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

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

Appendix C

Solution of the integral equation

The integral equation

$$f(x) = g(x) + \lambda \int_a^b K(x,y) f(y)\, dy, \tag{C.1}$$

where $g(x) \neq 0$ is a known function of x, λ is a constant parameter, and $K(x,y)$ is the kernel of the equation, is an inhomogeneous Fredholm equation of the second kind. If the kernel is of the form

$$K(x,y) = \sum_{i=1}^{n} \chi_i(x)\psi_i(y) \tag{C.2}$$

it is said to be degenerate and an analytic solution for $f(x)$ can be found by solving a system of linear equations.

The integral equation for $P_c(\boldsymbol{q},\boldsymbol{q}',\omega)$ from the mean field model of diffusion in two-dimensions (§2.3.4, equation (2.28)),

$$P_c(\boldsymbol{q},\boldsymbol{q}',\omega) = 2d_0(\boldsymbol{q}',\omega)\Big[(2\pi)^2\delta(\boldsymbol{q}-\boldsymbol{q}')-1\Big] + \frac{A}{(2\pi)^2}\int K(\boldsymbol{q}',\boldsymbol{q}_1)P_c(\boldsymbol{q},\boldsymbol{q}_1,\omega)\, d\boldsymbol{q}_1, \tag{C.3}$$

is an integral equation of the above type, where the kernel

$$K(\boldsymbol{q}',\boldsymbol{q}_1) = \frac{2}{\tau_c} d_0(\boldsymbol{q}',\omega)\Big\{1 + \phi(\boldsymbol{q}_1 - \boldsymbol{q}') - \phi(\boldsymbol{q}_1) - \phi(\boldsymbol{q}')\Big\} \tag{C.4}$$

is degenerate and where

$$d_0(\boldsymbol{q},\omega) = \frac{\tau_c}{2[1-\phi(\boldsymbol{q})] - i(\omega\tau_c)}. \tag{C.5}$$

The structure factor, $\phi(\boldsymbol{q})$, is defined as

$$\phi(\boldsymbol{q}) = \sum_k w_k \exp(i\boldsymbol{q}\cdot\mathbf{r}_k) \tag{C.6}$$

where w_k is the probability that the jump of a spin from the origin will be to $\mathbf{r}_k$, and τ_c is the mean time between jumps. The integral is over the first Brillouin zone and A is the area of the unit cell (Appendix A).

For the case of diffusion on a square lattice when only nearest neighbour jumps are allowed the structure factor is

$$\phi(\boldsymbol{q}') = \frac{1}{2}\Big[\cos(q_1'a) + \cos(q_2'a)\Big], \tag{C.7}$$

$$\phi(\boldsymbol{q}-\boldsymbol{q}') = \frac{1}{2}\sum_{i=1}^{2}\Big[\cos(q_ia)\cos(q_i'a) + \sin(q_ia)\sin(q_i'a)\Big], \tag{C.8}$$

and then the kernel of the integral equation becomes

$$K(\boldsymbol{q}',\boldsymbol{q}_1) = \frac{1}{2}d_0(\boldsymbol{q}',\omega)\sum_{i=1}^{2}\Big\{[1-\cos(q_i'a)][1-\cos(q_{1i}a)] + \sin(q_i'a)\sin(q_{1i}a)\Big\}. \tag{C.9}$$

The solution of the integral equation in this case is found by defining the functions

$$C_i(\boldsymbol{q}) = \frac{A}{(2\pi)^2}\int [1-\cos(q_{1i}a)]P(\boldsymbol{q},\boldsymbol{q}_1,\omega)\,d\boldsymbol{q}_1 \tag{C.10}$$

and

$$S_i(\boldsymbol{q}) = \frac{A}{(2\pi)^2}\int \sin(q_{1i}a)P(\boldsymbol{q},\boldsymbol{q}_1,\omega)\,d\boldsymbol{q}_1 \tag{C.11}$$

from the $\boldsymbol{q}_1$-components of the kernel and from which the integral equation (C.3), for the square lattice, can then be written

$$\begin{aligned} P_c(\boldsymbol{q},\boldsymbol{q}',\omega) &= 2d_0(\boldsymbol{q}',\omega)\Big[(2\pi)^2\delta(\boldsymbol{q}-\boldsymbol{q}') - 1\Big] \\ &\quad + \frac{1}{\tau_c}d_0(\boldsymbol{q}',\omega)\sum_{i=1}^{2}\Big\{[1-\cos(q_i'a)]C_i(\boldsymbol{q}) + \sin(q_i'a)S_i(\boldsymbol{q})\Big\}. \end{aligned} \tag{C.12}$$

Substitution of this equation into expression (C.10) for $C_i(\boldsymbol{q})$ gives the system of linear equations

$$\begin{pmatrix} 1-\alpha & -\beta \\ -\beta & 1-\alpha \end{pmatrix}\begin{pmatrix} C_1(\boldsymbol{q}) \\ C_2(\boldsymbol{q}) \end{pmatrix} = \begin{pmatrix} G_1 \\ G_2 \end{pmatrix} \tag{C.13}$$

where

$$\alpha = \frac{1}{\tau_c}\frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q}',\omega)\Big[1-2\cos(q_1'a)+\cos^2(q_1'a)\Big]\,d\boldsymbol{q}', \tag{C.14}$$

$$\beta = \frac{1}{\tau_c}\frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q}',\omega)\left[1 - 2\cos(q_1'a) + \cos(q_1'a)\cos(q_2'a)\right] d\boldsymbol{q}', \tag{C.15}$$

and

$$G_i = 2d_0(\boldsymbol{q},\omega)\left[1 - \cos(q_i a)\right] - 2\tau_c\gamma \tag{C.16}$$

where

$$\gamma = \frac{1}{\tau_c}\frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q}',\omega)\left[1 - \cos(q_1'a)\right] d\boldsymbol{q}', \tag{C.17}$$

and where the terms involving the $S_i(\boldsymbol{q})$ have vanished, by symmetry, on integrating over $\boldsymbol{q}_1$ in equation (C.10). The solution to the above system of linear equations is

$$C_i(\boldsymbol{q}) = \frac{2G_i - G_1 - G_2}{2(1-\alpha+\beta)} + \frac{G_1 + G_2}{2(1-\alpha-\beta)}. \tag{C.18}$$

Substitution of equation (C.12) into the expression (C.11) for $S_i(\boldsymbol{q})$ gives an equation in $C_i(\boldsymbol{q})$ and $S_i(\boldsymbol{q})$. In this equation for $S_i(\boldsymbol{q})$ the terms involving the $C_i(\boldsymbol{q})$ vanish, by symmetry, on integrating over $\boldsymbol{q}_1$ and the solution can then be found directly to be

$$S_i(\boldsymbol{q}) = \frac{2d_0(\boldsymbol{q},\omega)\sin(q_i a)}{1-\xi}, \tag{C.19}$$

where

$$\xi = \frac{1}{\tau_c}\frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q}',\omega)\sin^2(q_1'a)\, d\boldsymbol{q}'. \tag{C.20}$$

Expressions (C.18) and (C.19) for the $C_i(\boldsymbol{q})$ and $S_i(\boldsymbol{q})$ can then be substituted back into equation (C.12) for $P_c(\boldsymbol{q},\boldsymbol{q}',\omega)$ to give the solution

$$\begin{aligned} P_c(\boldsymbol{q},\boldsymbol{q}',\omega) = {} & 2d_0(\boldsymbol{q}',\omega)\left[(2\pi)^2\delta(\boldsymbol{q}-\boldsymbol{q}') - 1\right] + \frac{1}{\tau_c}d_0(\boldsymbol{q},\omega)d_0(\boldsymbol{q}',\omega)\sum_i \frac{\sin(q_i a)\sin(q_i'a)}{1-\xi} \\ & + \frac{1}{\tau_c}d_0(\boldsymbol{q}',\omega)\left[2 - \cos(q_1'a) - \cos(q_2'a)\right]\left\{2d_0(\boldsymbol{q},\omega)\sum_i \frac{\cos(q_i'a) - \cos(q_i a)}{1-\alpha+\beta}\right. \\ & \left. + \frac{d_0(\boldsymbol{q},\omega)[2 - \cos(q_1 a) - \cos(q_2 a)] - 2\tau_c\gamma}{1-\alpha-\beta}\right\}. \end{aligned} \tag{C.21}$$

Many of the terms in the above solution vanish by symmetry when the inverse spatial Fourier transform is taken in the evaluation of the spectral density functions (equation (2.22)). Only terms that contribute to the spectral density functions are included in the solution for $P(\boldsymbol{q},\boldsymbol{q}',\omega) = \Re\{P_c(\boldsymbol{q},\boldsymbol{q}',\omega)\}$ and the final solution is

$$P(\boldsymbol{q},\boldsymbol{q}',\omega) = \frac{2\tau(2\pi)^2[1-\phi(\boldsymbol{q})]}{[1-\phi(\boldsymbol{q})]^2 + (\omega\tau)^2}\delta(\boldsymbol{q}-\boldsymbol{q}') + \Re\left\{d_0(\boldsymbol{q},\omega)d_0(\boldsymbol{q}',\omega)\sum_l \frac{F_l(\boldsymbol{q})F_l(\boldsymbol{q}')}{B_l(\omega)}\right\} \tag{C.22}$$

where

$$d_0(\boldsymbol{q},\omega) = \frac{\tau}{[1-\phi(\boldsymbol{q})] - i(\omega\tau)},$$

$$F_1(\boldsymbol{q}) = 2 - \cos(q_1 a) - \cos(q_2 a), \qquad F_2(\boldsymbol{q}) = \cos(q_1 a) - \cos(q_2 a),$$

$$B_1(\omega) = 2\tau - \frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q},\omega)\Big\{2 - 4\cos(q_1 a) + \cos^2(q_1 a) + \cos(q_1 a)\cos(q_2 a)\Big\}\, d\boldsymbol{q},$$

$$B_2(\omega) = 2\tau - \frac{A}{(2\pi)^2}\int d_0(\boldsymbol{q},\omega)\Big\{\cos^2(q_1 a) - \cos(q_1 a)\cos(q_2 a)\Big\}\, d\boldsymbol{q},$$

where $\tau = \tau_c/2$ and the integrals in the above expressions for the $B_l(\omega)$ are over the first Brillouin zone of the two-dimensional reciprocal lattice.

Appendix D

Probability generating functions

The theory for calculating the displacement probability generating functions for a random walk on the cubic lattices, and some structures which are a Bravais lattice with b (≥ 1) basis vectors, is summarised below. The final expressions for the probabilities involve an integral over the first Brillouin zone which can be evaluated numerically.

The matrix elements P_{kl} (discussed in §3.2.2 after equation (3.24) on page 43) are the probability generating function

$$P(\boldsymbol{c}_k, \boldsymbol{c}_l; z) = \sum_{n=0}^{\infty} P_n(\boldsymbol{c}_k, \boldsymbol{c}_l) z^n \tag{D.1}$$

with $z = 1$, for $\boldsymbol{c}_k$ and $\boldsymbol{c}_l$, nearest neighbour vectors on the composite lattice and where $P_n(\boldsymbol{l}_2, \boldsymbol{l}_1)$ is the probability a random walker is displaced from $\boldsymbol{l}_1$ to $-\boldsymbol{l}_2$ in n steps. The random walk is on the interstitial lattice which, in general, is a Bravais lattice with b basis vectors. The case $b = 1$ corresponds to a random walk on a Bravais lattice.

For an infinite lattice the probability $P_n(\boldsymbol{l}_2, \boldsymbol{l}_1)$ is equal to the probability $P_n(\boldsymbol{l})$ that the random walker is displaced by $\boldsymbol{l} = -(\boldsymbol{l}_1 + \boldsymbol{l}_2)$ in n steps and the problem of calculating the probability generating function $P(\boldsymbol{c}_k, \boldsymbol{c}_l; z)$ reduces to one of calculating $P(\boldsymbol{l}; z)$, the probability generating function of $P_n(\boldsymbol{l})$. The first systems to be considered are the simple-cubic (s.c.), body-centred-cubic (b.c.c.) and face-centred-cubic (f.c.c.) lattices. On a cubic lattice; first, second and third nearest neighbour steps are allowed, and occur with normalised probabilities s_1, s_2 and s_3 respectively. If each lattice site has Z_j j^{th} nearest neighbour sites then the recurrence relation for

$P_n(\boldsymbol{l})$ is

$$P_n(\boldsymbol{l}) = \sum_{j=1}^{3} \left[\frac{s_j}{Z_j} \sum_{i=1}^{Z_j} P_{n-1}(\boldsymbol{l} - \boldsymbol{n}_i^{(j)}) \right]. \tag{D.2}$$

The $\boldsymbol{n}_i^{(j)}$ are the sets of lattice vectors to j^{th} nearest neighbour sites and the initial condition is $P_0(\boldsymbol{l}) = \delta_{\boldsymbol{l},0}$. The corresponding probability generating function is (Barber and Ninham 1970)

$$P(\boldsymbol{l}; z) = \frac{v}{(2\pi)^3} \int \frac{\exp(-i\boldsymbol{q} \cdot \boldsymbol{l})}{1 - zA(\boldsymbol{q})}\, d\boldsymbol{q}, \tag{D.3}$$

where the integral is over the first Brillouin zone, v is the volume of the unit cell, and

$$A(\boldsymbol{q}) = s_1\lambda_1(\boldsymbol{q}) + s_2\lambda_2(\boldsymbol{q}) + s_3\lambda_3(\boldsymbol{q}). \tag{D.4}$$

The reciprocal lattice vectors $\boldsymbol{q} = q_1\boldsymbol{b}_1 + q_2\boldsymbol{b}_2 + q_3\boldsymbol{b}_3$, where the $\boldsymbol{b}_i$ are defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = a\delta_{i,j}$, and the $\boldsymbol{a}_i$ are the vectors $\boldsymbol{a}_1 = a\hat{\boldsymbol{\imath}}$, $\boldsymbol{a}_2 = a\hat{\boldsymbol{\jmath}}$ and $\boldsymbol{a}_3 = a\hat{\boldsymbol{k}}$ where a is the lattice parameter. The structure factors, $\lambda_j(\boldsymbol{q})$, for the interstitial lattice are defined as

$$\lambda_j(\boldsymbol{q}) = \frac{1}{Z_j} \sum_{i=1}^{Z_j} \exp\left(i\boldsymbol{q} \cdot \boldsymbol{n}_i^{(j)}\right), \tag{D.5}$$

which for s.c., b.c.c. and f.c.c. lattices are given by

$$\lambda_1(\boldsymbol{q}) = \begin{cases} \frac{1}{3}\left[\cos(q_1a) + \cos(q_2a) + \cos(q_3a)\right], & \text{(s.c.)} \\ \cos(q_1a)\cos(q_2a)\cos(q_3a), & \text{(b.c.c.)} \\ \frac{1}{3}\left[\cos(q_1a)\cos(q_2a) + \cos(q_1a)\cos(q_3a) + \cos(q_2a)\cos(q_3a)\right], & \text{(f.c.c.)} \end{cases}$$

$$\lambda_2(\boldsymbol{q}) = \begin{cases} \frac{1}{3}\left[\cos(q_1a)\cos(q_2a) + \cos(q_1a)\cos(q_3a) + \cos(q_2a)\cos(q_3a)\right], & \text{(s.c.)} \\ \frac{1}{3}\left[\cos(2q_1a) + \cos(2q_2a) + \cos(2q_3a)\right], & \text{(b.c.c. and f.c.c.)} \end{cases} \tag{D.6}$$

$$\lambda_3(\boldsymbol{q}) = \begin{cases} \cos(q_1a)\cos(q_2a)\cos(q_3a), & \text{(s.c.)} \\ \frac{1}{3}\left[\cos(2q_1a)\cos(2q_2a) + \cos(2q_1a)\cos(2q_3a) + \cos(2q_2a)\cos(2q_3a)\right], & \text{(b.c.c.)} \\ \frac{1}{3}\left[\cos(q_1a)\cos(q_2a)\cos(2q_3a) + \cos(q_1a)\cos(2q_2a)\cos(q_3a) + \cos(2q_1a)\cos(q_2a)\cos(q_3a)\right], & \text{(f.c.c.).} \end{cases}$$

Equation (D.3), for the special case $\boldsymbol{l} = 0$ and $s_1 = 1$, with the remaining s_i equal to zero, and $z = 1$, are the Watson integrals which can be evaluated analytically

(Barber and Ninham 1970). Results for other $\boldsymbol{l}$ can be obtained numerically and these functions have been studied extensively (see for example Montroll and Weiss 1965; Joyce 1971; Sholl 1981c; and Koiwa and Ishioka 1983).

If the interstitial lattice has more than one basis vector ($b > 1$), there is more than one type of lattice site, each site of a particular type having the same configuration of surrounding sites. To obtain $P(\boldsymbol{l}; z)$ it is useful to introduce $P_n^{(\alpha)}(\boldsymbol{l})$, the probability $P_n(\boldsymbol{l})$ with the added restriction that $\boldsymbol{l}$ be a lattice site of type α ($1 \leq \alpha \leq b$) so that

$$P_n(\boldsymbol{l}) = \sum_{\alpha=1}^{b} P_n^{(\alpha)}(\boldsymbol{l}). \tag{D.7}$$

Recurrence relations can then be found for the $P_n^{(\alpha)}(\boldsymbol{l})$ which take into account the different possible jumps from each of the different types of lattice sites. As examples, the cases of random walks on the interstitial lattice of the NaCl structure (for which $b = 2$), the s.c.(f) system and the s.c.(e) system (for which $b = 3$) are considered below.

There are two types of lattice sites on the interstitial lattice of the NaCl structure (a f.c.c.(t) system). The first and second nearest neighbour jumps are the same for both lattice types and are the same as those on a simple-cubic lattice. The third nearest neighbour jumps are similar to jumps on a diamond structure and there is a different set of jump vectors for each of the two types of lattice sites. The recurrence relations for the $P_n^{(\alpha)}(\boldsymbol{l})$ in this system can be written

$$P_n^{(\alpha)}(\boldsymbol{l}) = \frac{s_1}{Z_1} \sum_{i=1}^{Z_1} P_{n-1}^{(\beta)}(\boldsymbol{l} - \boldsymbol{n}_i^{(1)}) + \frac{s_2}{Z_2} \sum_{i=1}^{Z_2} P_{n-1}^{(\alpha)}(\boldsymbol{l} - \boldsymbol{n}_i^{(2)}) + \frac{s_3}{Z_3} \sum_{i}^{\beta\alpha} P_{n-1}^{(\beta)}(\boldsymbol{l} - \boldsymbol{n}_i^{(3)}) \tag{D.8}$$

for $\alpha, \beta = 1, 2$ and $\alpha \neq \beta$, and where $\sum_{i}^{\beta\alpha}$ means to sum over all i which correspond to jumps from a type-β to a type-α lattice site. The initial condition is $P_0^{(\alpha)}(\boldsymbol{l}) = \delta_{\boldsymbol{l},0}\delta_{\alpha,1}$ if the random walker commences its walk at a type-1 site. The solution to the recurrence relations can be found as before, and the probability generating functions can be written

$$P(\boldsymbol{l}; z) = \frac{v}{(2\pi)^3} \int \left\{ \sum_{\alpha,\beta=1}^{b} [\mathbf{I} - z\mathbf{B}(\boldsymbol{q})]^{-1}_{\alpha\beta} \, P_0^{(\beta)}(\boldsymbol{q}) \right\} \exp(i\boldsymbol{q} \cdot \boldsymbol{l}) \; d\boldsymbol{q} \tag{D.9}$$

where $\mathbf{I}$ is the 2×2 identity matrix. The initial condition gives $P_0^{(\alpha)}(\boldsymbol{q}) = \delta_{\alpha,1}$, and

$\mathbf{B}(\boldsymbol{q})$ is the square matrix

$$\mathbf{B}(\boldsymbol{q}) = \begin{pmatrix} s_2\lambda_2(\boldsymbol{q}) & s_1\lambda_1 + s_3\lambda_3^{(2)}(\boldsymbol{q}) \\ s_1\lambda_1 + s_3\lambda_3^{(1)}(\boldsymbol{q}) & s_2\lambda_2(\boldsymbol{q}) \end{pmatrix}. \tag{D.10}$$

The $\lambda_j(\boldsymbol{q})$ are the structure factors defined by

$$\lambda_j(\boldsymbol{q}) = \frac{1}{Z_j}\sum_{i=1}^{Z_j} \exp\left(i\boldsymbol{q}\cdot\boldsymbol{n}_i^{(j)}\right) \tag{D.11}$$

for $j = 1$ and 2, and

$$\lambda_3^{(\alpha)}(\boldsymbol{q}) = \frac{1}{Z_3}\sum_{i}^{\alpha\beta} \exp\left(i\boldsymbol{q}\cdot\boldsymbol{n}_i^{(3)}\right) \tag{D.12}$$

for $j = 3$. If the nearest neighbour jump vectors are as defined in Table D.1, the structure factors are given by

$$\begin{aligned}
\lambda_1(\boldsymbol{q}) &= \frac{1}{3}\Big[\cos(q_1a) + \cos(q_2a) + \cos(q_3a)\Big], \\
\lambda_2(\boldsymbol{q}) &= \frac{1}{3}\Big[\cos(q_1a)\cos(q_2a) + \cos(q_1a)\cos(q_3a) + \cos(q_2a)\cos(q_3a)\Big], \\
\lambda_3^{(1)}(\boldsymbol{q}) &= \cos(q_1a)\cos(q_2a)\cos(q_3a) - i\sin(q_1a)\sin(q_2a)\sin(q_3a), \\
\lambda_3^{(2)}(\boldsymbol{q}) &= \left[\lambda_3^{(1)}(\boldsymbol{q})\right]^*.
\end{aligned} \tag{D.13}$$

The term inside the curly brackets in equation (D.9) can be evaluated either numerically for each value of $\boldsymbol{q}$, or algebraically. If it is evaluated algebraically then, for the above initial condition, the term can be written

$$\frac{1 + z\left[s_1\lambda_1(\boldsymbol{q}) - s_2\lambda_2(\boldsymbol{q}) + s_3\lambda_3^{(1)}(\boldsymbol{q})\right]}{\left[1 - zs_2\lambda_2(\boldsymbol{q})\right]^2 - z^2\left[s_1\lambda_1(\boldsymbol{q}) + s_3\lambda_3^{(1)}(\boldsymbol{q})\right]\left[s_1\lambda_1(\boldsymbol{q}) + s_3\lambda_3^{(2)}(\boldsymbol{q})\right]}. \tag{D.14}$$

The special cases $s_1 = 1$, $s_2 = 1$ and $s_3 = 1$ correspond to random walks on a s.c. lattice , a f.c.c. lattice and the diamond structure respectively. The probability generating function for diffusion on the diamond structure has been studied by Ishioka and Koiwa (1978).

Equation (D.9) is valid for any infinite, Bravais lattice with b basis vectors. The expression for the term inside the curly brackets, in terms of structure factors, will depend on the lattice, as will the expressions for the structure factors.

The interstitial lattices of the s.c.(f) and s.c.(e) structures are each f.c.c. lattices

Table D.1: First, second and third nearest neighbour vectors for the NaCl interstitial lattice. The vectors are $\boldsymbol{a}_1 = a\hat{\boldsymbol{\imath}}$, $\boldsymbol{a}_2 = a\hat{\boldsymbol{\jmath}}$ and $\boldsymbol{a}_3 = a\hat{\boldsymbol{k}}$ where a is the distance between adjacent interstitial lattice sites. The numbers of nearest neighbour sites to any lattice site are $Z_1 = 6$, $Z_2 = 12$ and $Z_3 = 4$.

$\boldsymbol{n}_i^{(1)}$	$\boldsymbol{n}_i^{(2)}$	$\boldsymbol{n}_i^{(3)}$	
both types	both types	type-1 to type-2	type-2 to type-1
$\pm\boldsymbol{a}_1$	$\pm(\boldsymbol{a}_1+\boldsymbol{a}_2)$	$\boldsymbol{a}_1+\boldsymbol{a}_2+\boldsymbol{a}_3$	$-\boldsymbol{a}_1-\boldsymbol{a}_2-\boldsymbol{a}_3$
$\pm\boldsymbol{a}_2$	$\pm(\boldsymbol{a}_1-\boldsymbol{a}_2)$	$\boldsymbol{a}_1-\boldsymbol{a}_2-\boldsymbol{a}_3$	$\boldsymbol{a}_2+\boldsymbol{a}_3-\boldsymbol{a}_1$
$\pm\boldsymbol{a}_3$	$\pm(\boldsymbol{a}_1+\boldsymbol{a}_3)$	$\boldsymbol{a}_2-\boldsymbol{a}_1-\boldsymbol{a}_3$	$\boldsymbol{a}_1+\boldsymbol{a}_3-\boldsymbol{a}_2$
	$\pm(\boldsymbol{a}_1-\boldsymbol{a}_3)$	$\boldsymbol{a}_3-\boldsymbol{a}_1-\boldsymbol{a}_2$	$\boldsymbol{a}_1+\boldsymbol{a}_2-\boldsymbol{a}_3$
	$\pm(\boldsymbol{a}_2+\boldsymbol{a}_3)$		
	$\pm(\boldsymbol{a}_2-\boldsymbol{a}_3)$		

that have three basis vectors, and so each have three different lattice types. In the present work it is necessary to consider only first and second nearest neighbour jumps in the s.c.(e) interstitial lattice, while up to fourth nearest neighbour jumps are allowed in the s.c.(f) interstitial lattice. The recurrence relation for $P_n^{(\alpha)}(\boldsymbol{l})$ in both systems, using the same notation as above, is

$$\begin{aligned} P_n^{(\alpha)}(\boldsymbol{l}) = \frac{s_1}{Z_1}\left[\sum_i{}^{\beta\alpha} P_{n-1}^{(\beta)}(\boldsymbol{l}-\boldsymbol{n}_i^{(1)}) + \sum_i{}^{\gamma\alpha} P_{n-1}^{(\gamma)}(\boldsymbol{l}-\boldsymbol{n}_i^{(1)})\right] \\ + \frac{s_2}{Z_2}\sum_i{}^{\alpha\alpha} P_{n-1}^{(\alpha)}(\boldsymbol{l}-\boldsymbol{n}_i^{(2)}) \\ + \frac{s_3}{Z_3}\left[\sum_i{}^{\beta\alpha} P_{n-1}^{(\beta)}(\boldsymbol{l}-\boldsymbol{n}_i^{(3)}) + \sum_i{}^{\gamma\alpha} P_{n-1}^{(\gamma)}(\boldsymbol{l}-\boldsymbol{n}_i^{(3)})\right] \\ + \frac{s_4}{Z_4}\sum_i{}^{\alpha\alpha} P_{n-1}^{(\alpha)}(\boldsymbol{l}-\boldsymbol{n}_i^{(4)}), \end{aligned} \tag{D.15}$$

where $\alpha, \beta, \gamma = 1$, 2 or 3, and $\alpha \neq \beta \neq \gamma$ and where, in the present work, for the s.c.(e) interstitial lattice $s_3 = s_4 = 0$ always, to exclude the possibility of third and fourth nearest neighbour jumps. This equation can be solved in a manner similar to the case for a random walk in the NaCl interstitial lattice, above, and the expression for the probability generating function $P(\boldsymbol{l}; z)$ is again given by equation (D.9). In this case, however, $\mathbf{B}(\boldsymbol{q})$ is a 3×3 matrix with diagonal elements

$$\mathrm{B}_{\alpha,\alpha}(\boldsymbol{q}) = s_2\lambda_2^{(\alpha\alpha)}(\boldsymbol{q}) + s_4\lambda_4^{(\alpha\alpha)}(\boldsymbol{q}), \tag{D.16}$$

and with the remaining elements

$$\mathrm{B}_{\alpha,\beta}(\boldsymbol{q}) = s_1\lambda_1^{(\alpha\beta)}(\boldsymbol{q}) + s_3\lambda_3^{(\alpha\beta)}(\boldsymbol{q}) \qquad (\alpha \neq \beta) \tag{D.17}$$

where the structure factors, defined by

$$\lambda_j^{(\alpha\beta)}(\boldsymbol{q}) = \frac{1}{Z_j}\sum_i{}^{\alpha\beta} \exp\left(i\boldsymbol{q}\cdot\boldsymbol{n}_i^{(j)}\right) \tag{D.18}$$

for the present two systems, satisfy the relation

$$\lambda_j^{(\alpha\beta)}(\boldsymbol{q}) = \lambda_j^{(\beta\alpha)}(\boldsymbol{q}). \tag{D.19}$$

For the choice of nearest neighbour lattice vectors and lattice site types defined in Table D.2 the structure factors for the s.c.(f) system are

$$\begin{gathered}
\lambda_1^{(12)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(q_2a), \qquad \lambda_1^{(13)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(q_3a), \\
\lambda_1^{(23)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_2a)\cos(q_3a), \\
\lambda_2^{(11)}(\boldsymbol{q}) = \tfrac{1}{2}[\cos(2q_2a) + \cos(2q_3a)], \qquad \lambda_2^{(22)}(\boldsymbol{q}) = \tfrac{1}{2}[\cos(2q_1a) + \cos(2q_3a)], \\
\lambda_2^{(33)}(\boldsymbol{q}) = \tfrac{1}{2}[\cos(2q_1a) + \cos(2q_2a)], \\
\lambda_3^{(12)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(q_2a)\cos(2q_3a), \qquad \lambda_3^{(13)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(2q_2a)\cos(q_3a), \\
\lambda_3^{(23)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(2q_1a)\cos(q_2a)\cos(q_3a), \\
\lambda_4^{(11)}(\boldsymbol{q}) = \cos(2q_2a)\cos(2q_3a), \qquad \lambda_4^{(22)}(\boldsymbol{q}) = \cos(2q_1a)\cos(2q_3a), \\
\lambda_4^{(33)}(\boldsymbol{q}) = \cos(2q_1a)\cos(2q_2a),
\end{gathered} \tag{D.20}$$

and for the s.c.(e) system are

$$\begin{gathered}
\lambda_1^{(12)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(q_2a), \quad \lambda_1^{(13)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_1a)\cos(q_3a), \\
\lambda_1^{(23)}(\boldsymbol{q}) = \tfrac{1}{2}\cos(q_2a)\cos(q_3a), \\
\lambda_2^{(11)}(\boldsymbol{q}) = \cos(2q_1a), \qquad \lambda_2^{(22)}(\boldsymbol{q}) = \cos(2q_2a), \qquad \lambda_2^{(33)}(\boldsymbol{q}) = \cos(2q_3a).
\end{gathered} \tag{D.21}$$

Once again, the term inside the curly brackets in equation (D.9) can be evaluated either numerically or algebraically. To evaluate the term algebraically a symbolic mathematics computer package is required and, for the initial condition $P_0^{(\alpha)}(\boldsymbol{l}) = \delta_{\boldsymbol{l},0}\delta_{\alpha,1}$, the term inside the curly brackets can be written

$$\frac{1 - z(b+c-d-e) + z^2(bc - cd - be + ef + df - f^2)}{1 - z(b+c-a) + z^2(bc + ac + ab - d^2 - e^2 - f^2) - z^3(abc + 2def - cd^2 - be^2 - af^2)} \tag{D.22}$$

where $a = B_{11}(\boldsymbol{q})$, $b = B_{22}(\boldsymbol{q})$, $c = B_{33}(\boldsymbol{q})$, $d = B_{12}(\boldsymbol{q})$, $e = B_{13}(\boldsymbol{q})$ and $f = B_{23}(\boldsymbol{q})$.

The integral in the expressions for $P(\boldsymbol{l};z)$ (equations (D.3) and (D.9)) can be evaluated efficiently using the special-points numerical integration technique of Chadi and Cohen (1973) (see Appendix A) and an extrapolation method (MacGillivray and Sholl 1983). The results of some of these calculations of $P(\boldsymbol{l};1)$ are shown in Tables D.3 to D.8 and Tables 3.1 to 3.3 for some of the j^{th} nearest neighbour vectors, $\boldsymbol{l}$, denoted P_j.

Table D.2: First, second, third and fourth nearest neighbour vectors for the s.c.(f) interstitial lattice, and first and second nearest neighbour lattice vectors for the s.c.(e) interstitial lattice. The vectors are $\boldsymbol{a}_1 = a\hat{\boldsymbol{i}}$, $\boldsymbol{a}_2 = a\hat{\boldsymbol{j}}$ and $\boldsymbol{a}_3 = a\hat{\boldsymbol{k}}$ where a is the distance between adjacent composite lattice sites. The numbers of nearest neighbour sites to any lattice site are $Z_1 = 8$, $Z_2 = 4$, $Z_3 = 16$ and $Z_4 = 4$ for the s.c.(f) interstitial lattice, while for the s.c.(e) interstitial lattice $Z_1 = 8$ and $Z_2 = 2$. The notation $\alpha \leftrightarrow \beta$ denotes possible jump vectors between type-α and type-β lattice sites.

s.c.(f)				s.c.(e)	
$\boldsymbol{n}_i^{(1)}$	$\boldsymbol{n}_i^{(2)}$	$\boldsymbol{n}_i^{(3)}$	$\boldsymbol{n}_i^{(4)}$	$\boldsymbol{n}_i^{(1)}$	$\boldsymbol{n}_i^{(2)}$
$1 \leftrightarrow 2$	$1 \leftrightarrow 1$	$1 \leftrightarrow 2$	$1 \leftrightarrow 1$	$1 \leftrightarrow 2$	$1 \leftrightarrow 1$
$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_2)$	$\pm 2\boldsymbol{a}_2$	$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_2 + 2\boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_2 + \boldsymbol{a}_3)$	$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_2)$	$\pm 2\boldsymbol{a}_1$
$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_2)$	$\pm 2\boldsymbol{a}_3$	$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_2 - 2\boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_2 - \boldsymbol{a}_3)$	$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_2)$	
		$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_2 + 2\boldsymbol{a}_3)$			
		$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_2 - 2\boldsymbol{a}_3)$			
$1 \leftrightarrow 3$	$2 \leftrightarrow 2$	$1 \leftrightarrow 3$	$2 \leftrightarrow 2$	$1 \leftrightarrow 3$	$2 \leftrightarrow 2$
$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_1$	$\pm(\boldsymbol{a}_1 + 2\boldsymbol{a}_2 + \boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_1 + \boldsymbol{a}_3)$	$\pm(\boldsymbol{a}_1 + \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_2$
$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_3$	$\pm(\boldsymbol{a}_1 + 2\boldsymbol{a}_2 - \boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_1 - \boldsymbol{a}_3)$	$\pm(\boldsymbol{a}_1 - \boldsymbol{a}_3)$	
		$\pm(\boldsymbol{a}_1 - 2\boldsymbol{a}_2 + \boldsymbol{a}_3)$			
		$\pm(\boldsymbol{a}_1 - 2\boldsymbol{a}_2 - \boldsymbol{a}_3)$			
$2 \leftrightarrow 3$	$3 \leftrightarrow 3$	$2 \leftrightarrow 3$	$3 \leftrightarrow 3$	$2 \leftrightarrow 3$	$3 \leftrightarrow 3$
$\pm(\boldsymbol{a}_2 + \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_1$	$\pm(2\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_1 + \boldsymbol{a}_2)$	$\pm(\boldsymbol{a}_2 + \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_3$
$\pm(\boldsymbol{a}_2 - \boldsymbol{a}_3)$	$\pm 2\boldsymbol{a}_2$	$\pm(2\boldsymbol{a}_1 + \boldsymbol{a}_2 - \boldsymbol{a}_3)$	$\pm 2(\boldsymbol{a}_1 - \boldsymbol{a}_2)$	$\pm(\boldsymbol{a}_2 - \boldsymbol{a}_3)$	
		$\pm(2\boldsymbol{a}_1 - \boldsymbol{a}_2 + \boldsymbol{a}_3)$			
		$\pm(2\boldsymbol{a}_1 - \boldsymbol{a}_2 - \boldsymbol{a}_3)$			

Table D.3: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first eleven nearest neighbour sites on the simple-cubic lattice. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of a (the lattice parameter). The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2,s_3					
$\boldsymbol{l}$	1,0,0	0,1,0	0,0,1	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{3},\frac{1}{3},\frac{1}{3}$
0,0,0	1.5163863	1.3446611	1.3932033	1.2679322	1.1424610	1.1764894
1,0,0	0.5163863	0	0	0.3007507	0.1090663	0.2039071
1,1,0	0.3311489	0.3446611	0	0.2351136	0.1359402	0.1638124
1,1,1	0.2614704	0	0.3932033	0.1776880	0.1489857	0.1617486
2,0,0	0.2573361	0.2299359	0.2909006	0.1589829	0.0964524	0.1149881
2,1,0	0.2155899	0	0	0.1423807	0.0821902	0.1043218
2,1,1	0.1917919	0.1954666	0	0.1299606	0.0734968	0.0974025
2,2,0	0.1683313	0.1708892	0.2295983	0.1132549	0.0718831	0.0860998
2,2,1	0.1569527	0	0	0.1058436	0.0657423	0.0807537
3,0,0	0.1652710	0	0	0.1060232	0.0603971	0.0776249
3,1,0	0.1531392	0.1496801	0	0.1006746	0.0591546	0.0743476

Table D.4: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first eleven nearest neighbour sites on the face-centred-cubic lattice. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of $a/2$, where a is the lattice parameter. The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2,s_3					
$\boldsymbol{l}$	1,0,0	0,1,0	0,0,1	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{3},\frac{1}{3},\frac{1}{3}$
0,0,0	1.3446611	1.5163881	1.0920099	1.2065504	1.1198210	1.1273305
1,1,0	0.3446611	0	0.0549560	0.1961962	0.0708944	0.1333177
2,0,0	0.2299359	0.5163881	0.0594701	0.2169047	0.1532518	0.1475308
2,1,1	0.1954666	0	0.0920099	0.1212752	0.0863901	0.1011431
2,2,0	0.1708892	0.3311506	0.0454183	0.1171477	0.0679846	0.0824935
3,1,0	0.1496801	0	0.0467365	0.1028574	0.0526685	0.0737941
2,2,2	0.1383631	0.2614721	0.0390827	0.0897728	0.0500035	0.0671462
3,2,1	0.1279530	0	0.0413390	0.0834487	0.0512619	0.0637574
4,0,0	0.1183354	0.2573379	0.0431288	0.0870572	0.0540742	0.0617325
3,3,0	0.1129709	0	0.0412775	0.0748562	0.0441468	0.0560164
3,3,2	0.1020796	0	0.0358834	0.0666873	0.0410739	0.0508415

Table D.5: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first eleven nearest neighbour sites on the body-centred-cubic lattice. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of $a/2$, where a is the lattice parameter. The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2,s_3					
$\boldsymbol{l}$	1,0,0	0,1,0	0,0,1	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{3},\frac{1}{3},\frac{1}{3}$
0,0,0	1.3932033	1.5163881	1.3446602	1.2989602	1.2679322	1.1790551
1,1,1	0.3932033	0	0	0.2985769	0	0.1885036
2,0,0	0.2909006	0.5163881	0	0.2993434	0.3007507	0.1979901
2,2,0	0.2295983	0.3311506	0.3446602	0.1902050	0.2351136	0.1506717
3,1,1	0.1885979	0	0	0.1651490	0	0.1105067
2,2,2	0.1909261	0.2614721	0	0.1547214	0.1776880	0.1100009
4,0,0	0.1547998	0.2573379	0.2299351	0.1411634	0.1589829	0.0964631
3,3,1	0.1479944	0	0	0.1242961	0	0.0869852
4,2,0	0.1413034	0.2155917	0	0.1222866	0.1423807	0.0863015
4,2,2	0.1303529	0.1917937	0.1954657	0.1109176	0.1299606	0.0786514
3,3,3	0.1244287	0	0	0.1041394	0	0.0729745

Table D.6: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first eight nearest neighbour sites on the interstitial lattice of the NaCl structure. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of a (the lattice parameter). The origin is a type-1 lattice site. The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2,s_3						
$\boldsymbol{l}$	1,0,0	0,1,0	0,0,1	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$0,\frac{1}{3},\frac{2}{3}$	$\frac{1}{3},\frac{1}{3},\frac{1}{3}$
0,0,0	1.5163863	1.3446611	1.7928802	1.2679322	1.1794606	1.2218536	1.1919798
1,0,0	0.5163863	0	0	0.3007507	0.1094808	0.0966142	0.2046404
1,1,0	0.3311489	0.3446611	0	0.2351136	0.1375198	0.1114850	0.1644149
1,1,1	0.2614704	0	0.7928802	0.1776880	0.2214014	0.2770379	0.2068841
1,1,−1	0.2614704	0	0	0.1776880	0.0774097	0.0640926	0.1170406
2,0,0	0.2573361	0.2299359	0	0.1589829	0.0780499	0.0630777	0.1074709
2,1,0	0.2155899	0	0	0.1423807	0.0822400	0.0738009	0.1041151
2,2,0	0.1683313	0.1708892	0.4595469	0.1132549	0.0815451	0.0949646	0.0899282
2,1,−1	0.1917919	0.1954666	0	0.1299606	0.0729860	0.0646976	0.0972454

Table D.7: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first five nearest neighbour sites on the interstitial lattice of the CsCl structure. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of a (the lattice parameter). The origin is a type-3 lattice site. The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2,s_3,s_4					
$\boldsymbol{l}$	1,0,0,0	0,0,1,0	$0,0,\frac{1}{2},\frac{1}{2}$	$0,0,\frac{1}{3},\frac{2}{3}$	$0,\frac{1}{3},\frac{1}{3},\frac{1}{3}$	$\frac{1}{4},\frac{1}{4},\frac{1}{4},\frac{1}{4}$
0,0,0	1.4762128	1.1326166	1.1412500	1.2049967	1.1598194	1.1453715
1,0,1	0.4762128	0.0704497	0.0695943	0.0635812	0.0824390	0.1370493
2,0,0	0.2971305	0.0762584	0.0548023	0.0458023	0.2058144	0.1778442
2,1,1	0.2539488	0.1326166	0.0862322	0.0728923	0.0895734	0.1080655
2,2,0	0.2118984	0.0542953	0.1962678	0.2710490	0.1840702	0.1585272

Table D.8: Values of the probability generating function $P(\boldsymbol{l};1)$ for the first three nearest neighbour sites on the interstitial lattice of the s.c.(e) structure. The $\boldsymbol{l}$ shown are representative nearest neighbour sites and the coordinates, relative to orthogonal axes, are in units of a (the lattice parameter). The origin is a type-1 lattice site. The s_i are the normalised probabilities that a jump of the random walker will be to an i^{th} nearest neighbour site.

	s_1,s_2		
$\boldsymbol{l}$	1,0	$\frac{1}{2},\frac{1}{2}$	$\frac{1}{3},\frac{2}{3}$
0,0,0	1.4762128	1.4321661	1.5770988
1,0,1	0.4762128	0.3249602	0.2959571
0,0,2	0.3403122	0.5393720	0.7176697

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Publications

The following papers, on the work in this thesis, have been accepted for publication.

1. Stephenson, P.C.L. and Sholl, C.A., 1993. NMR magnetic dipolar spectral density functions for two-dimensional lattice diffusion. *J. Phys.: Condens. Matter*, **5**, 2809–2824.

2. Stephenson, P.C.L. and Sholl, C.A., 1994. Tracer correlation factor and atomic displacements due to the collinear interstitialcy mechanism. *Phil. Mag. A*, **69**, 57–64.

3. Stephenson, P.C.L., 1994. Tracer correlation factor and atomic displacements due to the noncollinear interstitialcy mechanism. *Phil. Mag. A*, **70**, 775–792.