

3.4. ACCELERATED CONVERGENCE TREATMENT OF R^{-N} LATTICE SUMS

$$(1) + (3) = [1/\Gamma(n/2)] \sum_{j \neq k} Q_{jk} |\mathbf{R}_k - \mathbf{R}_j|^{-n} \\ \times \Gamma(n/2, \pi w^2 |\mathbf{R}_k - \mathbf{R}_j|^2),$$

which is the $\mathbf{d} = 0$, j unequal to k portion of the treated direct-lattice sum. The \mathbf{d} unequal to 0, j unequal to k portion corresponds to term (2) and the \mathbf{d} unequal to 0, $j = k$ portion corresponds to term (6). The direct-lattice terms may be consolidated as

$$(1) + (2) + (3) + (6) = [1/2\Gamma(n/2)] \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \\ \times \Gamma[n/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2].$$

Now let us combine terms (4) and (8), carrying out the \mathbf{h} summation first:

$$(4) + (8) = [1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h}} |\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\ \times \sum_j \sum_k Q_{jk} \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)].$$

Terms (5) and (9) may be combined:

$$(5) + (9) = [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} (n-3)^{-1} \left(\sum_j Q_{ij} + \sum_{j \neq k} Q_{jk} \right).$$

The final formula is shown below. The significance of the four terms is: (1) the treated direct-lattice sum; (2) a correction for the difference resulting from the removal of the origin term in direct space; (3) the reciprocal-lattice sum, except $\mathbf{h} = 0$; and (4) the $\mathbf{h} = 0$ term of the reciprocal-lattice sum.

$$V(n, \mathbf{R}_j) \\ = [1/2\Gamma(n/2)] \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \\ \times \Gamma(n/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2) \quad (1)$$

$$- [1/\Gamma(n/2)] \pi^{n/2} w^n n^{-1} \sum_j Q_{jj} \quad (2)$$

$$+ [1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_{\mathbf{h}} |\mathbf{H}(\mathbf{h})|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \\ \times \sum_j \sum_k Q_{jk} \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \quad (3)$$

$$+ [\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} (n-3)^{-1} \left(\sum_j \sum_k Q_{jk} \right). \quad (4)$$

3.4.6. The case of $n = 1$ (Coulombic lattice energy)

As taken above, the limit of the reciprocal-lattice $\mathbf{h} = 0$ term of $S'(n, \mathbf{R})$ or $S'(n, 0)$ existed only if n was greater than 3. The corresponding contributions to $V(n, \mathbf{R}_j)$ were terms (5) and (9) of Section 3.4.5. To extend the method to $n = 1$ we will show in this section that these $\mathbf{h} = 0$ terms vanish if conditions of unit-cell neutrality and zero dipole moment are satisfied.

The integral representation of the term (5) is

$$[1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_{j \neq k} Q_{jk} \int \delta(0) |\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] \\ \times \exp[2\pi i \mathbf{H} \cdot (\mathbf{R}_k - \mathbf{R}_j)] d\mathbf{H}$$

and for term (9) is

$$[1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \sum_j Q_{jj} \int \delta(0) |\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] d\mathbf{H}.$$

Combining these two sums of integrals into one integral sum gives

$$[1/2\Gamma(n/2)] V_d^{-1} \pi^{n-(3/2)} \int \delta(0) |\mathbf{H}|^{n-3} \\ \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] \sum_j \sum_k Q_{jk} \\ \times \exp[2\pi i \mathbf{H} \cdot (\mathbf{R}_k - \mathbf{R}_j)] d\mathbf{H}.$$

For $n = 1$, suppose q_j are net atomic charges so that the geometric combining law holds for $Q_{jk} = q_j q_k$. Then the double sum over j and k can be factored so that the limit that needs to be considered is

$$\lim_{|\mathbf{H}| \rightarrow 0} \frac{[\sum_k q_k \exp(2\pi i \mathbf{H} \cdot \mathbf{R}_k)] [\sum_j q_j \exp(-2\pi i \mathbf{H} \cdot \mathbf{R}_j)]}{|\mathbf{H}|^2}.$$

If the unit cell does not have a net charge, the sum over the q 's goes to zero in the limit and this is a 0/0 indeterminate form. Let $|\mathbf{H}|$ approach zero along the polar axis so that $\mathbf{H} \cdot \mathbf{R}_k = H_3 R_{3k}$, where subscript 3 indicates components along the polar axis. To find the limit with L'Hospital's rule the numerator and denominator are differentiated twice with respect to H_3 . Represent the numerator of the limit by the product (uv) and note that

$$\frac{d^2(uv)}{dx^2} = u \frac{d^2v}{dx^2} + v \frac{d^2u}{dx^2} + 2 \frac{du}{dx} \frac{dv}{dx}.$$

It is seen that in addition to cell neutrality the product of the first derivatives of the sums must exist. These sums are

$$\left[2\pi i \sum_k q_k R_{3k} \exp(2\pi i H_3 R_{3k}) \right]$$

and

$$\left[-2\pi i \sum_j q_j R_{3j} \exp(-2\pi i H_3 R_{3j}) \right],$$

which vanish if the unit cell has no dipole moment in the polar direction, that is, if $\sum q_j R_{3j} = 0$. Since the second derivative of the denominator is a constant, the desired limit is zero under the specified conditions. Now the polar direction can be chosen arbitrarily, so the unit cell must not have a dipole moment in any direction for the limit of the numerator to be zero. Thus we have the formula for the Coulombic lattice sum

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$$\begin{aligned}
 V(\mathbf{1}, \mathbf{R}_j) &= [1/2\Gamma(1/2)] \sum_j \sum_k' Q_{jk} \sum_{\mathbf{d}} |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-1} \\
 &\quad \times \Gamma(1/2, \pi w^2 |\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2) \\
 &\quad + [1/2\Gamma(1/2)V_d^{-1} \pi^{-1/2} \sum_{\mathbf{h}} |\mathbf{H}(\mathbf{h})|^{-2} \\
 &\quad \times \Gamma(1/2, \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2) \sum_j \sum_k Q_{jk} \\
 &\quad \times \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot (\mathbf{R}_k - \mathbf{R}_j)] \\
 &\quad - [1/\Gamma(1/2)] \pi^{1/2} w \sum_j q_j^2,
 \end{aligned}$$

which holds on conditions that the unit cell be electrically neutral and have no dipole moment. If the unit cell has a dipole moment, the limiting value discussed above depends on the direction of \mathbf{H} . For methods of obtaining the Coulombic lattice sum where the unit cell does have a dipole moment, the reader is referred to the literature (DeWette & Schacher, 1964; Cummins *et al.*, 1976; Bertaut, 1978; Massidda, 1978).

3.4.7. The cases of $n = 2$ and $n = 3$

If $n = 2$ the denominator considered for the limit in the preceding section is linear in $|\mathbf{H}|$ so that only one differentiation is needed to obtain the limit by L'Hospital's method. Since a term of the type $\sum_j q_j \exp(2\pi i \mathbf{H} \cdot \mathbf{R}_j)$ is always a factor, the requirement that the unit cell have no dipole moment can be relaxed. For $n = 2$ the zero-charge condition is still required: $\sum_j q_j = 0$. When $n = 3$ the expression becomes determinate and no differentiation is required to obtain a limit. In addition, factoring the Q_{jk} sums into q_j sums is not necessary so that the only remaining requirement for this term to be zero is $\sum_j \sum_k Q_{jk} = 0$, which is a further relaxation beyond the requirement of cell neutrality.

3.4.8. Derivation of the accelerated convergence formula via the Patterson function

The structure factor with generalized coefficients q_j is defined by

$$F[\mathbf{H}(\mathbf{h})] = \sum_j q_j \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}_j].$$

The corresponding Patterson function is defined by

$$P(\mathbf{X}) = V_d^{-1} \sum_{\mathbf{h}} |F[\mathbf{H}(\mathbf{h})]|^2 \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{X}].$$

The physical interpretation of the Patterson function is that it is nonzero only at the intersite vector points $\mathbf{R}_k + \mathbf{X}(\mathbf{h}) - \mathbf{R}_j$. If the origin point is removed, the lattice sum may be expressed as an integral over the Patterson function. This origin point in the Patterson function corresponds to intersite vectors with $j = k$ and $\mathbf{H}(\mathbf{h}) = 0$:

$$S_n = (1/2V_d) \int |\mathbf{X}|^{-n} [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})] d\mathbf{X}.$$

Using the incomplete gamma function as a convergence function, this formula expands into two integrals

$$\begin{aligned}
 S_n &= [1/2V_d \Gamma(n/2)] \int |\mathbf{X}|^{-n} \\
 &\quad \times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})] \Gamma(n/2, \pi w^2 |\mathbf{X}|^2) d\mathbf{X} \\
 &\quad + [1/2V_d \Gamma(n/2)] \int |\mathbf{X}|^{-n} \\
 &\quad \times [P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})] \gamma(n/2, \pi w^2 |\mathbf{X}|^2) d\mathbf{X}.
 \end{aligned}$$

The first integral is shown only for a consistent representation; actually it will be reconvered to a sum and evaluated in direct space. The first part of the second integral will be evaluated with Parseval's theorem and the second part in the limit as $|\mathbf{X}|$ approaches zero:

$$\begin{aligned}
 &[1/2V_d \Gamma(n/2)] \int FT_3[P(\mathbf{X})] \\
 &\quad \times FT_3[|\mathbf{X}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{X}|^2)] d\mathbf{H} \\
 &\quad - \lim_{\mathbf{X} \rightarrow 0} [1/2V_d \Gamma(n/2)] [P(0) |\mathbf{X}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{X}|^2)].
 \end{aligned}$$

The first Fourier transform (of the Patterson function) is the set of amplitudes of the structure factors and the second Fourier transform has already been discussed above; the method for obtaining the limit (for n equal to or greater than 1) was also discussed above. The result obtained is

$$\begin{aligned}
 &[1/2V_d \Gamma(n/2)] \pi^{n-(3/2)} \int |F[\mathbf{H}(\mathbf{h})]|^2 |\mathbf{H}|^{n-3} \\
 &\quad \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] d\mathbf{H} \\
 &\quad - [1/2V_d \Gamma(n/2)] |F(0)|^2 2\pi^{n/2} w^n n^{-1}.
 \end{aligned}$$

The integral can be converted into a sum, since $|F[\mathbf{H}(\mathbf{h})]|$ is nonzero only at the reciprocal-lattice points:

$$\begin{aligned}
 &[1/2V_d \Gamma(n/2)] \pi^{n-(3/2)} \sum_{\mathbf{h}} |F[\mathbf{H}(\mathbf{h})]|^2 |\mathbf{H}(\mathbf{h})|^{n-3} \\
 &\quad \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2].
 \end{aligned}$$

The term with $\mathbf{H}(\mathbf{h}) = 0$ is evaluated in the limit, for n greater than 3, as

$$[\Gamma(n/2)]^{-1} V_d^{-1} \pi^{n/2} w^{n-3} (n-3)^{-1} |F(0)|^2.$$

Since $|F(0)|^2 = \sum_j \sum_k q_j q_k$, this term is identical with the third term of $V(n, \mathbf{R}_j)$ as derived earlier. The case of $n = 1$ is handled in the same way as previously discussed, where the limit of this term is zero provided the unit cell has no net charge or dipole moment.

3.4.9. Evaluation of the incomplete gamma function

The incomplete gamma function may be expressed in terms of commonly available functions such as the exponential integral and the complement of the error function. The definition of the exponential integral is

$$E_1(x^2) = \int_{x^2}^{\infty} t^{-1} \exp(-t) dt = \Gamma(0, x^2).$$

The definition of the complement of the error function is

$$\operatorname{erfc}(x) = \int_x^{\infty} \exp(-t^2) dt = \pi^{-1/2} \Gamma(1/2, x^2).$$