International Tables for Crystallography (2010). Vol. B, Section 3.4.4, pp. 450–452.

Table 3.4.2.2. *Untreated lattice-sum results for the dispersion energy (n = 6) of crystalline benzene (kJ mol^{-1}, Å)*

Truncation limit	Number of molecules	Number of terms	Calculated energy
6.0	26	524	−69.227
8.0	51	1313	−76.007
10.0	77	2631	−78.179
12.0	126	4718	−79.241
14.0	177	7531	−79.726
16.0	265	11274	−80.013
18.0	344	15904	−80.178
20.0	439	22049	−80.295
Converged value			−80.589

the original sum, which contains the difference terms, is not increased.

$$V_n = (1/2)\sum_j^{\text{one cell}} \sum_k^{\text{all cells}}{}' Q_{jk}R_{jk}^{-n}W(R) + (1/2)\sum_j^{\text{one cell}} \sum_k^{\text{all cells}}{}' Q_{jk}R_{jk}^{-n}[1-W(R)].$$

In the accelerated-convergence method the difference terms are expressed as an integral of the product of two functions. According to Parseval's theorem (described below) this integral is equal to an integral of the product of the two Fourier transforms of the functions. Finally, the integral over the Fourier transforms of the functions is converted to a sum in reciprocal (or Fourier-transform) space. The choice of the convergence function $W(R)$ is not unique; an obvious requirement is that the relevant Fourier transforms must exist and have correct limiting behaviour. Nijboer and DeWette suggested using the incomplete gamma function for $W(R)$. More recently, Fortuin (1977) showed that this choice of convergence function leads to optimal convergence of the sums in both direct and reciprocal space:

$$W(R) = \Gamma(n/2, \pi w^2R^2)/\Gamma(n/2),$$

where $\Gamma(n/2)$ and $\Gamma(n/2, \pi w^2R^2)$ are the gamma function and the incomplete gamma function, respectively:

$$\Gamma(n/2, \pi w^2R^2) = \int_{\pi w^2R^2}^{\infty} t^{(n/2)-1}\exp(-t)\,\mathrm{d}t$$

and

$$\Gamma(n/2) = \Gamma(n/2, 0).$$

The complement of the incomplete gamma function is

$$\gamma(n/2, \pi w^2R^2) = \Gamma(n/2) - \Gamma(n/2, \pi w^2R^2).$$

3.4.4. Preliminary derivation to obtain a formula which accelerates the convergence of an R^{-n} sum over lattice points X(d)

The three-dimensional direct-space crystal lattice is specified by the origin vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. A general vector in direct space is defined as

$$\mathbf{X}(\mathbf{x}) = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3,$$

where x_1, x_2, x_3 are the fractional cell coordinates of $\mathbf{X}$. A lattice vector in direct space is defined as

$$\mathbf{X}(\mathbf{d}) = d_1\mathbf{a}_1 + d_2\mathbf{a}_2 + d_3\mathbf{a}_3,$$

where d_1, d_2, d_3 are integers (specifying particular values of x_1, x_2, x_3) designating a lattice point. $V_{\rm d}$ is the direct-cell volume which is equal to $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$. A general point in the direct lattice is $\mathbf{X}(\mathbf{x})$; the contents of the lattice are by definition identical as the components of $\mathbf{x}$ are increased or decreased by integer amounts.

The reciprocal-lattice vectors are defined by the relations

$$\begin{aligned} \mathbf{a}_j \cdot \mathbf{b}_k &= 1 \qquad j = k \\ &= 0 \qquad j \neq k. \end{aligned}$$

A general vector in reciprocal space $\mathbf{H}(\mathbf{r})$ is defined as

$$\mathbf{H}(\mathbf{r}) = r_1\mathbf{b}_1 + r_2\mathbf{b}_2 + r_3\mathbf{b}_3.$$

A reciprocal-lattice vector $\mathbf{H}(\mathbf{h})$ is defined by the integer triplet h_1, h_2, h_3 (specifying particular values of r_1, r_2, r_3) so that

$$\mathbf{H}(\mathbf{h}) = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3.$$

In other sections of this volume a shortened notation $\mathbf{h}$ is used for the reciprocal-lattice vector. In this section the symbol $\mathbf{H}(\mathbf{h})$ is used to indicate that it is a particular value of $\mathbf{H}(\mathbf{r})$.

The three-dimensional Fourier transform $g(\mathbf{t})$ of a function $f(\mathbf{x})$ is defined by

$$g(\mathbf{t}) = FT_3[f(\mathbf{x})] = \int f(\mathbf{x})\exp(2\pi i\mathbf{x}\cdot\mathbf{t})\,\mathrm{d}\mathbf{x}.$$

The Fourier transform of the set of points defining the direct lattice is the set of points defining the reciprocal lattice, scaled by the direct-cell volume. It is useful for our purpose to express the lattice transform in terms of the Dirac delta function $\delta(x - x_{\rm o})$ which is defined so that for any function $f(\mathbf{x})$

$$f(\mathbf{x}_{\rm o}) = \int \delta(\mathbf{x} - \mathbf{x}_{\rm o})f(\mathbf{x})\,\mathrm{d}\mathbf{x}.$$

We then write

$$FT_3\{\sum_{\mathbf{d}}\delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})]\} = V_{\rm d}^{-1}\sum_{\mathbf{h}}\delta[\mathbf{H}(\mathbf{r}) - \mathbf{H}(\mathbf{h})].$$

First consider the lattice sum over the direct-lattice points $\mathbf{X}(\mathbf{d})$, relative to a particular point $\mathbf{X}(\mathbf{x}) = \mathbf{R}$, with omission of the origin lattice point.

$$S'(n, \mathbf{R}) = \sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n}.$$

The special case with $\mathbf{R} = 0$ will also be needed:

$$S'(n, 0) = \sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})|^{-n}.$$

Now define a sum of Dirac delta functions

$$f'[\mathbf{X}(\mathbf{d})] = \sum_{d \neq 0} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})].$$

Then S' can be represented as an integral

$$S'(n, \mathbf{R}) = \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} \, \mathrm{d}\mathbf{X},$$

in which a term is contributed to S' whenever the direct-space vector $\mathbf{X}$ coincides with the lattice vector $\mathbf{X}(\mathbf{d})$, except for $\mathbf{d} = 0$. Now apply the convergence function to S':

$$\begin{aligned} S'(n, \mathbf{R}) = {} & [\Gamma(n/2)]^{-1} \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} \\ & \times \Gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) \, \mathrm{d}\mathbf{X} \\ & + [\Gamma(n/2)]^{-1} \int f'[\mathbf{X}(\mathbf{d})] |\mathbf{X} - \mathbf{R}|^{-n} \\ & \times \gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) \, \mathrm{d}\mathbf{X}. \end{aligned}$$

The first integral is shown here only for the purpose of giving a consistent representation of S'; in fact, the first integral will be reconverted back into a sum and evaluated in direct space. The second integral will be transformed to reciprocal space using Parseval's theorem [see, for example, Arfken (1970)], which states that

$$\int f(\mathbf{X}) g^*(\mathbf{X}) \, \mathrm{d}\mathbf{X} = \int FT_3[f(\mathbf{X})] FT_3[g^*(\mathbf{X})] \, \mathrm{d}\mathbf{H}.$$

Considering only the second integral in the formula for S' and explicitly introducing the $\mathbf{d} = 0$ term we have

$$\begin{aligned} & [\Gamma(n/2)]^{-1} \int f[\mathbf{X}(\mathbf{d})] |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) \, \mathrm{d}\mathbf{X} \\ & \quad - [\Gamma(n/2)]^{-1} \int \delta(\mathbf{X}) |\mathbf{R}|^{-n} \gamma(n/2, \pi w^2 |\mathbf{R}|^2) \, \mathrm{d}\mathbf{X}, \end{aligned}$$

where the unprimed f includes the $\mathbf{h} = 0$ term which was earlier omitted from f':

$$f(\mathbf{X}) = \sum_{\mathbf{d}} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})].$$

Using Parseval's theorem, and evaluating the origin term, we have

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

The Fourier transform of the complement of the incomplete gamma function divided by $|\mathbf{X}|^n$ is (Nijboer & DeWette, 1957)

$$\begin{aligned} & FT_3[\gamma(n/2, \pi w^2 |\mathbf{X}|^2) |\mathbf{X}|^{-n}] \\ & \quad = \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2]. \end{aligned}$$

If there is a change of origin and the point $(\mathbf{X} - \mathbf{R})$ is used instead of $\mathbf{X}$ the transform is

$$\begin{aligned} & FT_3[\gamma(n/2, \pi w^2 |\mathbf{X} - \mathbf{R}|^2) |\mathbf{X} - \mathbf{R}|^{-n}] \\ & \quad = \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \Gamma[(-n/2) \\ & \qquad + (3/2), \pi w^{-2} |\mathbf{H}|^2] \exp(2\pi i \mathbf{H} \cdot \mathbf{R}). \end{aligned}$$

Evaluation of the two Fourier transforms in the first term gives

$$\begin{aligned} & [\Gamma(n/2)]^{-1} \int V_{\mathrm{d}}^{-1} \sum_{\mathbf{h}} \delta[\mathbf{H}(\mathbf{h}) - \mathbf{H}] \pi^{n-(3/2)} |\mathbf{H}|^{n-3} \\ & \quad \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2] \exp(2\pi i \mathbf{H} \cdot \mathbf{R}) \, \mathrm{d}\mathbf{H}. \end{aligned}$$

Because of the presence of the Dirac delta function in each integral, we can convert the integrals with $\mathbf{h}$ unequal to zero into a sum

$$\begin{aligned} & [\Gamma(n/2)]^{-1} V_{\mathrm{d}}^{-1} \pi^{n-(3/2)} \sum_{h \neq 0} |\mathbf{H}(\mathbf{h})|^{n-3} \\ & \quad \times \Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}(\mathbf{h})|^2] \exp[2\pi i \mathbf{H}(\mathbf{h}) \cdot \mathbf{R}]. \end{aligned}$$

The $\mathbf{h} = 0$ term needs to be evaluated in the limit. Clearly, the complex exponential goes to unity. If n is greater than 3 the limit of the indeterminate form infinity/infinity is needed:

$$\begin{aligned} & \lim_{|\mathbf{H}| \to 0} \frac{\Gamma[(-n/2) + (3/2), \pi w^{-2} |\mathbf{H}|^2]}{|\mathbf{H}|^{3-n}} \\ & \quad = \lim_{|\mathbf{H}| \to 0} \frac{\int_{\pi w^{-2} |\mathbf{H}|^2}^{\infty} t^{(-n/2)+(1/2)} \exp(-t) \, \mathrm{d}t}{|\mathbf{H}|^{3-n}}. \end{aligned}$$

The limit can be found by L'Hospital's rule [see, for example, Widder (1961)] which states that if $f(x)$ and $g(x)$ both approach infinity as x approaches a constant, c, and the limit of the ratio of the first derivatives $f'(x)$ and $g'(x)$ exists, that limit is also true for the limit of the ratio of the functions:

$$\lim_{x \to c} \frac{f(x)}{g(x)} = \lim_{x \to c} \frac{f'(x)}{g'(x)}.$$

To differentiate the definite integral function, Leibnitz's formula may be used [see, for example, Arfken (1970)]. This formula states that

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}x} \int_{g(x)}^{h(x)} f(t, x) \, \mathrm{d}t = {} & \int_{g(x)}^{h(x)} \frac{\mathrm{d}f(t, x)}{\mathrm{d}x} \, \mathrm{d}t \\ & + f[h(x)] \frac{\mathrm{d}h(x)}{\mathrm{d}x} - f[g(x)] \frac{\mathrm{d}g(x)}{\mathrm{d}x}. \end{aligned}$$

In our case, x becomes $|\mathbf{H}|$; f becomes $t^{(-n/2)+(1/2)} \exp(-t)$ which is independent of $|\mathbf{H}|$; g becomes $\pi w^{-2} |\mathbf{H}|^2$; and h is infinite. Thus only the last term of Leibnitz's formula is nonzero and we obtain for the ratio of the first derivatives

$$\begin{aligned} & \lim_{|\mathbf{H}| \to 0} \frac{-(\pi w^{-2} |\mathbf{H}|^2)^{(-n/2)+(1/2)} \exp(-\pi w^2 |\mathbf{H}|^2) 2\pi w^{-2} |\mathbf{H}|}{(3 - n) |\mathbf{H}|^{2-n}} \\ & \quad = \pi^{(-n/2)+(3/2)} w^{n-3} [2/(n-3)], \end{aligned}$$

so that the limiting value for the $\mathbf{h} = 0$ term for n greater than 3 is

$$+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n/2}w^{n-3}[2/(n-3)].$$

The final result for S' is

$$\begin{aligned}S'(n,\mathbf{R}) &= [\Gamma(n/2)]^{-1}\sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})-\mathbf{R}|^{-n}\\ &\quad\times \Gamma(n/2,\pi w^2|\mathbf{X}(\mathbf{d})-\mathbf{R}|^2)\\ &\quad-[\Gamma(n/2)]^{-1}|\mathbf{R}|^{-n}\gamma(n/2,\pi w^2|\mathbf{R}|^2)\\ &\quad+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3}\\ &\quad\times\Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2]\\ &\quad\times\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot\mathbf{R}]\\ &\quad+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}.\end{aligned}$$

The significance of the terms is as follows. The first term represents the convergence-accelerated direct sum, which does not include the origin term; the next term, also in direct space, corrects for the remainder resulting from the subtraction of the origin term; the third term comes from Parseval's theorem and is a sum over the nonzero $\mathbf{h}$ reciprocal-lattice points; and the last term is the reciprocal-lattice $\mathbf{h}=0$ term.

If $\mathbf{R}=0$ the second term becomes an indeterminate form 0/0. The limit can be found with use of L'Hospital's rule again, this time for the 0/0 form. We need the limit of $f(x)/g(x)$, where $f(R)=\gamma(n/2,\pi w^2R^2)$ and $g(R)=R^n$. To differentiate the incomplete gamma function, we can again use Leibnitz's formula. In this case only the second term of the formula is nonzero and we obtain for the ratio of the first derivatives

$$\frac{2\pi^{n/2}w^n|\mathbf{R}|^{n-1}\exp(-\pi w^2|\mathbf{R}|^2)}{n|\mathbf{R}|^{n-1}},$$

so that the limiting value for this term as $|\mathbf{R}|$ approaches zero is

$$-[\Gamma(n/2)]^{-1}2\pi^{n/2}w^nn^{-1}.$$

Therefore, the value of the sum when $\mathbf{R}=0$ is

$$\begin{aligned}S'(n,0) &= [\Gamma(n/2)]^{-1}\sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})|^{-n}\Gamma(n/2,\pi w^2|\mathbf{X}(\mathbf{d})|^2)\\ &\quad-[\Gamma(n/2)]^{-1}2\pi^{n/2}w^nn^{-1}\\ &\quad+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3}\\ &\quad\times\Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2]\\ &\quad+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}.\end{aligned}$$

3.4.5. Extension of the method to a composite lattice

Define a general lattice sum over direct-space points $\mathbf{R}_j$ which interact with pairwise coefficients Q_{jk}, where $Q_{jk}=Q_{kj}$:

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

where the prime indicates that when $\mathbf{d}=0$ the self-terms with $j=k$ are omitted. For convenience the terms may be divided into three groups: the first group of terms has $\mathbf{d}=0$, where j is unequal to k; the second group has $\mathbf{d}$ not zero and j not equal to k; and the third group had $\mathbf{d}$ not zero and $j=k$. (A possible fourth group with $\mathbf{d}=0$ and $j=k$ is omitted, as defined.)

$$\begin{aligned}V(n,\mathbf{R}_j) &= (1/2)\sum_{j\neq k}Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n}\\ &\quad+(1/2)\sum_{j\neq k}Q_{jk}S'(n,|\mathbf{R}_j-\mathbf{R}_k|)+(1/2)\sum_j Q_{jj}S'(n,0).\end{aligned}$$

By expanding this expression we obtain

$$\begin{aligned}V(n,\mathbf{R}_j) &= (1/2)\sum_{j\neq k}Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} &(1)\\ &\quad+\Big\{[1/2\Gamma(n/2)]\sum_{j\neq k}Q_{jk}\sum_{\mathbf{d}\neq 0}|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^{-n}\\ &\quad\times\Gamma(n/2,\pi w^2|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^2)\Big\} &(2)\\ &\quad-\Big\{[1/2\Gamma(n/2)]\sum_{j\neq k}Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n}\\ &\quad\times\gamma(n/2,\pi w^2|\mathbf{R}_k-\mathbf{R}_j|^2)\Big\} &(3)\\ &\quad+\Big\{[1/2\Gamma(n/2)]V_{\rm d}^{-1}\pi^{n-(3/2)}\sum_{j\neq k}Q_{jk}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3}\\ &\quad\times\Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2]\\ &\quad\times\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k-\mathbf{R}_j)]\Big\} &(4)\\ &\quad+[1/2\Gamma(n/2)]V_{\rm d}^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}\sum_{j\neq k}Q_{jk} &(5)\\ &\quad+\Big\{[1/2\Gamma(n/2)]\sum_j Q_{jj}\sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})|^{-n}\\ &\quad\times\Gamma(n/2,\pi w^2|\mathbf{X}(\mathbf{d})|^2)\Big\} &(6)\\ &\quad-[1/\Gamma(n/2)]\pi^{n/2}w^nn^{-1}\sum_j Q_{jj} &(7)\\ &\quad+\Big\{[1/2\Gamma(n/2)]V_{\rm d}^{-1}\pi^{n-(3/2)}\sum_j Q_{jj}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3}\\ &\quad\times\Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2]\Big\} &(8)\\ &\quad+[1/2\Gamma(n/2)]V_{\rm d}^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}\sum_j Q_{jj}. &(9)\end{aligned}$$

This expression for V has nine terms, which are numbered on the right-hand side. Term (3) can be expressed in terms of Γ rather than γ:

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

It is seen that cancellation occurs with term (1) so that

references