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Determination of density correlation functions from scattering of polychromatic light

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Abstract

It is shown that for some many-particle systems with a high degree of symmetry, i.e. systems with homogeneous and/or isotropic density correlations, the density correlation function may be determined by measurements of the changes in the spectrum of polychromatic light scattered by the particles. The use of spectral measurements for such inverse problems may appreciably reduce the number of measurements required to uniquely determine the system structure. © 1999 Elsevier Science B.V. All rights reserved.

The inverse scattering problem is concerned with the reconstruction of the scattering potential from field measurements outside the scatterer. This is usually done by measuring the scattered field generated by scattering an incident monochromatic field for many directions of incidence and scattering. Recent work, however, has demonstrated that some information about source structure may be determined from measurements of changes in the spectrum of the scattered radiation [1–3]. More recently, it has been shown [4] that the spectrum of light scattered off of systems of particles depends upon the generalized structure function of the system. In this paper, we demonstrate that for certain particle systems, the density correlation function may be determined by illuminating the scatterer by polychromatic light and measuring the complete spectrum of the scattered light in a finite number of directions of scattering, provided that some information about the system is known.

Consider a polychromatic plane wave with spectrum $S^{(i)}(\omega)$, ω being the frequency, incident on a random distribution of identical particles in a direction specified by a unit vector $\boldsymbol{u}_0$, and let us examine the scattered field at a distance r in the far zone of the scatterer, in direction specified by a unit vector $\boldsymbol{u}$ (see Fig. 1). It follows from the analysis given in a recent paper [4] that the spectrum $S^{(\infty)}(r\boldsymbol{u},\omega)$ of the field in the far zone is given by the expression

$$S^{(\infty)}(r\boldsymbol{u},\omega) = \frac{1}{r^2}|\tilde{U}[k(\boldsymbol{u}-\boldsymbol{u}_0),\omega]|^2 \times \mathscr{S}[k(\boldsymbol{u}-\boldsymbol{u}_0)]S^{(i)}(\omega), \quad (1)$$

where $k=\omega/c$, c is the speed of light in vacuum, and

$$\tilde{U}(\boldsymbol{K},\omega) = \int U(\boldsymbol{r}',\omega)\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}'} d^3r' \quad (2)$$

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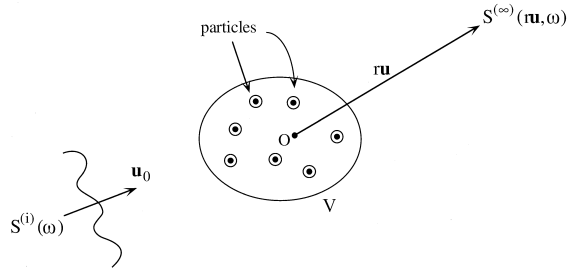

Fig. 1. Illustration of the notation relating to Eq. (1).

is the spatial Fourier transform of the scattering potential of each particle. Furthermore,

$$\mathscr{S}(\boldsymbol{K}) \equiv \left\langle \left| \sum_j e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_j} \right|^2 \right\rangle = \left\langle \sum_j \sum_{j'} e^{i\boldsymbol{K}\cdot(\boldsymbol{r}_j - \boldsymbol{r}_{j'})} \right\rangle \tag{3}$$

is the generalized structure function of the particle system, and the angular brackets denote the average, taken over the ensemble of positions $\boldsymbol{r}_j$ of the particles. Eq. (1) applies to systems for which the scattering is sufficiently weak, i.e. systems for which the first Born approximation applies.

One is frequently interested in determining the average positions of the particles relative to one another. If the system consists of N 'point particles', we may define a density function by the relation

$$n(\boldsymbol{r}) = \sum_{j=1}^{N} \delta^{(3)}(\boldsymbol{r} - \boldsymbol{r}_j), \tag{4}$$

where $n(\boldsymbol{r})d^3r$ represents the number of particles in a volume element d^3r, centered on the point $\boldsymbol{r}$, and $\delta^{(3)}$ is the three-dimensional Dirac delta function. The two-point density correlation function is then defined by the equation

$$C_n(\boldsymbol{r}_1,\boldsymbol{r}_2) = \langle n(\boldsymbol{r}_1)\, n(\boldsymbol{r}_2)\rangle = \left\langle \sum_j \sum_{j'} \delta^{(3)}(\boldsymbol{r}_1 - \boldsymbol{r}_j)\, \delta^{(3)}(\boldsymbol{r}_2 - \boldsymbol{r}_{j'}) \right\rangle, \tag{5}$$

where $\langle \cdots \rangle$ again represents the ensemble average. If

$$\tilde{C}_n(\boldsymbol{q}_1,\boldsymbol{q}_2) \equiv \iint C_n(\boldsymbol{r}_1,\boldsymbol{r}_2)\, e^{-i\boldsymbol{q}_1\cdot\boldsymbol{r}_1} e^{-i\boldsymbol{q}_2\cdot\boldsymbol{r}_2} d^3r_1 d^3r_2 \tag{6}$$

denotes the spatial Fourier transform of the correlation function, we find on substituting Eq. (5) into Eq. (6) that

$$\tilde{C}_n(\boldsymbol{q}_1,\boldsymbol{q}_2) = \left\langle \sum_j \sum_{j'} e^{-i\boldsymbol{q}_1\cdot\boldsymbol{r}_j} e^{-i\boldsymbol{q}_2\cdot\boldsymbol{r}_{j'}} \right\rangle. \tag{7}$$

Comparison of Eqs. (7) and (3) shows that the structure function may be written as [5]

$$\mathscr{S}(\boldsymbol{q}) = \tilde{C}_n(-\boldsymbol{q},\boldsymbol{q}), \tag{8}$$

i.e. it is equal to the 'antidiagonal' element of the Fourier transform of the density correlation function. On substituting from Eq. (8) into Eq. (1) it follows that

$$\tilde{C}_n\big[-k(\boldsymbol{u}-\boldsymbol{u}_0), k(\boldsymbol{u}-\boldsymbol{u}_0)\big] = \frac{r^2}{|\tilde{U}\big[k(\boldsymbol{u}-\boldsymbol{u}_0),\omega\big]|^2} \left[\frac{S^{(\infty)}(r\boldsymbol{u},\omega)}{S^{(i)}(\omega)} \right]. \tag{9}$$

Eq. (9) shows that the far zone field spectrum contains information about the 'antidiagonal' elements of $\tilde{C}_n$. However, such information is, in general, not sufficient to reconstruct the density correlation function. For certain systems of high symmetry, though, the antidiagonal elements do provide useful information, as we will now show.

Let us restrict our attention to systems in a fluid state, for which the density correlation function is homogeneous and isotropic. Then the density correlation function has the form

$$C_n(\boldsymbol{r}_1,\boldsymbol{r}_2) = C_n(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \text{ when } \boldsymbol{r}_1 \in V, \boldsymbol{r}_2 \in V = 0 \text{ otherwise}, \tag{10}$$

V denoting the volume containing the system. We will consider, for simplicity, a system confined to a spherical domain of radius R. It can then be shown that the structure function for the system is given by the equation (see Appendix)

$$\mathscr{S}(\boldsymbol{q}) = \int_{(4\pi)} \int_0^{2R} \left[\frac{4}{3}\pi R^3 - \pi R^2 r + \frac{\pi}{12} r^3 \right] \times C_n(r)\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d^3r. \tag{11}$$

We see that the structure function is related to the Fourier transform of the product of the density correlation function and a factor that depends upon the size of the entire system. This equation may be

simplified by using the so-called Ursell function [5], defined by the expression

$$H_n(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\equiv C_n(|\boldsymbol{r}_1-\boldsymbol{r}_2|)-\langle n\rangle^2, \tag{12}$$

$\langle n\rangle$ being the average density of the particles. Rewriting Eq. (11) in terms of the Ursell function, we have

$$\begin{aligned}\mathscr{S}(\boldsymbol{q}) = &\int_{(4\pi)}\int_0^{2R}\left[\frac{4}{3}\pi R^3-\pi R^2 r+\frac{\pi}{12}r^3\right]\\ &\times H_n(r)\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d^3r\\ &+\langle n\rangle^2\int_{(4\pi)}\int_0^{2R}\left[\frac{4}{3}\pi R^3-\pi R^2 r\right.\\ &\left.+\frac{\pi}{12}\boldsymbol{r}^3\right]e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d^3r.\end{aligned} \tag{13}$$

If correlations between particle positions are sufficiently short-ranged, as in liquids and gases at temperatures far from critical transitions, the Ursell function will have an essentially zero value for values of r larger than a few particle diameters, a distance much smaller than the size of the system R. The first term of Eq. (13) may then be simplified and one finds that

$$\begin{aligned}&\int_{(4\pi)}\int_0^{2R}\left[\frac{4}{3}\pi R^3-\pi R^2 r+\frac{\pi}{12}r^3\right]H_n(r)\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d^3r\\ &\quad\approx\frac{4}{3}\pi R^3\int_{(4\pi)}\int_0^{2R}H_n(r)\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}d^3r.\end{aligned} \tag{14}$$

On examining the second term of Eq. (13), it becomes clear that for large values of $|\boldsymbol{q}|R$ this term will be negligible. To see this, we may evaluate the second part of Eq. (13), denoted $\mathscr{S}_2(\mathbf{q})$, and arrive at the result

$$\mathscr{S}_2(\boldsymbol{q})=\frac{(4\pi)^2\langle n\rangle^2}{q^6}\left[-qR\cos qR+\sin qR\right]^2. \tag{15}$$

In the limit $qR\gg 1$, this function will have the limiting form

$$\mathscr{S}_2(\boldsymbol{q})\approx\langle n\rangle^2(4\pi)^2\frac{R^2}{q^4}\cos^2 qR\sim V^{2/3}. \tag{16}$$

It is clear from Eq. (14) that the first part of the structure function depends linearly upon V. In the limit $qR\gg 1$, then, the structure factor will be dominated by the first term in Eq. (13). In the opposite limit $qR\ll 1$, we may use the approximate relations $\sin qR\approx qR$ and $\cos qR\approx 1-(qR)^2/2$ to write $\mathscr{S}_2(\boldsymbol{q})$ as

$$\mathscr{S}_2(\boldsymbol{q})\approx(4\pi)^2\frac{R^6}{4}\sim V^2, \tag{17}$$

and this term will dominate the structure factor for sufficiently small qR. Neglecting this forward scattering contribution in particle scattering calculations is standard practice in X-ray diffraction. See, for instance, Ref. [6]. As long as the scattered field is measured in directions not too close to the forward direction, we may neglect the second term in Eq. (13). Under these conditions, the structure function may be expressed in a simple form as

$$\mathscr{S}(\boldsymbol{q})=V\tilde{H}_n(q), \tag{18}$$

where the Fourier transform of $H_n(r)$,

$$\tilde{H}_n(q)=\int H_n(r')\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}'}d^3r', \tag{19}$$

is a spherically symmetric function of $q=|\boldsymbol{q}|$.

It is now straightforward to obtain an approximate solution to the inverse problem. Substituting Eq. (18) into Eq. (9), we find that the Ursell function is related to the measured spectra by the expression

$$\begin{aligned}\tilde{H}_n\left[k|\boldsymbol{u}-\boldsymbol{u}_0|\right]=&\frac{r^2}{V}\frac{1}{|\tilde{U}\left[k(\boldsymbol{u}-\boldsymbol{u}_0),\omega\right]|^2}\\ &\times\left[\frac{S^{(\infty)}(r\boldsymbol{u},\omega)}{S^{(i)}(\omega)}\right].\end{aligned} \tag{20}$$

The spectrum of the incident and the scattered field can be determined by experiment. If we assume that the potential U of the particles is known, one can then determine $\tilde{H}_n[k|\boldsymbol{u}-\boldsymbol{u}_0|]$.

Note that $\tilde{H}_n$ depends only upon the magnitude of the momentum transfer vector, $q=|k(\boldsymbol{u}-\boldsymbol{u}_0)|$. In the conventional inversion techniques one varies $\boldsymbol{u}$ and $\boldsymbol{u}_0$ to determine all the components of $\tilde{H}_n$ within a sphere of radius $|\boldsymbol{q}|\le 2\omega/c$ (the Ewald limiting sphere; see Fig. 2(a).) However, because the unknown function H_n does not depend upon frequency, we may fix the directions $\boldsymbol{u}$ and $\boldsymbol{u}_0$ and

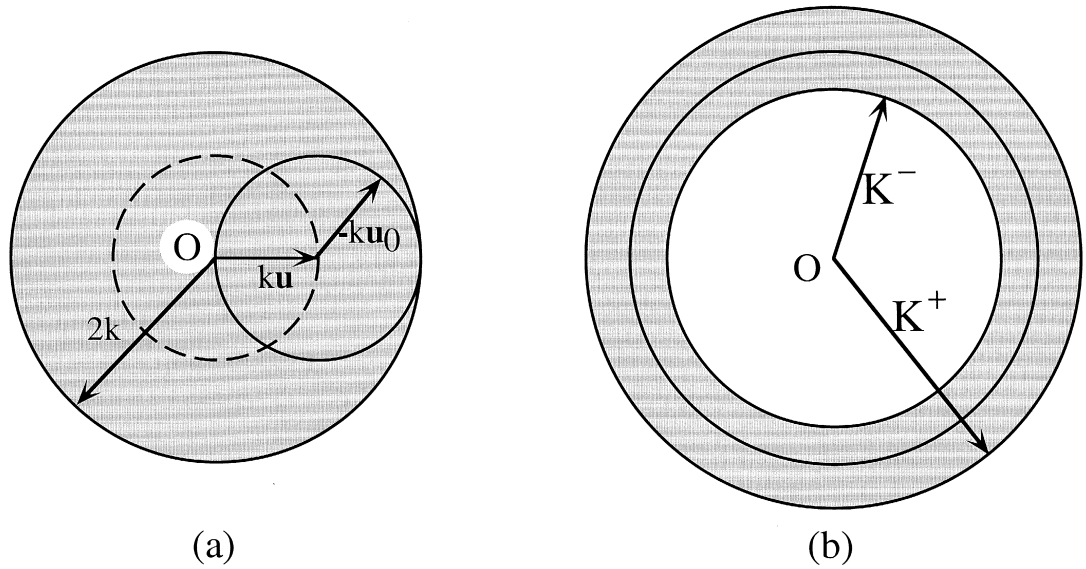

Fig. 2. The region of Fourier space available for reconstructions using: (a) the Ewald sphere method; and (b) the method outlined in this paper. The radii K^+, K^- in Fourier space are defined by the formula:
$K^{\pm} = \frac{1}{c}\left[\omega_0 \pm \frac{\Delta\omega}{2}\right]|\boldsymbol{u} - \boldsymbol{u}_0|$.

vary ω to determine all of the values of $\tilde{H}_n$ in a spherical shell defined by the $\boldsymbol{q}$ values such that

$$\left[\omega_0 - \frac{\Delta\omega}{2}\right]\frac{|\boldsymbol{u}-\boldsymbol{u}_0|}{c} \le |\boldsymbol{q}| \le \left[\omega_0 + \frac{\Delta\omega}{2}\right]\frac{|\boldsymbol{u}-\boldsymbol{u}_0|}{c}. \tag{21}$$

Here ω_0 is the center frequency of the spectrum of the incident field and $\Delta\omega$ is the spectral width (see Fig. 2(b).)

If incident light with a sufficiently broadband spectrum (e.g. $\Delta\omega \sim 2\omega_0$) is used to illuminate the scatterer, it can be seen from Eq. (21) that a measurement of the spectrum of the backscattered light ($|\boldsymbol{u} - \boldsymbol{u}_0| = 2$) will provide nearly all the Fourier components of $\tilde{H}_n$ within a sphere of radius

$$|\boldsymbol{q}| \le \frac{4\omega_0}{c}, \tag{22}$$

i.e. within a sphere whose radius is twice the radius of the Ewald limiting sphere associated with the frequency ω_0. One may then obtain a band-limited reconstruction of the Ursell function $H_n(r)$ by measuring the scattered spectrum for a *single* direction of incidence and a *single* direction of scattering.

If the incident light has a narrower spectral width, a single scattering measurement will not provide information about the Fourier components of significantly low frequencies, as seen from Eq. (21). But by varying $\boldsymbol{u}$, $\boldsymbol{u}_0$ over a *finite* number of directions, we may fill almost all of a spherical domain in $\boldsymbol{q}$ space of radius

$$|\boldsymbol{q}| \le \frac{2\omega_0 + \Delta\omega}{c}. \tag{23}$$

(see Fig. 3.) Data obtained in this way would still likely exclude a small region around the origin, because of the difficulty encountered with the forward scattering direction, noted earlier [associated with the second term in Eq. (13)].

It should be noted that if the incident field contains frequencies resonant with the individual particle potentials $U(\boldsymbol{r},\omega)$, those frequencies will be strongly scattered, making the use of Eq. (1) for the analysis invalid. But this difficulty may be avoided

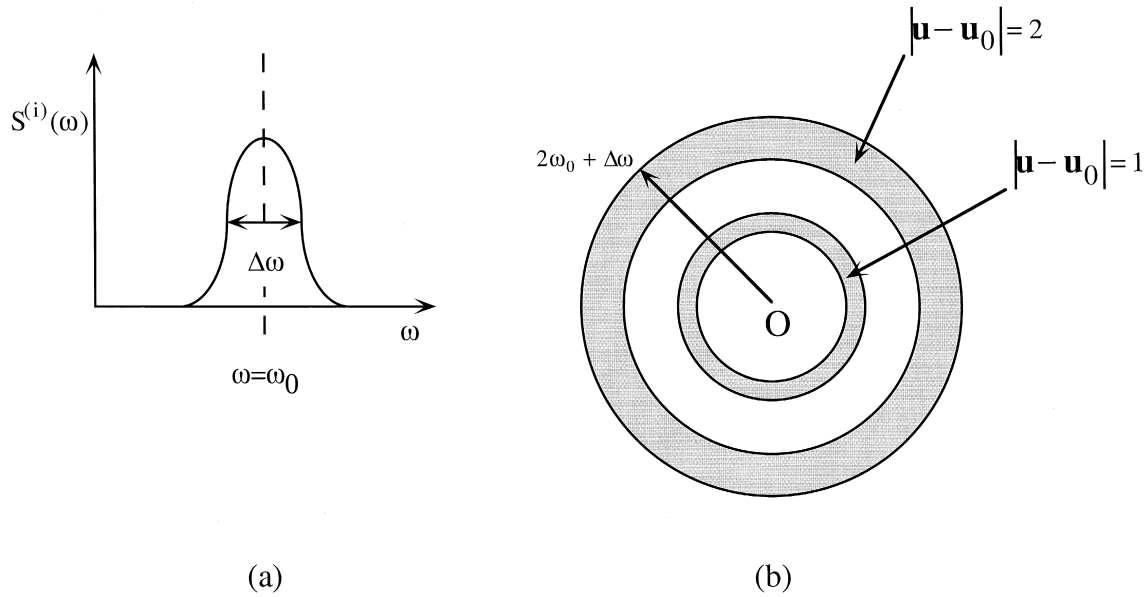

Fig. 3. Illustration of the method by which the Fourier components represented by points within the Ewald limiting sphere may be obtained using the measured spectrum for only a finite number of directions of scattering and/or of incidence. The spectrum (a) of the incident field has a width of $\Delta\omega$ and a center frequency of ω_0. With two different measurement positions, one can obtain values on shells of two different thicknesses and diameters (b). For a larger, but still finite, number of measurement positions, one can, in principle, fill almost the whole sphere of radius $2\omega_0 + \Delta\omega$.

by using a narrower-band off-resonance spectrum for the measurements and making measurements for several directions of incidence and scattering.

So far we have concerned ourselves with systems which possess a high degree of symmetry. We have seen that when the Ursell function is homogeneous and isotropic one may reconstruct it by the use of spectral information from one direction of incidence and one direction of scattering. Spectral methods may still, however, appreciably reduce the amount of measurements required for reconstructing systems which are not isotropic.

Consider a system for which the density correlation function is homogeneous, but depends upon direction, i.e.

$$C_n(\boldsymbol{r}_1,\boldsymbol{r}_2) = C_n(\boldsymbol{r}_2-\boldsymbol{r}_1) \text{ when } \boldsymbol{r}_1 \in V, \boldsymbol{r}_2 \in V$$
$$= 0 \text{ otherwise.} \qquad (24)$$

If the correlations between the positions of the particles are sufficiently short-ranged, and one avoids measurements of the scattered field close to the forward direction, one finds that

$$\tilde{H}_n[k(\boldsymbol{u}-\boldsymbol{u}_0)] = \frac{r^2}{V}\frac{1}{|\tilde{U}[k(\boldsymbol{u}-\boldsymbol{u}_0,\omega)]|^2} \times\left[\frac{S^{(\infty)}(r\boldsymbol{u},\omega)}{S^{(i)}(\omega)}\right]. \qquad (25)$$

This equation differs from Eq. (20) in that $\tilde{H}_n$ now depends upon both the direction and magnitude of the momentum transfer vector $\boldsymbol{q} = k(\boldsymbol{u}-\boldsymbol{u}_0)$. For this case, one may fix the magnitude of the difference vector $(\boldsymbol{u}-\boldsymbol{u}_0)$ and allow the direction of this difference vector to vary over all possible directions. This would be equivalent to fixing the relative orientation of the incident field and detector and rotating the sample through all possible directions. From this information, using the complete spectrum, one will again obtain all of the Fourier components of $\tilde{H}_n(\boldsymbol{q})$ within a spherical shell whose boundaries are given by the inequality (21). This method makes it possible

to keep the incident field and the detector in fixed positions relative to one another.

These methods of inversion would seem to have some advantages over the traditional methods using the concept of Ewald's spheres. In neutron scattering experiments, spectral methods have been used in a restricted form to investigate the structure of particle systems. In the von Laue method, for instance, the spectrum of elastically scattered neutrons is measured for a single direction of incidence and scattering to determine the Bragg scattering peaks. This method applies only to scattering from periodic structures, while the present analysis applies more generally (cf. Ref. [7]). By using the data provided by the full continuous spectrum of the scattered field, one can avoid the need to take a large number of measurements for different directions of the incident and the scattered field.

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Appendix A. Derivation of Eq. (11)

We wish to determine the value of $\tilde{C}_n(-\boldsymbol{q},\boldsymbol{q})$ when $C_n(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is a homogeneous, isotropic function

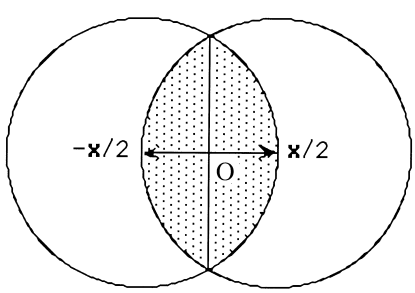

Fig. 4. Illustration of the region of overlap (shaded) of two spheres of the same radii whose centers are separated by a distance $|\boldsymbol{x}|$.

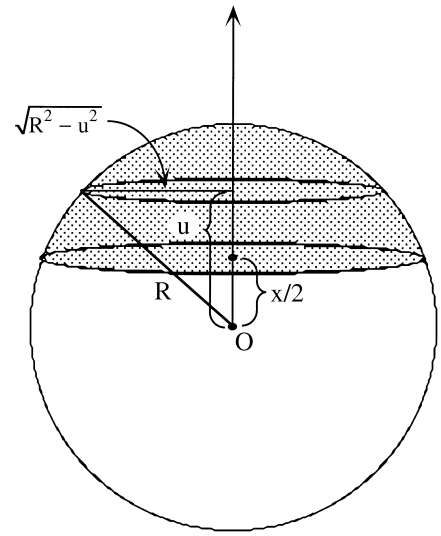

Fig. 5. Illustration of the notation used to evaluate the overlap volume defined by Eq. (A4).

of the form of Eq. (10). We may rewrite Eq. (10) in the equivalent form

$$C_n(\boldsymbol{r}_1,\boldsymbol{r}_2) = B(\boldsymbol{r}_1)\,B(\boldsymbol{r}_2)\,C_n(|\boldsymbol{r}_1-\boldsymbol{r}_2|), \tag{A1}$$

where

$$B(\boldsymbol{r}) = \begin{cases} 1 & \text{when } |\boldsymbol{r}| \le R \\ 0 & \text{when } |\boldsymbol{r}| > R \end{cases} \tag{A2}$$

Defining new variables $\boldsymbol{x} \equiv (\boldsymbol{r}_1+\boldsymbol{r}_2)/2$ and $\boldsymbol{x}' \equiv \boldsymbol{r}_2 - \boldsymbol{r}_1$, the antidiagonal Fourier components of $C_n(\boldsymbol{r}_1,\boldsymbol{r}_2)$ can readily be shown to be given by the formula:

$$\tilde{C}_n(-\boldsymbol{q},\boldsymbol{q}) = \iint B(\boldsymbol{x}+\boldsymbol{x}'/2)\,B(\boldsymbol{x}-\boldsymbol{x}'/2) \times C_n(\boldsymbol{x}')\,e^{-i\boldsymbol{q}\cdot\boldsymbol{x}'}d^3x d^3x'. \tag{A3}$$

The domain of integration of the $\boldsymbol{x}$ variable is the overlap volume of two spheres separated by a distance x as shown in Fig. 4, and the value of this integral is then just the volume of the overlap, which will depend upon the magnitude of $\boldsymbol{x}$. The overlap region consists of two spherical caps, each of which may be expressed as an integral over a series of thin disks. As may be seen from Fig. 5, the overlap volume is given by the expression

$$(\text{overlap volume}) = 2\times\int_{x/2}^{R}\pi(R^2-u^2)\,\mathrm{d}u. \tag{A4}$$

The integration is straightforward, and leads to the result that

$$\int B(\boldsymbol{X}+\boldsymbol{x}/2)\,B(\boldsymbol{X}-\boldsymbol{x}/2)\,d^3X = \begin{cases} \frac{4}{3}\pi R^3 - \pi R^2 x + \frac{\pi}{12}x^3 & |\boldsymbol{x}| \le 2R \\ 0 & |\boldsymbol{x}| > 2R \end{cases}. \quad \text{(A5)}$$

Substituting Eq. (A5) into Eq. (A3), one finds that

$$\tilde{C}_n(-\boldsymbol{q},\boldsymbol{q}) = \int_{(4\pi)}\int_0^{2R}\left[\frac{4}{3}\pi R^3 - \pi R^2 x + \frac{\pi}{12}x^3\right] \times C_n(x)\,e^{-i\boldsymbol{q}\cdot\boldsymbol{x}}d^3x. \quad \text{(A6)}$$

If Eq. (8) is now used, Eq. (11) follows.

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