of ε values, support the prediction of the scaling theory as given in Eq. (15) and drawn schematically in Figure 4.

The small random displacements from a crystal lattice we have used to describe volume fluctuations are reminiscent of thermally induced displacements in a real crystal lattice. Thermally induced fluctuations lead to a decreased scattered intensity of diffraction lines that remain sharp, the Debye–Waller factor (Kittel, 1971). Thermal fluctutations, however, are random with time, and it is the time averaging of the detector that yields the decreased intensity. The fluctuations we introduce are stationary with time and hence are not described by the Debye–Waller factor.

Equation (15) and Figure 4 describe the most general case for scattering of waves from a system of scatterers. As such it can be used to describe nearly any single scattering situation. (The problem of a porous sphere will be considered in a latter publication.) When $\epsilon = 0$, Figure 4 simplifies to Figure 2, and we saw above that this can be used to describe scattering from single, compact spheres and fractal aggregates. Below we describe a common experimental situation.

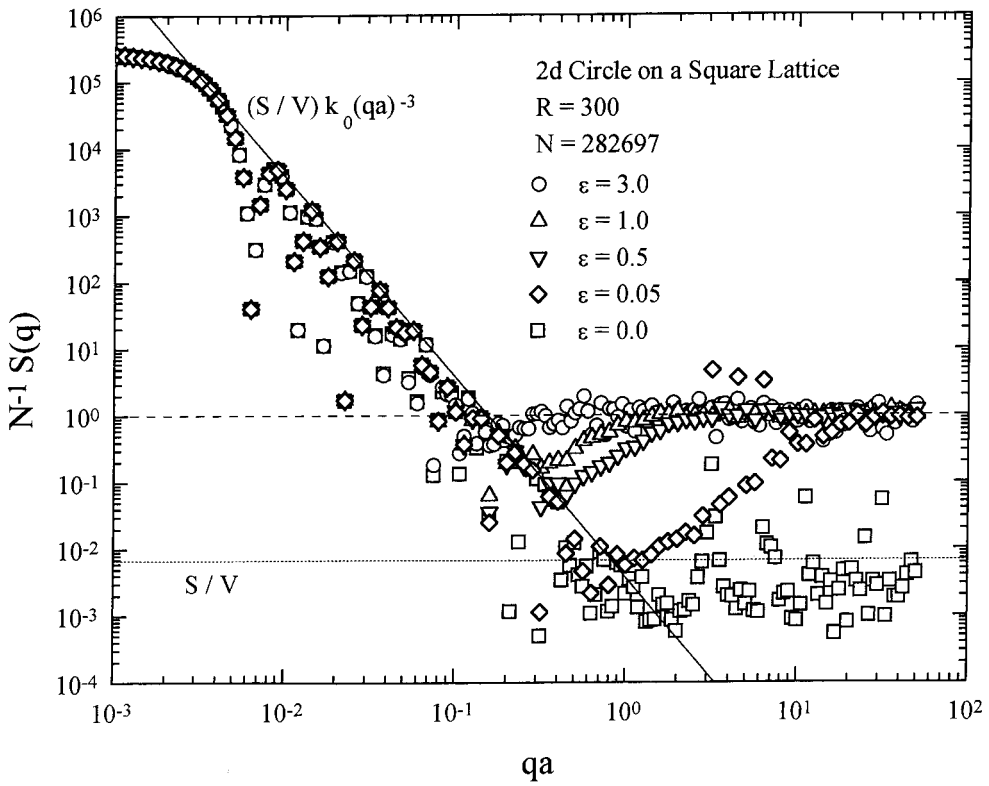

Figure 5. Structure factor normalized by N calculated using Eq. (1) (hence exact) for a system of $N = 282697$ point scatterers in a $d = 2$, $R = 300a$, circular region. When $\varepsilon = 0$ the scatters all reside on a square lattice of spacing $2a$. Curves for increasing ϵ show enhance scattering for $q > (\varepsilon a)^{-1}$ due to volume fluctuations in accord with the scaling prediction of Eq. (15).

a. An ensemble of particles in a scattering volume. We now extend Eq. (15) and Figure 4 to the common situation of an ensemble of particles, either solid spheres or fractal aggregates, in a scattering volume. This extension begins with the approximation that the total structure factor of the entire ensemble is a product of individual structure factors as

$$S_{\mathrm{TOT}}(q) = S_{\mathrm{cc}}(q)S_{\mathrm{sc}}(q)S_{\mathrm{m}}(q). \tag{18}$$

In (18) 'm' means monomer structure factor, 'sc' means the single cluster structure factor representing the monomers that make it up as points, and 'cc' means the cluster–cluster structure factor due to the entire ensemble of clusters in the scattering volume representing each cluster as a point. The equality in Eq. (18) is true only if the clusters are monodisperse. Polydispersity breaks the exact equality, but it still holds to a good approximation (Huang et al., 1998, see, however, Haw et al., 1997).

Each of these three structure factors is described by Eq. (15) and Figure 4 and each is represented in Figure 6. In this example we take the monomers as uniform, compact spheres of radius a. The clusters each have N monomers, have a radius of R, and a fractal dimension of D_{m}. Since D_{m} is still arbitrary, the clusters could be solid spheres ($D_{\mathrm{m}} = d, d \geq D_{\mathrm{s}} \geq d-1$) or fractal aggregates ($D_{\mathrm{m}} = D_{\mathrm{s}} < d$). The ensemble of clusters is contained in a scattering volume of size L. There are N_{c} clusters, $N_{\mathrm{c,s}}$ of which are on the surface of the scattering volume. They are separated by average spacing of $2R_{\mathrm{nn}}$ (the nearest neighbor distance) but the fractional deviation from uniformity is $\varepsilon R_{\mathrm{nn}}$. All three of these, the monomers, the clusters, the scattering volume are a 'system of scatterers', and they each have structure factors in accord with Eq. (15). We draw these structure factors to scale in Figure 6. Their product is the total structure factor and is drawn as the lowest curve in Figure 6.

The total structure factor in Figure 6 can be described as follows. At smallest $q, q < L^{-1}$, the total scattering according to Figure 6 is $N_{\mathrm{c}}^2 N^2$. Note that the total number of monomers in the entire scattering volume is $N_{\mathrm{m}} = N_{\mathrm{c}}N$, hence the total scattering for $q < L^{-1}$ is N_{m}^2. This, of course, follows from condition 1 above; since q^{-1} is larger than the entire scattering volume, all the monomers scatter in phase regardless of the state of aggregation. Next, for $L^{-1} < q < R_{\mathrm{nn}}^{-1}$ fluctuations in density only occur from the surface of the scattering volume; thus, in complete analogy to compact, uniform sphere scattering, a Porod regime for the scattering

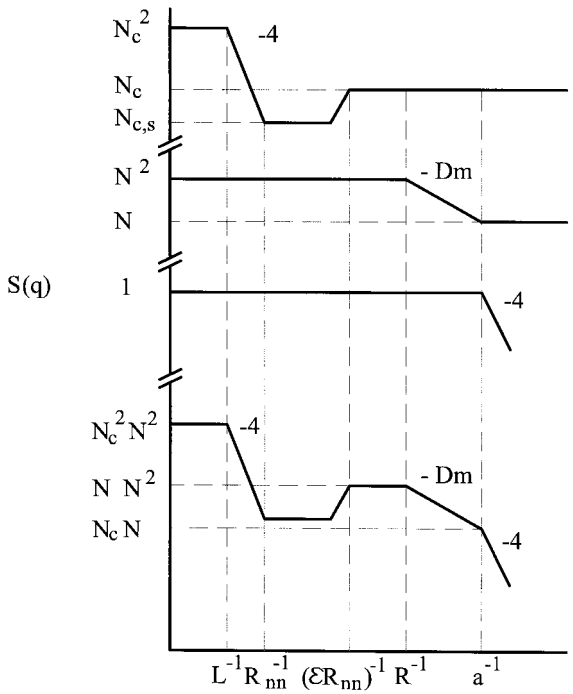

Figure 6. Prediction of Eq. (15) for a system of N_{c} fractal aggregates of mass fractal dimension D_{m} and radius R composed of N uniform spherical monomers of radius a. These aggregates reside in a scattering volume of size L and have a mean nearest neighbor separation of $2R_{\mathrm{nn}}$. The upper curve is the structure factor for the system of clusters in the scattering volume taking them as points. The second curve is the structure factor for a single cluster taking its monomers as points. The third curve is the structure factor for the monomers. The fourth, lowest, curve is the product of the upper three to yield, by Eq. (18), the complete structure factor. The factor $\varepsilon \geq 0$ allows for variation in the ordering of the cluster ensemble. If $\varepsilon = 0$ the cluster ensemble has long range order. As ε increases the ensemble randomizes.

volume is encountered with slope $-(d+1)$, which is -4 in three dimensions. Most often L is much too large hence L^{-1} is much too small to be detected by q in a real experiment. However, it is important to realize that this *scattering volume Porod regime* which begins at $q \simeq L^{-1}$ can continue with increasing q for many orders of magnitude until it can be seen experimentally near R_{nn}^{-1}. This regime is often ignored, neglected, or discounted in the literature (see below). Despite this the scattering volume Porod regime appears in experimental measurements, and its identification can be important for interpretation of structure factor data (Sorensen et al., 1998).

The regime $R_{\mathrm{nn}}^{-1} < q < (\varepsilon R_{\mathrm{nn}})^{-1}$ is system dependent. A dilute system of clusters, where 'dilute' implies

$R_{nn} \gg R$, with no long range cluster–cluster interactions, will have the clusters randomly distributed which is represented by $\varepsilon \to 1$. Then this regime disappears and the total scattering for $R_{nn}^{-1} < q < R^{-1}$ is $N^2 N_c$. From the scaling point of view, one could say that for $\varepsilon \to 1$ the scattering is dominated by volume fluctuations so every cluster scatterers with a strength of N^2 (because $q < R^{-1}$) and the sum of cluster scattering is N_c, because $q > R_{nn}^{-1}$ implies random phase cluster–cluster scattering. On the otherhand, in a dense system, i.e., as $R_{nn} \to R$ cluster crowding causes correlation in their positions hence ε approaches zero as crowding increases. Then the region $R_{nn}^{-1} < q < (\varepsilon R_{nn})^{-1}$ appears with an intensity $N_{c,s} N^2 < N_c N^2$. This is our simple scaling picture (Huang et al., 1998) of why a peak occurs in dense aggregating systems such as sols approaching the gel point (Carpineti & Giglio, 1992, 1993; Bibette et al., 1992; Schatzel & Ackerson, 1992; Robinson & Earnshaw, 1993) and spinodally decomposing fluids (Furukawa, 1985; Hashimoto et al., 1992; Butler et al., 1995). Strong correlations may enhance this peak, but our scaling approach does not account for such effects.

It is of value to compare our generic results of Figures 4–6 to more detailed calculations of the structure factor for an ensemble of N scatterers, be they molecules in a fluid system or particles in a colloid, based on statistical mechanical theory (Klein & D'Aguanno, 1996). In this more traditional approach a delta function at $q = 0$, i.e., $\delta(q)$, results which is customarily omitted because it contributes only to scattering at zero angle. Moreover, what remains at $q \to 0$ is closely related to the isothermal compressibility of the system. Both these features reside in the scaling approach we have presented. To see the similarity one must take the thermodynamic limit, $L \to \infty$, $N \to \infty$ with N/L^d constant, of the scaling approach, a limit which is implicit in the statistical mechanical approach. Consider the scaling $L \to \alpha L$ with $\alpha > 1$. Then $V \to \alpha^d V$ so $N \to \alpha^d N$. The thermodynamic limit occurs as $\alpha \to \infty$. Now consider $N^{-1} S(q)$ as $\alpha \to \infty$. Then the low q peak of the scattering volume Porod regime will increase in magnitude proportional to α^d, i.e., $N^{-1} S(q) \sim \alpha^d$ while its boundary at L^{-1} will decrease proportional to α. Since the slope of this scattering volume Porod regime is $-(d+1)$, the overall effect will be both to heighten and narrow this regime until at $\alpha \to \infty$ it limits to $\delta(q)$ as in statistical mechanic theory. By omitting $\delta(q)$ previous approaches have in essence discarded the scattering volume term in $S(q)$.

With the scattering volume term removed, $S(q) = k_0 N_s$ for $q < (\varepsilon a)^{-1}$. Again normalize as $N^{-1} S(q) = k_0 N_s / N$. Scalings with α are $N \to \alpha^d N$, and $N_s \to \alpha^{d-1} N_s$; so for $q < (\varepsilon a)^{-1}$, $N^{-1} S(q) \to 0$ as $\alpha \to \infty$, the thermodynamic limit. This means the compressibility of our system is zero which is correct because we have assumed no physics for our system that would lead to anything else than an incompressible system. Inclusion of fluctuations with various length scales would create various compressibilities, but this is beyond the scope of our paper.

As mentioned above for $(\varepsilon R_{nn})^{-1} < q < R^{-1}$ the scattering is due to every cluster in the ensemble scattering with phases random with respect to the rest. The regions $R^{-1} < q < a^{-1}$ and $a^{-1} < q$ were described above in reference to Figure 3.

Discussion and conclusion

The scaling approach that we have presented cannot account for some quantitative aspects of the structure factor. It does not give the coefficients of the power law dependencies. Such information is not entirely lacking, however, because the approach does yield correct functional dependencies for these magnitudes such as volume and surface dependencies. The proper coefficients are quite complexly dependent on a variety of parameters. For fractal aggregates the coefficient of $(qR)^{-D_m}$ depends on the cutoff function of the density correlation function for the aggregates and the polydispersity of the aggregates (Nicolai et al., 1994). These details are not part of our general scaling approach.

Classical light scattering theory for hard spheres in the small refractive index limit, the Rayleigh–Debye–Gans theory (Kerker, 1969), yields a series of maxima and minima for $S(q)$ the enveloped of which follows the Porod Law $(qR)^{-(d+1)}$. The coefficients of this envelope are $8/\pi$ and 9, for $d = 2$ and 3, respectively; whereas the scaling approach simply predicts unity for each dimension (see Eq. (13)). Thus the scaling approach both fails to predict these interference ripples and the correct coefficients. It is often observed, however, that modest polydispersity in the sphere diameter washes out these interference 'ripples' leaving only the Porod envelope for the experimentalist to measure. Scattering from random aggregates or associations may not

always yield linear power laws due to other, poorly characterized length scales not considered here.

On the other hand, the scaling approach we have presented makes up for these deficiencies by yielding a general picture of power laws and length scale dependent cross overs for the structure factor for a system of scatterers. Perhaps the most attractive feature of the approach is that the concept of a system of scatterers is general enough to describe a wide variety of experimental situations including solid spheres with both smooth and fractally rough surfaces, fractal aggregates, and any of these particulate systems in a scattering volume with or without correlations between the particulates. Thus all these scattering phenomena are unified and physical insight is gained.

Acknowledgement

This work was supported by NSF grant CTS9709764.

References

Beaucage G., 1996. J. Appl. Crystallogr. 29, 134.
Berry M.V. & I.C. Percival, 1986. Optica Acta 33, 577 .
Bianco H., M. Narkis & Y. Cohen, 1998. J. Appl. Crystallogr. 31, 369.
Bibette J., T.G. Manson, H. Gang & D.A. Weitz, 1992. Phys. Rev. Lett. 69, 981.
Butler B.D., H.J.M. Hanley, D. Hansen & D.J. Evans, 1995. Phys. Rev. Lett. 74, 4468.
Carpineti M. & M. Giglio, 1992. Phys. Rev. Lett. 68, 3327.
Carpineti M. & M. Giglio, 1993. Phys. Rev. Lett. 70, 3828.
Charalampopoulos T.T., 1992. Prog. Energy Combust. Sci. 18, 13.
Dobbins R.A. & C.M. Megaridis, 1991. Applied Optics 30, 4747.
Freltoft T., J.K. Kjems & S. Sinha, 1986. Phys. Rev. B33, 269.
Furukawa H., 1985. Adv. Phys. 34, 703.
Gangopadhyay S., I. Elminyawi & C.M. Sorensen, 1991. Applied Optics 30, 4859.
Glatter, O. & O. Kratky, eds. Small Angle X-Ray Scattering. 1982. Academic Press, New York.
Guinier A., G. Fournet C.B. Walker & K.L. Yudowitch, 1955. Small Angle Scattering of X-Rays. Wiley, New York.
Hashimoto T., M. Takenaka & T. Izumitani, 1992. J. Chem. Phys. 97, 679.
Hasmy A., M. Foret, J. Pelous & R. Jullien, 1993. Phys. Rev. B48, 9345.
Hasmy A., E. Anglaret, M. Foret, J. Pelous & R. Jullien, 1994. Phys. Rev. B50, 6006.
Haw M.D., W.C.K. Poon & P.N. Pusey, 1997. Phys. Rev. E56, 1918.
Hecht E., Optics 1998. Addison-Wesley, Reading, MA.
Huang, H., C. Oh & C.M. Sorensen, 1998. Phys. Rev. E57, 875.
Kerker, M., The Scattering of Light and Other Electromagnetic Radiation. 1969. Academic, New York.
Kittel, C., Introduction to Solid State Physics. 1971. Wiley, New York.
Klein R. & B. D'Aguanno, 1996. In: Brown, W. ed. Light Scattering Principles and Development, Clarendon, Oxford, p. 30.
Köylü, U.O., G.M. Faeth, T.L. Farias & M.G. Carvalho, 1995. Combust. Flame 100, 621.
Martin, J.E. & A.J. Hurd, 1987. J. Appl. Cryst. 20, 61.
Nicolai, T., D. Durand & J.-C. Gimel, 1994. Phys. Rev. B50, 16357.
Porod, G., Kolloid Z. 1951. 124, 83.
Robinson, D.J. & J.C. Earnshaw, 1993. Phys. Rev. Lett. 71, 715.
Schaefer D.W., J.E. Martin & K.D. Keefer, 1986. Phys. Rev. Lett. 56, 2199.
Schätzel, K. & B.J. Ackerson, 1992. Phys. Rev. Lett. 68, 337.
Schmidt, P.W., 1995. In: Brumberger H., ed. Modern Aspects of Small-Angle Scattering. Kluwer, Dordrecht, p. 1.
Sorensen C.M., J. Cai & N. Lu, 1992. Applied Optics 31, 6547.
Sorensen, C.M., 1997. In: Birdi, K.S., ed. Handbook of Surface and Colloidal Chemistry. CRC, Boca Raton, FL.
Sorensen C.M., C. Oh, P.W. Schmidt & T. Rieker, 1998. Phys. Rev. E58, 4666.
Vacher R., T. Woignier, J. Pelous & E. Courtens, 1988. Phys. Rev. B37, 6500.