In the general case of a random isotropic fractal, the *fractal* or *Hausdorff* dimension d_f is defined via

$$n(r) \sim (r/a)^{d_f}. \tag{2.12.12}$$

This is a generalization of the relation $n \sim r^d$ valid for normal compact objects. The fractal dimension of a polymer is thus $1/\nu$. The pair distribution function and static structure factor for a general fractal are given by

$$\begin{aligned} g_F(r) &\sim n/r^d \sim 1/(a_f^d r^{d-d_f}), \qquad \text{or } \alpha = d - d_f \\ S(q) &\sim (qa)^{-d_f}. \end{aligned} \tag{2.12.13}$$

It is very easy to get a physical feel for what the correlation and scattering functions mean by looking at Figs. 2.12.4 and 2.12.5. Fig. 2.12.4 is an electron micrograph of an aggregate of gold particles formed under highly nonequilibrium conditions. The uniform-size 50Å particles were in stable suspension because of repulsion between the like surface charges. The charges were then chemically removed. The particles diffused until they collided and then stuck wherever they hit. The process is known as *diffusion limited aggregation* (DLA). The mass correlation function was calculated from the electron micrograph by randomly picking a point in the cluster, drawing a circle of radius r and counting the number of particles intersecting the circle. The process was repeated for many origins and many radii. Since the picture is a projection of the structure in two dimensions, it is fractal with $g(r) \sim 1/r^{2-d_f}$, and the log-log plot indicates a slope of 0.25 ($d_f = 1.75 \pm 0.05$) until r approaches the size of the cluster at which point it rapidly decreases.

The same system was studied by both neutron scattering and light scattering. The resulting structure function is shown in Fig. 2.12.5. $S(q)$ should have the form q^{-d_f} until q reaches a crossover value. The $S(q)$ data on this sample give $d_f \sim 1.80$. For higher q the scattering probes distances smaller than a particle size, and the objects no longer look fractal. Fig. 2.12.5 also serves as a good example of the range covered by light ($q \geq 2\pi/\lambda \geq 2\pi/1500\text{Å}$) and neutron scattering ($q \geq 2\pi/1\text{Å}$).

Appendix 2A Fourier transforms

In this appendix, we will review Fourier transforms for functions of one- and d-dimensional continuous variables and for functions defined at lattice sites on one- and d-dimensional lattices.

1 One dimension

We begin with a function $f(x)$ of a single variable x in the interval $[-L/2, L/2]$ (i.e. $-L/2 \leq x \leq L/2$). If $f(x)$ satisfies reasonable continuity and boundedness conditions (e.g. it does not have an infinite number of zeros in some finite interval of x), it can be expanded in a uniformly convergent Fourier series:

$$f(x) = \sum_q \psi_q(x) f(q) , \tag{2A.1}$$

where $\psi_q(x)$ satisfies the same boundary conditions as $f(x)$. Common boundary conditions on $f(x)$ are $f(x = \pm L/2) = 0$ or $f'(x = \pm L/2) = 0$. In condensed matter physics, one is often interested in bulk systems in the thermodynamic limit, $L \to \infty$, for which most physical properties of interest do not depend on the boundary conditions. In this case, any physically reasonable boundary condition can be imposed. The periodic boundary condition requiring $f(x)$ to be a periodic function of period L,

$$f(x) = f(x + L) , \tag{2A.2}$$

is computationally the simplest and is almost universally used in situations where surface properties are not relevant. The condition (2A.2) is equivalent to wrapping the line of length L on a circle of circumference L and tying the two ends together. The functions $\psi_q(x)$ must satisfy the periodic boundary condition and can be chosen to be

$$\psi_q(x) = Ae^{iqx} , \tag{2A.3}$$

where

$$q = \frac{2\pi}{L} n, \qquad n = 0, \pm 1, \pm 2, \ldots \tag{2A.4}$$

and where A is an arbitrary normalization constant. The functions e^{iqx} satisfy the *orthogonality condition,*

$$\int_{-L/2}^{L/2} dx e^{i(q-q')x} = \frac{\sin[(q-q')L/2]}{[(q-q')/2]} = L\delta_{n,n'} = L\delta_{q-q',0} , \tag{2A.5}$$

where $\delta_{a,b}$ is the Kronecker delta ($\delta_{a,b} = 1$ if $a = b$ and $\delta_{a,b} = 0$ otherwise) and the *completeness condition,*

$$\sum_q e^{-iqx} = \lim_{N\to\infty} \sum_{N-1}^{N-1} e^{-i(2\pi n/L)x} = \lim_{N\to\infty} \frac{\sin[2\pi(N - 1/2)x/L]}{\sin(\pi x/L)} = L\delta(x) , \tag{2A.6}$$

where $\delta(x)$ is the Dirac delta that is zero except at $x = 0$ but whose integral over x is unity. Thus, for periodic boundary conditions,

$$\left.\begin{aligned} f(x) &= A\textstyle\sum_q e^{iqx} f(q), \\ f(q) &= \frac{1}{AL} \textstyle\int_{-L/2}^{L/2} e^{-iqx} f(x) dx. \end{aligned}\right\} \tag{2A.7}$$

To treat systems in the limit $L \to \infty$, one takes the continuum limit in which $q = (2\pi/L)n$ is treated as a continuous variable and

$$\sum_q \equiv \sum_n \Delta n = \frac{L}{2\pi} \sum_q \Delta q \to L \int_{-\infty}^{\infty} \frac{dq}{2\pi} , \tag{2A.8}$$

where $\Delta n = 1$. Thus Eqs. (2A.7) can be rewritten as

$$f(x) = AL \int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{iqx} f(q) \overset{LA=1}{\to} \int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{iqx} f(q), \tag{2A.9}$$

$$f(q) = \frac{1}{AL} \int_{-\infty}^{\infty} dx e^{-iqx} f(q) \overset{LA=1}{\to} \int_{-\infty}^{\infty} dx e^{-iqx} f(q) . \tag{2A.10}$$

The normalization constant A is often chosen to be equal to L^{-1} so that the factors LA and $(LA)^{-1}$ become unity as shown in the final form on the right hand side of Eqs. (2A.9) and (2A.10). Other choices, such as $A = L^{-1/2}$ so that $L^{-1/2}$ appears as a factor in both Eqs. (2A.9) and (2A.10), are also used. In the continuum limit, the orthogonality and completeness relations (2A.5) and (2A.6) become

$$\int_{-\infty}^{\infty} dx e^{i(q-q')x} = \lim_{L\to\infty} L\delta_{q-q',0} \equiv 2\pi\delta(q-q') \tag{2A.11}$$

and

$$\int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{-iq(x-x')} = \delta(x-x'). \tag{2A.12}$$

The identification of $L\delta_{q,q'}$ with $2\pi\delta(q-q')$ can be seen from

$$\sum_q \delta_{q,0} = 1 = \frac{L}{2\pi}\int dq\delta_{q,0} \to \int_{-\infty}^{\infty} dq\delta(q)\,. \tag{2A.13}$$

2 *d dimensions*

The generalization of the above formulae to d dimensions is straightforward. Let $f(\mathbf{x})$ be a function of a d-component vector $\mathbf{x} = (x_1, x_2, ..., x_d)$ and impose periodic boundary conditions on each of the components of $\mathbf{x}$:

$$f(x_1, ..., x_i, ..., x_d) = f(x_1, ..., x_i + L_i, ..., x_d)\,, \qquad i = 1, 2, ..., d\,. \tag{2A.14}$$

Then $f(\mathbf{x})$ can be expanded in a Fourier series similar to Eqs. (2A.7):

$$f(\mathbf{x}) = A\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{q}) \tag{2A.15}$$

$$f(\mathbf{q}) = \frac{1}{AV}\int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{x})\,, \tag{2A.16}$$

where $V = L_1 L_2 ... L_d$ and

$$\mathbf{q} = \left(\frac{2\pi}{L_1}n_1, \frac{2\pi}{L_2}n_2, ..., \frac{2\pi}{L_d}n_d\right)\,, \tag{2A.17}$$

where the coefficients n_i are integers. In the infinite volume limit, these relations become

$$f(\mathbf{x}) = A\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{q}) = AV\int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{q})$$

$$\overset{AV=1}{\to} \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{q}) \tag{2A.18}$$

$$f(\mathbf{q}) = \frac{1}{AV}\int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{x}) \overset{AV=1}{\to} \int d^d x e^{-i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{x}), \tag{2A.19}$$

where again the normalization factor A is often chosen to be equal to V^{-1} as indicated by the final form of these equations. It is understood that the $\mathbf{x}$- and $\mathbf{q}$-integrals in Eqs. (2A.18) and (2A.19) are over all space. Finally, in the infinite volume, continuum limit, the orthogonality and completeness conditions become

$$\int d^d x e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{x}} = V\delta_{\mathbf{q},\mathbf{q}'} = (2\pi)^d \delta^{(d)}(\mathbf{q}-\mathbf{q}') \tag{2A.20}$$

and

$$\int \frac{d^d q}{(2\pi)^d} e^{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')} = \delta^{(d)}(\mathbf{x}-\mathbf{x}')\,, \tag{2A.21}$$

where $\delta^{(d)}(\mathbf{x})$ is a d-dimensional Dirac delta function.

3 Transforms on a lattice

Often one is interested in functions that are defined only at points on a regular periodic lattice rather than at all points in space. The Fourier transformation of these functions is the subject of this sub-section.

One-dimensional lattices Let f_l be a function of the integer l indexing the lattice site located at position $R_l = la$ of a one-dimensional lattice with lattice spacing a (see Sec. 2.5). The function f_l can be expanded in a discrete Fourier series

$$f_l = \sum_q \tilde{\psi}_q(l) f_q, \tag{2A.22}$$

where $\tilde{\psi}_q(l)$ satisfies the same boundary conditions as f_l. Again, we choose the periodic boundary condition,

$$f_l = f_{l+N}, \tag{2A.23}$$

where N is an integer. In this case, we can choose

$$\tilde{\psi}_q(l) = Ae^{iqR_l} = \tilde{\psi}_q(l+N), \tag{2A.24}$$

where

$$q = \frac{2\pi}{Na} n, \tag{2A.25}$$

where n is an integer. Because R_l is an integral multiple of the lattice spacing a, the function $\tilde{\psi}_q(x)$ in Eq. (2A.23) is periodic in q as well as in l:

$$\tilde{\psi}_q(l) = \tilde{\psi}_{q+(2\pi)/a}(l). \tag{2A.26}$$

Thus all the functions $\tilde{\psi}_q(l)$ and $f(q)$ are completely characterized by q in the interval $[-\pi/a, \pi/a]$, i.e., by q in the first *Brillouin zone* (BZ) of the one-dimensional lattice.

The number of points in the first BZ is equal to the number of sites N in the direct lattice. This follows because the number of points in some region of space is equal to its "volume" divided by the "volume" per point. The volume of the first BZ of a one-dimensional lattice is $2\pi/a$ and volume per point is simply $\Delta q = (2\pi)/Na$, so that

$$\text{number of points in first BZ} = \frac{2\pi}{a}\frac{1}{\Delta q} = \frac{2\pi/a}{(2\pi)/Na} = N. \tag{2A.27}$$

The functions e^{iqR_l} satisfy an orthogonality condition similar to that of the functions e^{iqx}:

$$\sum_{l=0}^{N} e^{i(q-q')R_l} = N\delta_{q,q'} \overset{N\to\infty}{\to} \frac{2\pi}{a}\delta(q-q'), \tag{2A.28}$$

where Eq. (2A.11) with $L = Na$ was used to relate the Kronecker delta to the Dirac delta. The completeness condition is

$$\sum_{q\in \text{1st BZ}} e^{iqR_l} = \frac{1-e^{iNl}}{1-e^{il}} = N\delta_{l,0}. \tag{2A.29}$$

In the continuum limit, this equation becomes

$$a\int_{-\pi/a}^{\pi/a} \frac{dq}{2\pi} e^{iqR_l} = \delta_{l,0}. \tag{2A.30}$$

When the above results are combined, the lattice Fourier transforms can be written as

$$f_l = A\sum_{q\in \text{1st BZ}} e^{iqR_l} f_q \overset{N\to\infty}{\to} A(Na)\int_{-\pi/a}^{\pi/a} \frac{dq}{2\pi} e^{iqR_l} f_q$$

$$\overset{ANa=1}{\rightarrow} \quad \int_{-\pi/a}^{\pi/a} \frac{dq}{2\pi} e^{iqR_l} f_q \tag{2A.31}$$

$$f_q = \frac{1}{NA} \sum_l e^{-iqR_l} f_l \overset{ANa=1}{\rightarrow} a \sum_l e^{-iqR_l} f_l. \tag{2A.32}$$

Again, the choice of A is arbitrary. Often the choice $A = (1/Na)$ is made as shown on the far right hand side of these equations. In this case, $(NA)^{-1} = a$, and the sum over l in Eq. (2A.32) could be replaced by an integral over R_l in a spatial continuum limit.

***d*-dimensional lattices** The generalization of lattice Fourier transforms to d-dimensional lattices is again straightforward. If $f_\mathbf{l}$ is a function of the lattice index $\mathbf{l}$ satisfying periodic boundary conditions, $f_\mathbf{l} = f_{\mathbf{l}+\mathbf{N}}$, where $\mathbf{N} = (N_1, N_2, ..., N_d)$, then

$$f_\mathbf{l} = \sum_\mathbf{q} \tilde{\psi}_\mathbf{q}(\mathbf{l}) f_\mathbf{q}, \tag{2A.33}$$

where, since $\mathbf{R}_{\mathbf{l}+\mathbf{N}} = \mathbf{R}_\mathbf{l} + \mathbf{R}_\mathbf{N}$,

$$\tilde{\psi}_\mathbf{q}(\mathbf{l}) = A e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} \tag{2A.34}$$

with

$$\mathbf{q} = \left(\frac{2\pi}{N_1 a} n_1, \frac{2\pi}{N_2 a} n_2, ..., \frac{2\pi}{N_d a} n_d \right) . \tag{2A.35}$$

The restriction of $\mathbf{R}_\mathbf{l}$ to lattice points leads to

$$\tilde{\psi}_{\mathbf{q}+\mathbf{G}}(\mathbf{l}) = \tilde{\psi}_\mathbf{q}(\mathbf{l}) , \tag{2A.36}$$

where $\mathbf{G}$ is a reciprocal lattice vector. Thus, as in the one-dimensional case, only wave vectors $\mathbf{q}$ in the first Brillouin zone need be considered. The number of points in the first Brillouin zone is again equal to the number of points, $N = N_1 N_2 ... N_d$ in the lattice. The orthogonality and completeness conditions are now

$$v_0 \sum_\mathbf{l} e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}_\mathbf{l}} = V \delta_{\mathbf{q},\mathbf{q}'} = (2\pi)^d \delta^{(d)}(\mathbf{q} - \mathbf{q}'), \tag{2A.37}$$

and

$$\frac{1}{N} \sum_\mathbf{q} e^{-i\mathbf{q}\cdot(\mathbf{R}_\mathbf{l} - \mathbf{R}_{\mathbf{l}'})} \rightarrow v_0 \int \frac{d^d q}{(2\pi)^d} e^{-i\mathbf{q}\cdot(\mathbf{R}_\mathbf{l} - \mathbf{R}_{\mathbf{l}'})} = \delta_{\mathbf{l},\mathbf{l}'}, \tag{2A.38}$$

where $v_0 = V/N$ is the volume of a unit cell and the q-integral is over the first BZ. The Fourier transform equations are

$$f_\mathbf{l} = A \sum_\mathbf{q} e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} f_\mathbf{q} \rightarrow AV \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} f_\mathbf{q}$$

$$\overset{AV=1}{\rightarrow} \quad \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} \tag{2A.39}$$

and

$$f_\mathbf{q} = \frac{1}{NA} \sum_\mathbf{l} e^{-i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} f_\mathbf{l} \overset{AV=1}{\rightarrow} v_0 \sum_\mathbf{l} e^{-i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} . \tag{2A.40}$$

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Appendix A

Brillouin zone summations

Many types of equations can be solved, and infinite lattice summations can be evaluated efficiently using spatial Fourier transform and reciprocal space techniques (as in §2.3.3, §4.3.2 and Appendix D). In the following, some of these techniques (and in particular the methods of evaluating summations over reciprocal lattice sites) are outlined.

A lattice vector $\mathbf{r}$ is defined in terms of the set of primitive vectors $\boldsymbol{a}_i$ as

$$\mathbf{r} = \sum_{i=1}^{d} \lambda_i \boldsymbol{a}_i, \tag{A.1}$$

where the λ_i are integers, d is the dimension of the lattice and $|\boldsymbol{a}_i| = a$, the lattice parameter. The spatial Fourier transform of a function $f(\mathbf{r})$ is defined to be

$$F(\boldsymbol{q}) = \sum_{\mathbf{r}} f(\mathbf{r}) \exp(i\boldsymbol{q} \cdot \mathbf{r}), \tag{A.2}$$

where the sum is over all lattice vectors. The reciprocal lattice vector is

$$\boldsymbol{q} = \sum_{j=1}^{d} q_j \boldsymbol{b}_j, \tag{A.3}$$

where the primitive vectors of the reciprocal lattice, $\boldsymbol{b}_j$, are defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = a\delta_{i,j}$ and the q_j have dimensions of reciprocal length. The inverse Fourier transform is then

$$f(\mathbf{r}) = \frac{1}{N} \sum_{\boldsymbol{q}} F(\boldsymbol{q}) \exp(-i\boldsymbol{q} \cdot \mathbf{r}), \tag{A.4}$$

where N is the number of lattice sites and the sum is over all reciprocal lattice vectors.

An example of importance is where $f(\mathbf{r}) = \exp(-i\boldsymbol{q}'\cdot\mathbf{r})$, and the Fourier transform of $f(\mathbf{r})$ vanishes by symmetry for all values of $\boldsymbol{q}$ except $\boldsymbol{q} = \boldsymbol{q}'$, in which case $F(\boldsymbol{q}) = N$; that is,

$$F(\boldsymbol{q}) = N\delta_{\boldsymbol{q},\boldsymbol{q}'}. \tag{A.5}$$

The Kronecker delta function is

$$\delta_{\boldsymbol{q},\boldsymbol{q}'} \doteq \prod_{j=1}^{d} \delta_{q_j,q_j'} \tag{A.6}$$

where $\delta_{q_j,q_j'} = 1$ if $q_j = q_j'$ and is zero otherwise. It is straightforward to confirm that the inverse Fourier transform (equation (A.4)) of $N\delta_{\boldsymbol{q},\boldsymbol{q}'}$ is the original function $f(\mathbf{r}) = \exp(-i\boldsymbol{q}'\cdot\mathbf{r})$.

It is possible to define a finite region of reciprocal space, called the first Brillouin zone, which simplifies the summation over all possible reciprocal lattice vectors in the inverse Fourier transform. From the definition of the Fourier transform (equation (A.2)), $F(\boldsymbol{q})$ is periodic so that for any reciprocal space vector $\boldsymbol{q}$ there is an equivalent vector, $\boldsymbol{q}'$, that can be written

$$\boldsymbol{q}' = \boldsymbol{q} + \frac{2\pi}{a}\sum_{j=1}^{d} n_j\boldsymbol{b}_j, \tag{A.7}$$

where the n_j are integers, so that $F(\boldsymbol{q}) = F(\boldsymbol{q}')$ for any n_j. In particular, any vector $\boldsymbol{q}$ has an equivalent vector, $\boldsymbol{q}'$, in the first Brillouin zone, which is the region in reciprocal space of vectors whose components satisfy the inequality $a|q_j'| \leq \pi$. This region of reciprocal space is sufficient to completely specify $F(\boldsymbol{q})$ for any vector $\boldsymbol{q}$ since the period of the exponential of a purely imaginary number is 2π.

The inverse Fourier transform of $F(\boldsymbol{q})$ (equation (A.4)) includes a summation over all reciprocal lattice sites, $\boldsymbol{q}$, and can, by the periodicity of the argument, be written as a summation over the equivalent vectors in the first Brillouin zone. The summation over a finite volume involves a quasi-infinite number of terms and can therefore be well approximated by an integral of the continuum over the first Brillouin zone, multiplied by the density of reciprocal lattice vectors, $v/(2\pi)^d$ where v is the volume (area) of the primitive cell of the real lattice. The following notations are then equivalent:

$$\frac{1}{N}\sum_{\boldsymbol{q}} \equiv \frac{v}{(2\pi)^d}\int_{BZ} d\boldsymbol{q} \tag{A.8}$$

where $v = V/N$ and V is the total volume (area) of the lattice. In three-dimensional lattices $v = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ and

$$\frac{v}{(2\pi)^3}\int_{BZ} d\boldsymbol{q} \doteq \frac{v}{(2\pi)^3}\iiint_{-\pi/a}^{\pi/a} \frac{a^3}{v}\, dq_1\, dq_2\, dq_3 \tag{A.9}$$

since $\boldsymbol{b}_1 \cdot (\boldsymbol{b}_2 \times \boldsymbol{b}_3) = a^3/v$, and a similar relation holds for two-dimensional lattices, where $v = |\boldsymbol{a}_1 \times \boldsymbol{a}_2|$. Expression (A.9) is valid only for lattices where the condition $|\boldsymbol{a}_i| = a$ for $1 \leq i \leq d$ holds. The above finite, one-dimensional integrals can be evaluated numerically using the Gauss-Legendre technique (Abramowitz and Stegun 1972) to high accuracy in most cases.

The Kronecker delta function notation, $N\delta_{\boldsymbol{q},\boldsymbol{q}'}$, used with the summation notation in the above example becomes the delta function

$$(2\pi)^d \delta(\boldsymbol{q} - \boldsymbol{q}') \doteq \left(\frac{2\pi}{a}\right)^d \prod_{j=1}^{d} \delta(q_j - q_j') \tag{A.10}$$

in the integral approximation since

$$F(\boldsymbol{q}') = \frac{1}{N}\sum_{\boldsymbol{q}} N\delta_{\boldsymbol{q},\boldsymbol{q}'} F(\boldsymbol{q}) = \frac{v}{(2\pi)^d}\int_{BZ} (2\pi)^d \delta(\boldsymbol{q} - \boldsymbol{q}') F(\boldsymbol{q})\, d\boldsymbol{q}. \tag{A.11}$$

Some types of integrals over the Brillouin zone of the the cubic lattices, particularly lattice generating functions, are especially time consuming to calculate accurately using the Gauss-Legendre technique. In these cases it is advantageous to use the special points integration technique of Chadi and Cohen (1973) which makes use of the 48 symmetry operators R_i of the cubic point group (see, for example, Burns and Glazer 1990) to define the function

$$F_1(\boldsymbol{q}) = \sum_{i=1}^{48} F(R_i \boldsymbol{q}) \tag{A.12}$$

which has the complete symmetry of the lattice. The Brillouin zone integral can then be written

$$\int_{BZ} F(\boldsymbol{q})\, d\boldsymbol{q} = \int_{IR} F_1(\boldsymbol{q})\, d\boldsymbol{q} \tag{A.13}$$

where the integral of $F_1(\boldsymbol{q})$ is over the irreducible Brillouin zone which is 1/48 of the Brillouin zone volume and which generates the whole (first) Brillouin zone by the application of the 48 symmetry opperators R_i. The irreducible Brillouin zones of the

simple-cubic (s.c.), face-centred-cubic (f.c.c.) and body-centred-cubic (b.c.c.) lattices are

$$\begin{aligned} &0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a}, && \text{(s.c.)} \\ 0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a} \quad &\text{and} \quad q_1 + q_2 + q_3 \le \frac{3\pi}{2a}, && \text{(f.c.c.)} \\ 0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a} \quad &\text{and} \quad 0 \le q_1 + q_2 \le \frac{\pi}{a}. && \text{(b.c.c.)} \end{aligned} \tag{A.14}$$

In the special points technique the integral is evaluated using the approximation

$$\int_{IR} F_1(\boldsymbol{q})\, d\boldsymbol{q} = \sum_{i=1}^{n} \alpha_i F_1(\boldsymbol{q}_i') \tag{A.15}$$

where the α_i are weights and the $\boldsymbol{q}_i'$ are n distinct special points in the irreducible Brillouin zone, generated from two reciprocal space vectors, $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, using the equation

$$\boldsymbol{q}_i = \boldsymbol{k}_1 + R_i \boldsymbol{k}_2. \tag{A.16}$$

These $\boldsymbol{q}_i$ are then transformed, using the R_i opperators, into the irreducible Brillouin zone to the vectors $\boldsymbol{q}_i'$ and the α_i are the numbers of $\boldsymbol{q}_i$ equivalent to each distinct $\boldsymbol{q}_i'$, normalised to unity. The $\boldsymbol{q}_i'$ so generated can then be used as seed vectors, $\boldsymbol{k}_1$, to generate an additional group of special points and this process can be repeated to improve the accuracy of the integral approximation. The base special-points sets are

$$\boldsymbol{k}_1 = \frac{\pi}{2a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \quad \boldsymbol{k}_2 = \frac{\pi}{4a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \tag{A.17}$$

with successive values of $\boldsymbol{k}_2$ for generating additional groups of points given by

$$\boldsymbol{k}_2 = \frac{\pi}{2^{m+1}a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \qquad m = 2, 3, \ldots \tag{A.18}$$

for the Brillouin zone of the s.c. lattice, and

$$\boldsymbol{k}_1 = \frac{\pi}{a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \quad \boldsymbol{k}_2 = \frac{\pi}{2a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \tag{A.19}$$

with successive values of $\boldsymbol{k}_2$ for generating additional groups of points given by

$$\boldsymbol{k}_2 = \frac{\pi}{2^m a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \qquad m = 2, 3, \ldots \tag{A.20}$$

for the Brillouin zones of the f.c.c. and b.c.c. lattices.

Appendix B

Transformation of $\mathrm{T}_p(\mathbf{q},\mathbf{j},z)$ and $\mathrm{T}_p(\mathbf{q})$

The functions $T_p(\boldsymbol{q},\boldsymbol{j},z)$ and $T_p(\boldsymbol{q})$ are the spatial Fourier transforms of $Y_{2p}(\Omega)/r^3$ in two- and three-dimensional systems respectively, where $\mathbf{r} = (r,\Omega)$. The transformations of these functions are each treated separately in the following two sections.

B.1 The two-dimensional case

The function $T_p(\boldsymbol{q},\boldsymbol{j},z)$ is defined by (see §2.3.3)

$$T_p(\boldsymbol{q},\boldsymbol{j},z) = \sum_{\boldsymbol{l}} \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3} \exp(i\boldsymbol{q}\cdot\mathbf{r}_\alpha) \tag{B.1}$$

where $\mathbf{r}_\alpha$ are the vectors $\boldsymbol{l}+\boldsymbol{j}+z\hat{\boldsymbol{k}}$ and where the summation is over the lattice vectors in an infinite plane. In terms of basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, where $|\boldsymbol{a}_i| = a$, and two-dimensional reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, defined by $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = a\delta_{ij}$, the vectors $\mathbf{r}_\alpha$ and $\boldsymbol{q}$ are

$$\mathbf{r}_\alpha = z\hat{\boldsymbol{k}}+\boldsymbol{j}+\boldsymbol{l} = z\hat{\boldsymbol{k}}+(j_1\boldsymbol{a}_1+j_2\boldsymbol{a}_2)+(\lambda_1\boldsymbol{a}_1+\lambda_2\boldsymbol{a}_2), \tag{B.2}$$

$$\boldsymbol{q} = q_1\boldsymbol{b}_1+q_2\boldsymbol{b}_2. \tag{B.3}$$

The summation over $\boldsymbol{l}$ in equation (B.1) then corresponds to λ_1 and λ_2 summed over integers from $-\infty$ to ∞. This two-dimensional sum can be transformed into a

sum over two-dimensional reciprocal lattice co-ordinates μ_1 and μ_2, using the Poisson summation formula in a similar way to the case $\boldsymbol{q} = 0$ considered by Sholl (1966). The result is, for $p \geq 0$,

$$T_p(\boldsymbol{q},\boldsymbol{j},z) = A_p \sum_{\mu_1,\mu_2=-\infty}^{\infty} F_p(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2} \exp\{-2\pi(z/a) f_{\mu_1,\mu_2}\} \tag{B.4}$$

where

$$A_p = \frac{4\pi^2(-i)^p}{a|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\left[\frac{5}{4\pi(2-p)!\,(2+p)!}\right]^{1/2},$$

$$F_p(\mu_1,\mu_2,j_1,j_2) = \exp\Big\{i[p\omega_{\mu_1,\mu_2} - 2\pi(j_1\mu_1 + j_2\mu_2)]\Big\},$$

$$f_{\mu_1,\mu_2} = |(\mu_1 + a\rho_1)\boldsymbol{b}_1 + (\mu_2 + a\rho_2)\boldsymbol{b}_2|,$$

$$\omega_{\mu_1,\mu_2} = \arctan\left[\frac{-a_{2x}(\mu_1 + a\rho_1) + (\mu_2 + a\rho_2)}{a_{2y}(\mu_1 + a\rho_1)}\right],$$

$a_{2x} = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2/a^2$, $a_{2y} = \sqrt{1 - a_{2x}^2}$ and $\boldsymbol{q} = 2\pi\boldsymbol{\rho}$. The values of $T_p(\boldsymbol{q},\boldsymbol{j},z)$ for $p < 0$ can be obtained from

$$T_{-p}(\boldsymbol{q},\boldsymbol{j},z) = (-1)^p T_p^*(-\boldsymbol{q},\boldsymbol{j},z). \tag{B.5}$$

The expression (B.4) is not valid for $z = 0$. In this case the transformation can be made to a rapidly converging form by using an auxiliary function (Nijboer and DeWette 1957). The results are

$$T_0(\boldsymbol{q},\boldsymbol{j},0) = \frac{-\sqrt{5}}{2\pi a^3}\left[\sum_{\lambda_1,\lambda_2}{}' \frac{\exp(i\boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})}{\sigma_{\lambda j}^3}\Gamma\left(\frac{3}{2},\pi\sigma_{\lambda j}^2\right) - \frac{2}{3}\pi^{3/2}\delta_{\boldsymbol{j},0}\right.$$
$$\left. + \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2} F_0(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2}\Gamma\left(-\frac{1}{2},\pi f_{\mu_1,\mu_2}^2\right)\right], \tag{B.6}$$

$$T_1(\boldsymbol{q},\boldsymbol{j},0) = 0, \tag{B.7}$$

$$T_2(\boldsymbol{q},\boldsymbol{j},0) = \frac{\sqrt{5}}{\sqrt{6}\pi a^3}\left[\sum_{\lambda_1,\lambda_2}{}' \frac{\exp[i(2\phi_{\lambda j} + \boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})]}{\sigma_{\lambda j}^3}\Gamma\left(\frac{5}{2},\pi\sigma_{\lambda j}^2\right)\right.$$
$$\left. - \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2}{}' F_2(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2}\Gamma\left(\frac{1}{2},\pi f_{\mu_1,\mu_2}^2\right)\right] \tag{B.8}$$

where the prime on the summation over λ_1, λ_2 denotes the exclusion of the $\lambda_1 = \lambda_2 = 0$ term when $\boldsymbol{j} = 0$, and the prime on the summation over μ_1, μ_2 denotes the exclusion of the $\mu_1 = \mu_2 = 0$ term if $\boldsymbol{q} = 0$, and where $\boldsymbol{\sigma}_{\lambda j}$ is the projection of the vector $\mathbf{r}_\alpha$ on to the xy-plane; that is, $\boldsymbol{\sigma}_{\lambda j} = \mathrm{r}_\alpha - z\hat{\boldsymbol{k}} = \boldsymbol{l} + \boldsymbol{j}$. $\Gamma(x,\pi\sigma^2)$ is the incomplete gamma function.

B.2 The three-dimensional case

The function $T_p(\boldsymbol{q})$ is defined by (see §4.3.2)

$$T_p(\boldsymbol{q}) = \sum_{\boldsymbol{m}} \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3} \exp(i\boldsymbol{q}\cdot\mathbf{r}_\alpha) \tag{B.9}$$

where the $Y_{2p}(\Omega)$ are spherical harmonics, and where the $\mathbf{r}_\alpha$ are the vectors $\boldsymbol{m}+\boldsymbol{j}$, where $\boldsymbol{m}$ are lattice vectors, and $\boldsymbol{j}$ is the nonzero relative displacement between the two sublattices in the crystal structure. The summation is over all the lattice vectors in the three-dimensional lattice. In terms of basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$, where $|\boldsymbol{a}_i| = a$ and which need not be orthogonal, and reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ and $\boldsymbol{b}_3$, defined by $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = a\delta_{ij}$, the vectors $\mathbf{r}_\alpha$ and $\boldsymbol{q}$ are

$$\mathbf{r}_\alpha = \boldsymbol{m}+\boldsymbol{j} = (\lambda_1\boldsymbol{a}_1+\lambda_2\boldsymbol{a}_2+\lambda_3\boldsymbol{a}_3)+(j_1\boldsymbol{a}_1+j_2\boldsymbol{a}_2+j_3\boldsymbol{a}_3), \tag{B.10}$$

$$\boldsymbol{q} = q_1\boldsymbol{b}_1+q_2\boldsymbol{b}_2+q_3\boldsymbol{b}_3. \tag{B.11}$$

The summation over $\boldsymbol{m}$ in equation (B.9) then corresponds to λ_1, λ_2 and λ_3 summed over integers from $-\infty$ to ∞. This summation can be transformed into a rapidly converging two-dimensional sum over reciprocal space co-ordinates μ_1 and μ_2, using the planewise summation technique developed by Nijboer and DeWette (1957) and discussed by Barton and Sholl (1980) for the case of orthogonal basis vectors. The result is, for $p \geq 0$ and $j_3 \neq 0$,

$$T_p(\boldsymbol{q}) = A_p \sum_{\mu_1,\mu_2=-\infty}^{\infty} F_p(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2} \left[(-)^p h(j_3,\mu_1,\mu_2) + h^*(1-j_3,\mu_1,\mu_2)\right] \tag{B.12}$$

where

$$A_p = \frac{4\pi^2(-i)^p}{a|\boldsymbol{a}_1\times\boldsymbol{a}_2|}\left[\frac{5}{4\pi(2+p)!\,(2-p)!}\right]^{1/2},$$

$$F_p(\mu_1,\mu_2,j_1,j_2) = \exp\Big\{i[p\omega_{\mu_1\mu_2} - 2\pi(j_1\mu_1+j_2\mu_2)]\Big\},$$

$$f_{\mu_1,\mu_2} = |(\mu_1+a\rho_1)\boldsymbol{b}_1' + (\mu_2+a\rho_2)\boldsymbol{b}_2'|,$$

$$\omega_{\mu_1\mu_2} = \arctan\left[\frac{a_{2x}(\mu_1+a\rho_1)-(\mu_2+a\rho_2)}{-a_{2y}(\mu_1+a\rho_1)}\right],$$

$$h(j,\mu_1,\mu_2) = \frac{\exp\{-2\pi j[a_{3z}f_{\mu_1,\mu_2} + i[t_1(\mu_1+a\rho_1)+t_2(\mu_2+a\rho_2)-a\rho_3]]\}}{1-\exp\{-2\pi[a_{3z}f_{\mu_1,\mu_2}+i[t_1(\mu_1+a\rho_1)+t_2(\mu_2+a\rho_2)-a\rho_3]]\}},$$

$$t_1 = \left(a_{3x} - \frac{a_{3y}a_{2x}}{a_{2y}}\right), \qquad t_2 = \frac{a_{3y}}{a_{2y}},$$

$a_{kx} = \boldsymbol{a}_k \cdot \boldsymbol{a}_1/a^2$ and $a_{ky} = \sqrt{1 - a_{kx}^2}$, for $k = 2$ and 3, and $2\pi\boldsymbol{\rho} = q_1\boldsymbol{b}'_1 + q_2\boldsymbol{b}'_2$ where the $\boldsymbol{b}'_i$ are the two-dimensional reciprocal lattice vectors defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}'_j = a\delta_{ij}$ for i and $j = 1$, 2. The values of $T_p(\boldsymbol{q})$ for $p < 0$ can be obtained from

$$T_{-p}(\boldsymbol{q}) = T_p^*(-\boldsymbol{q}). \tag{B.13}$$

In the special case when $j_1 = j_2 = 0$ or $1/2$, as in the NaCl structure, $T_p(\boldsymbol{q}) = T_p(-\boldsymbol{q})$ in which case equation (B.13) becomes

$$T_{-p}(\boldsymbol{q}) = T_p^*(\boldsymbol{q}). \tag{B.14}$$

It is convenient to choose the basis vectors used to calculate the $T_p(\boldsymbol{q})$ for the NaCl structure to be the primitive lattice vectors of the f.c.c. lattice. The resulting spectral density functions, $g'_{pp'}(\omega\tau)$, will be for a magnetic field in the direction $\left(\arccos(1/\sqrt{3}), 3\pi/4\right)$ with respect to the crystallographic axes. The spectral density functions, $g_{pp'}(\omega\tau)$, corresponding to a magnetic field along the crystallographic axis are obtained from the spectral density functions for a magnetic field in the direction (β,α) using the rotation matrix $R(\alpha,\beta,0)$ as discussed by Sholl (1986) and where $\alpha = 3\pi/4$ and $\beta = \arccos(1/\sqrt{3})$. Crystal symmetry greatly simplifies the problem and the rotation can be achieved using the result, for $p = 0$ and 1,

$$g_{pp} = g'_{pp} + C_p(\sin^2 2\beta + \sin^4\beta \sin^2 2\alpha), \tag{B.15}$$

where

$$C_0 = \frac{3}{4}(g'_{11} - g'_{00}), \qquad \text{and} \qquad C_1 = \frac{1}{2}(g'_{00} - g'_{11}).$$