

Coulomb Energy of Polar Crystals

Bouke P. van Eijck* and Jan Kroon

Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received: September 11, 1996[⊗]

A simple derivation is given to arrive at an expression for the Coulomb energy of a polar crystal with emphasis on its dependence on the external form of the crystal. It is found that the existing treatments are incomplete, since they refer to the central cell in the crystal, which may have an energy different from the average one. It is stressed that there is a very simple relation between results from calculations using a cutoff scheme and results from Ewald summation. Explicit formulas for the form-dependent contribution are developed for the case of a rectangular crystal. However, the usual approach in which that contribution is neglected appears to be a reasonable one for practical applications.

I. Introduction

It is a well-known fact that the lattice energy of a polar crystal, i.e., a crystal where the unit cell has a nonzero dipole moment, depends in principle on the external shape of the crystal. This is immediately obvious from the consideration that a head-to-tail stacking of dipole moments has a more favorable energy than side-to-side stacking (Figure 1), so a needle in the dipole direction must be energetically favorable with respect to platelets in a plane perpendicular to that direction.

Consequently, the energy of a polar crystal cannot be given unless its external form is specified. Without such specifications tabulation of thermodynamic quantities is meaningless. Nevertheless, few people seem to be worried by this problem; usually, it is assumed that external conditions exist that exactly compensate for the effect of crystal form.

The theory has been discussed by various authors.^{1–4} However, to our knowledge, it has always been treated in conjunction with convergence acceleration techniques, notably Ewald summations. This is, of course, entirely correct, but the mathematical complexity of these treatments tends to obscure the underlying physical principles. It is the first goal of this paper to present a direct and simple derivation of the relevant formulas. In doing so, we find that the discussions mentioned above are not complete, since they refer to a region of the crystal that has not been clearly defined—usually a central unit cell. Implicitly or explicitly, it is assumed that the energy of that cell is representative of the average unit cell in a large crystal, which we shall find to be incorrect. We further give some development of the theory for crystals with a simple form and speculate a little on the implications for the prediction of the internal structure of polar crystals.

II. Derivation of the Energy Equation

Let us denote the position of the origin of a certain unit cell i by a vector \mathbf{R}_i and the vector between two cells i and j by $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. In each cell there are various atoms k with charge q_k and position vector ρ_k with respect to the origin of the cell. The total charge of each cell is zero ($\sum_k q_k = 0$), and the dipole moment of one unit cell is defined as

$$\mathbf{p} = \sum_k q_k \rho_k \quad (1)$$

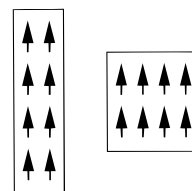


Figure 1. Two different arrays of polar unit cells (symbolized by arrows) are seen to have different energies.

The volume of each cell is V , and the total number of unit cells is N . Thus, the crystal is considered as finite from the beginning, and there are no convergence problems.

The average Coulomb energy of one unit cell is then

$$U = \frac{1}{2N} \sum_i \sum_k \sum_j \sum_{k'}' \frac{q_k q_{k'}}{|\mathbf{R}_{ij} + \rho_k - \rho_{k'}|} \quad (2)$$

where the prime indicates that terms $i = j, k = k'$ must be absent. The factor $1/(4\pi\epsilon_0)$, required in SI units, will be omitted throughout.

Now let us divide the total Coulomb energy into two parts: U_1 and U_2 . The first one refers to those combinations of cells i and j whose distance is smaller than a certain cutoff radius R_c . In U_1 all terms with different indices i will give the same contribution except cells that are closer than R_c to a crystal surface. The number of those is negligible in the thermodynamic limit, so the first term needs only to be evaluated for one representative cell i :

$$U_1 = \frac{1}{2} \sum_k \sum_j \sum_{k'}' \frac{q_k q_{k'}}{|\mathbf{R}_{ij} + \rho_k - \rho_{k'}|} \quad R_{ij} < R_c \quad (3)$$

If desired, the intramolecular interactions could be omitted or treated differently here.

The second part, U_2 , refers to the remaining terms. If the cutoff radius is chosen large enough, we can use the dipole–dipole interaction formula

$$U_2 = \frac{1}{2N} \sum_i \sum_j \left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{R_{ij}^3} - 3 \frac{(\mathbf{p}_i \cdot \mathbf{R}_{ij})(\mathbf{p}_j \cdot \mathbf{R}_{ij})}{R_{ij}^5} \right] \quad R_{ij} \geq R_c \quad (4)$$

where the indices i and j on the dipole moments are only written for clarity and will be omitted further on, since all moments are, of course, equal. When eq 4 is a good approximation, we

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

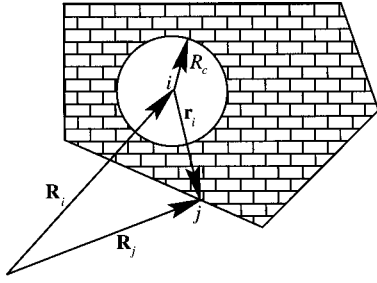


Figure 2. Unit cells j , which contribute to the i th summand in eq 5, are symbolized as bricks in a wall. The cutoff sphere is enormously exaggerated in comparison with the crystal boundary.

can also take the unit cells to be distributed homogeneously with a density V^{-1} for distances larger than R_c . So the summation over j can be replaced by an integration:

$$U_2 = \frac{1}{N} \sum_i \frac{1}{2V} \int \left[\frac{p^2}{R_{ij}^3} - 3 \frac{(\mathbf{p} \cdot \mathbf{R}_{ij})^2}{R_{ij}^5} \right] d^3 \mathbf{R}_j \quad (5)$$

where \mathbf{R}_j is integrated over the entire crystal volume except a sphere with radius R_c centered on unit cell i (Figure 2). Since \mathbf{R}_i is fixed for every integral, we can change the integration variable from \mathbf{R}_j to $\mathbf{r}_i = \mathbf{R}_j - \mathbf{R}_i$. Using Gauss's theorem, we can transform this volume integral into a surface integral:

$$U_2 = \frac{1}{N} \sum_i \frac{1}{2V} \int \frac{(\mathbf{p} \cdot \mathbf{r}_i)(\mathbf{p} \cdot \mathbf{n}_i)}{r_i^3} dA_i \quad (6)$$

where \mathbf{n}_i denotes a unit vector perpendicular to the surface element dA_i , pointing outward from the volume under consideration, which is different for every cell i . This transformation is performed using the relation

$$\text{div} \left[\frac{(\mathbf{p} \cdot \mathbf{r}) \mathbf{p}}{r^3} \right] = \frac{p^2}{r^3} - 3 \frac{(\mathbf{p} \cdot \mathbf{r})^2}{r^5} \quad (7)$$

without possible problems due to singularities, since we always have $r \geq R_c$.

Each summand in eq 6 can be interpreted as the energy of one dipole \mathbf{p}_i in the field of a surface charge density $\mathbf{p} \cdot \mathbf{n}_i/V$, with a factor $1/2$ to prevent a double count of the interactions.

The vector \mathbf{r}_i in eq 6 originates from cell i and ends on the surface of the volume under consideration (Figure 2). There are contributions from the inner as well as the outer surface. The former one concerns the surface of the cutoff sphere and is readily evaluated by integration over the spherical coordinates θ and ϕ since $\mathbf{n}_i = -\mathbf{r}_i/r_i$:

$$U_2^{\text{inner}} = \frac{1}{N} \sum_i \frac{1}{2V} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \frac{(pR_c \cos \theta)(-p \cos \theta)}{R_c^3} R_c^2 \sin \theta d\theta d\phi = -\frac{2\pi p^2}{3V} \quad (8)$$

The second integral covers the outside area of the crystal and introduces the shape dependence of the energy:

$$U_2^{\text{outer}} = \frac{1}{N} \sum_i S_i = \frac{1}{N} \sum_i \frac{1}{2V} \int \frac{(\mathbf{p} \cdot \mathbf{r}_i)(\mathbf{p} \cdot \mathbf{n})}{r_i^3} dA_{\text{outer}} \quad (9)$$

where, for later reference, we have defined S_i as the energy of cell i due to the surface charges. Again, we can replace the summation over all cells by an integration over the entire crystal volume.

The final result is thus

$$U = U_1 + U_2^{\text{inner}} + U_2^{\text{outer}} \quad (10)$$

where the three individual terms are given by eqs 3, 8, and 9. The derivation shows that the cutoff radius must be chosen to be large so that eq 4 can be used. In practice this will be the case when U_1 remains unchanged upon further increase of R_c , which adds a spherical shell to the cutoff sphere. Since the contribution of the dipole moments in a spherical shell is zero, and the influence of higher multipole moments decays faster than r^{-3} , convergence can always be obtained. However, convergence acceleration by Ewald summation, as discussed in the next section, may be quite effective.

In the Appendix we derive expressions for U_2^{outer} for orthogonal crystals with edges L_x, L_y, L_z . A few special cases are

$$L_x = L_y = L_z \text{ (cubic crystal form): } U_2^{\text{outer}} = 2\pi p^2/(3V)$$

$$L_z \rightarrow 0 \text{ (platelet): } U_2^{\text{outer}} = 2\pi p_z^2/V$$

$$L_x \rightarrow 0, L_y \rightarrow 0 \text{ (needle): } U_2^{\text{outer}} = \pi(p_x^2 + p_y^2)/V$$

It is seen that this term is zero for a needle-shaped crystal with the dipole moment in the needle direction and for a platelet with the dipole moment in its plane. This result is intuitively obvious, since these crystals have only a negligible number of charged surfaces; any other form has a higher energy. Notably, for a crystal with a cubic form (which is, of course, something completely different from a crystal with a unit cell of cubic symmetry) the two contributions to U_2 cancel exactly.

It is quite usual to omit the shape-dependent term U_2^{outer} . This is justified by assuming that external charges will accumulate on the surface to annul the surface charge on the crystal exactly (sometimes described as "tin foil boundary conditions"), equivalent to putting the crystal in a medium of very high dielectric constant.

III. Discussion

A. Ewald Summation. As noted in the Introduction, the usual treatment of Coulomb interactions in a periodic system is by Ewald summation. The equations are well-known and can be summarized as

$$U = U_0^{\text{Ewald}} + U_2^{\text{outer}} \quad (11)$$

The first term is given by⁵

$$U_0^{\text{Ewald}} = \frac{1}{2} \sum_k \sum_j \sum_{k'} \frac{q_k q_{k'} \text{erfc}(|\mathbf{R}_{ij} + \boldsymbol{\rho}_k - \boldsymbol{\rho}_{k'}|/\eta)}{|\mathbf{R}_{ij} + \boldsymbol{\rho}_k - \boldsymbol{\rho}_{k'}|} + \frac{1}{2\pi V} \sum_{\mathbf{h} \neq 0} \frac{|F_{\mathbf{h}}|^2}{h^2} \exp(-\pi^2 h^2 \eta^2) - \frac{1}{\pi^{1/2} \eta} \sum_k q_k^2 \quad (12)$$

where \mathbf{h} is a vector in reciprocal space and $F_{\mathbf{h}}$ is defined as

$$F_{\mathbf{h}} = \sum_k q_k \exp(2\pi i \mathbf{h} \cdot \boldsymbol{\rho}_k) \quad (13)$$

comparable in form to the structure factor in diffraction theory.

The parameter η can be chosen at will, which is useful for optimizing the efficiency of the method.

The second term in eq 11, which depends on the surface charge and the crystal shape, follows only from a careful development of the theory. It is a correction for the omission of the $\mathbf{h} = \mathbf{0}$ term in the reciprocal space summation in eq 12. The formulas reported in the literature¹⁻⁴ refer, in fact, to the center cell and thus represent S_{center} (defined as S_i for the center cell, cf. eq 9) rather than U_2^{outer} . These two quantities are sometimes, but not always, equal. A more detailed discussion is given in the next section and in the Appendix.

In any case, comparison of eqs 10 and 11 shows

$$U_0^{\text{Ewald}} = U_1 - \frac{2\pi p^2}{3V} \quad (14)$$

When crystal energies are calculated directly with a sufficiently large cutoff radius, we obtain U_1 , which is obviously different from the Ewald energy U_0^{Ewald} . Likewise, U_1 is different from the vacuum energy U except for some very special crystal forms (for instance, a cube). These differences are not always recognized, or appreciated correctly. For instance, in a recent paper Roberts and Schnitker⁶ define a “direct lattice sum energy” E_{vacuum} (equal to our U) and suggest strongly that this can be obtained by using spherical cutoff conditions. We further disagree with their view that there is some inherent relation between the Ewald procedure and tin foil boundary conditions: one should omit the $\mathbf{h} = \mathbf{0}$ term if those conditions are expected physically and include it otherwise.

As a numerical illustration of the formulas, we have calculated the Coulomb energy for the CsCl lattice: a unit cell with length 1 and charges +1 at (0, 0, 0) and -1 at (0.5, 0.5, 0.5). The results are

$$U_1 = -0.46457 \quad (\text{eq 3, } R_c = 15)$$

$$U_2^{\text{inner}} = -\pi/2 \quad (\text{eq 8})$$

$$U_0^{\text{Ewald}} = -2.03536 \quad (\text{eq 12})$$

These values satisfy eq 14; the Madelung constant is defined as $-\frac{1}{\sqrt{3/2}} U_0^{\text{Ewald}}$ and has the accepted value. Direct calculation of U by eq 2 is extremely time-consuming, and we could not obtain the thermodynamic limit: $U = -0.519, -0.490, -0.481, -0.477$ for cubes of 10, 20, 30, 40 cells, respectively, in each direction.

B. Comparison with the Literature. The surface term U_2^{outer} is often discussed under the assumption of a spherical or cubic crystal, where it is equal to $2\pi p^2/(3V)$. Although earlier work exists, this result is usually attributed to de Leeuw, Perram, and Smith.¹ Older references can be found in the article by Smith,² which gives an elaborate discussion of the shape dependence of the crystal energy. Unfortunately, there seems to be a mix-up in his key equation (3.14), which in our opinion should read (adapted to our notation)

$$S_i = \frac{2}{\pi^2 V} \int_{-\infty}^{\infty} \frac{(\mathbf{p} \cdot \mathbf{w})^2}{w^2} \left[\int_C \exp(2i\mathbf{r}_i \cdot \mathbf{w}) d^3 \mathbf{r}_i \right] d^3 \mathbf{w} \quad (15)$$

We have reconstructed this equation from the discussions that precede and follow it. The subscript C denotes that the integration over \mathbf{r}_i should cover the entire crystal volume. It is important to note that the origin of the vector \mathbf{r}_i is not really specified; the discussion implies that the result should be the same for every cell: $U_2^{\text{outer}} = S_i$. This conclusion is explicitly

TABLE 1: Selected Values for b_z and c_z in a Rectangular Crystal^a

L_x	L_y	L_z	b_z	c_z	
0	0	10	0	0	(needle)
1	1	10	0.0396	0.2873	
5	5	10	0.8054	1.2461	
10	10	10	2.0944	2.0944	($2\pi/3$, cube)
10	10	5	3.7092	3.1160	
10	10	1	5.7198	5.0585	
10	10	0	6.2832	6.2832	(2π , platelet)
10	0	0	3.1416	3.1416	(π , needle)
0	5	10	0	0	(platelet)
1	3	10	0.1144	0.4499	
10	1	3	1.2309	1.5737	
3	10	1	4.9379	4.2596	

^a Crystal dimensions of zero are to be interpreted as limiting values; the results for $L_y = L_z = 0$ implies $L_y/L_z = 1$ and is very sensitive to changes in that ratio. For definition of b_z and c_z see eqs 30 and 28, respectively.

confirmed by Smith's eq 4.23. We disagree, suspecting the discussion of the orders of magnitude in the integration of eq 4.22. A simple counterexample is given in Table 1 of the Appendix. In a later paper⁷ Smith formulated his results differently, and in our opinion correctly. His eq 2.4 in our notation reads

$$U_2^{\text{outer}} = \frac{2}{\pi^2 V^2 N} \int_{-\infty}^{\infty} \frac{(\mathbf{p} \cdot \mathbf{w})^2}{w^2} \left| \int_C \exp(2i\mathbf{r} \cdot \mathbf{w}) d^3 \mathbf{r} \right|^2 d^3 \mathbf{w} \quad (16)$$

To show that eq 15 is equivalent to our eq 9, the integral over the crystal volume can be divided into two parts as in Figure 2. The spherical volume gives a contribution of $2\pi p^2/(3V)$, as shown by Smith. The contribution of the rest of the crystal can be found using Smith's eq 3.24:

$$w^{-2} = \int_0^{\infty} \exp(-t\mathbf{w} \cdot \mathbf{w}) dt \quad (17)$$

Evaluating first the three w integrals and then the t integral leads to

$$S_i = \frac{2\pi p^2}{3V} + \frac{1}{2V} \int_{r_i > R_c} \left[\frac{p^2}{r_i^3} - 3 \frac{(\mathbf{p} \cdot \mathbf{r}_i)^2}{r_i^5} \right] d^3 \mathbf{r}_i \quad (18)$$

By use of eqs 7 and 8, it can be seen that this result is the same as our eq 9. A similar discussion is possible for eq 16.

Another formulation has been presented by Hansen,³ whose eq 3.18 can be written in the form

$$S_i = -\frac{1}{2V} \sum_g \sum_{g'} p_g p_{g'} \int_C \frac{\partial^2}{\partial r_g \partial r_{g'}} \frac{1}{r} d^3 \mathbf{r} \quad (19)$$

where g and g' denote x, y, z . This result can be reduced to eq 18. Again, the implication is that S_i is independent of i .

Deem, Newsam, and Sinha⁴ were the first to express S_i in the elegant form of a surface integral as in eq 9. They stated explicitly the *assumption* that S_{center} is representative for the entire crystal in the thermodynamic limit.

C. Practical Considerations. The key question, of course, is whether or not U_2^{outer} should be included in the energy. In other words, is the assumption of tin foil boundary conditions physically justified? This question is relevant for the theoretical prediction of crystal structures, which is becoming a subject under active investigation. In the comparison of different possible structures the treatment of the surface term is important for polar space groups. To our knowledge, the surface term has never been explicitly included, an exception being the recent

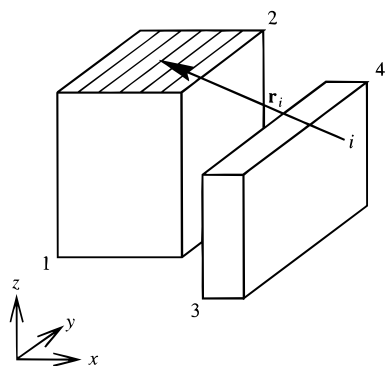


Figure 3. Two parts of a crystal built from rectangular blocks. The energy of one unit cell i due to the surface charge on the hatched area is given by eq 22.

work of Gibson and Sheraga⁸ who use Ewald summation with a surface term corresponding to a spherical crystal. Like for a cubic crystal form, this is equivalent to just calculating U_1 .

In crystal structure prediction it may be quite important to specify the conditions under which the crystal is supposed to be grown. In crystallization from solvents with a high dielectric constant such as water the tin foil boundary conditions seem quite realistic. A nice illustration is given by the lattice energy of glycine, a zwitterion and therefore extremely polar. Derissen, Smit, and Voogd⁹ found that a cutoff radius of even 30 Å gave unacceptably large energy differences for three crystal modifications (two of which are polar), whereas Ewald summation gave three comparable energies as expected for polymorphs. The authors attributed the difference to lack of convergence of the direct lattice sum, but their figures do not support that statement convincingly. In fact, we find that addition of the neglected term U_2^{inner} (−35.7 kcal/mol for γ -glycine!) to these energies gives almost exactly the same result as that calculated by the authors using Ewald summations. And this also shows that no significant term U_2^{outer} should be added because that would have the same order of magnitude and spoil the agreement again.

However, when a crystal is formed in a medium with low dielectric constant, especially by sublimation, the situation may be quite different. In fact, the influence of the solvent on crystal shape is well-known.¹⁰ Recently, a case was described¹¹ where extremely needle-shaped crystals (the needle axis coinciding with the dipole moment) were grown from toluene and then used as a seed in a methanol solution for expansion into the other directions. These phenomena are usually explained kinetically in terms of different growth rates, but the possibility of real energy differences due to various crystal shapes should be kept in mind.

There appears to have existed a notion (recently refuted¹² by a statistical analysis) that polar molecules tend to crystallize in centrosymmetric space groups. Munn and Hurst suggested earlier¹³ that this notion might be connected to a destabilizing surface energy in polar space groups. They criticized this idea, referring to “the experimental observation that polar molecular crystals do not usually exhibit a macroscopic dipole moment”. Contrarily, Roberts and Schnitzer⁶ advocate the use of vacuum conditions for crystals (in contrast to periodic systems simulating the liquid state).

We think that it is the best course of action to omit U_2^{outer} in crystal structure predictions: either the crystal surroundings annul the surface charge or the crystal can find a shape (needle or platelet) where this term vanishes and the energy is at its lowest. In that case one may calculate either U_0^{Ewald} or $U_1 + U_2^{\text{inner}}$, the choice is only a matter of computational convenience. The result has the pleasant property of being independent

of the crystal shape. Thus, the calculation of U_2^{outer} would be only of academic interest. Nevertheless, in the Appendix we develop the theory for a simple crystal form with only right angles.

Appendix

The calculation of U_2^{outer} involves a five-dimensional integral. For a crystal with a general set of plane faces only a numerical approach seems feasible. However, for the simple case of a crystal that is built from parallel rectangular parallelepipeds, an analytical development is possible.

Consider first the contribution of one upper face (the hatched area in Figure 3), which is part of a parallelepiped defined by the vectors \mathbf{R}_1 and \mathbf{R}_2 . Here, \mathbf{n} corresponds to the positive z -axis, so from eq 9 we find for cell i

$$S_i^{\text{upper}} = \frac{1}{2V} \int_{y_1-Y_i}^{Y_2-Y_i} \int_{x_1-X_i}^{X_2-X_i} \frac{\mathbf{p} \cdot \mathbf{r}_i}{r_i^3} p_z dx dy \quad (20)$$

We define

$$\int \int \frac{r_g}{r^3} dx dy = B_{gz}(x, y, z) \quad (21)$$

where g denotes x, y, z . Analogous relations for B_{gx} and B_{gy} can be defined for the other two directions. Then the integral can be written as

$$S_i^{\text{upper}} = \frac{p_z}{2V} \sum_g p_g [B_{gz}(X_2 - X_i, Y_2 - Y_i, z_i) - B_{gz}(X_1 - X_i, Y_2 - Y_i, z_i) + B_{gz}(X_1 - X_i, Y_1 - Y_i, z_i) - B_{gz}(X_2 - X_i, Y_1 - Y_i, z_i)] \quad (22)$$

with $z_i = Z_2 - Z_i$. By addition of the other five faces of the parallelepiped,

$$S_i = \frac{1}{2V} \sum_g \sum_{g'} p_g p_{g'} \sum_{\alpha=1,2} \sum_{\beta=1,2} \sum_{\gamma=1,2} (-1)^{\alpha+\beta+\gamma} B_{gg'}(X_\alpha - X_i, Y_\beta - Y_i, Z_\gamma - Z_i) \quad (23)$$

Now let the cell i be situated in a second parallelepiped, defined by the vectors \mathbf{R}_3 and \mathbf{R}_4 (Figure 3). We first sum our results over all cells in this parallelepiped, which is equivalent to integrating over its volume. To perform this integration, we define

$$\iiint B_{gg'}(x, y, z) dx dy dz = C_{gg'}(x, y, z) \quad (24)$$

and find

$$\sum_i S_i = \frac{1}{V} \int S_i d^3\mathbf{R}_i = \frac{-1}{2V^2} \sum_g \sum_{g'} p_g p_{g'} \sum_{\alpha=1,2} \sum_{\beta=1,2} \sum_{\gamma=1,2} \sum_{\alpha'=3,4} \sum_{\beta'=3,4} \sum_{\gamma'=3,4} (-1)^{\alpha+\beta+\gamma+\alpha'+\beta'+\gamma'} C_{gg'}(X_\alpha - X_{\alpha'}, Y_\beta - Y_{\beta'}, Z_\gamma - Z_{\gamma'}) \quad (25)$$

The total U_2^{outer} is found by summing this result over all possible combinations of parallelepipeds and dividing by the total number of cells N .

With aid of the MATHEMATICA¹⁴ program explicit formulas for $B_{gg'}$ and $C_{gg'}$ could be obtained:

$$\begin{aligned}
 B_{xz} &= -\frac{1}{2} \ln \frac{r+y}{r-y} \\
 B_{yz} &= -\frac{1}{2} \ln \frac{r+x}{r-x} \\
 B_{zz} &= \arctan \frac{xy}{zr}
 \end{aligned} \quad (26)$$

$$\begin{aligned}
 C_{yz} &= \frac{yzr}{3} + \frac{xz^2}{2} \arctan \frac{xy}{zr} + \frac{xy^2}{2} \arctan \frac{xz}{yr} + \frac{x^3}{6} \arctan \frac{yz}{xr} - \\
 &\quad \frac{xyz}{2} \ln \frac{r+x}{r-x} + \frac{z(z^2-3x^2)}{12} \ln \frac{r+y}{r-y} + \frac{y(y^2-3x^2)}{12} \ln \frac{r+z}{r-z} \\
 C_{zz} &= \frac{r(r^2-3z^2)}{6} + xyz \arctan \frac{xy}{zr} + \frac{y(z^2-x^2)}{4} \ln \frac{r+y}{r-y} + \\
 &\quad \frac{x(z^2-y^2)}{4} \ln \frac{r+x}{r-x} \quad (27)
 \end{aligned}$$

The other expressions can be found by any permutation of x , y , z . Of course, these indefinite integrals are by no means unique; the forms chosen here are either symmetric or antisymmetric for each variable.

A simple case is a crystal that consists of just one rectangular parallelepiped: $\mathbf{R}_1 = \mathbf{R}_3$, $\mathbf{R}_2 = \mathbf{R}_4$. Let the lengths of the crystal edges in the three coordinate directions be L_x , L_y , L_z , so $L_x L_y L_z = NV$. From symmetry considerations it can be seen that terms with $g \neq g'$ do not contribute, and the result can be written in the form

$$U_2^{\text{outer}} = \frac{1}{V} \sum_g c_g p_g^2 \quad (28)$$

with c_g from eq 25:

$$\begin{aligned}
 c_g &= 4[C_{gg}(L_x, L_y, L_z) - C_{gg}(L_x, L_y, 0) - C_{gg}(L_x, 0, L_z) - \\
 &\quad C_{gg}(0, L_y, L_z) + C_{gg}(L_x, 0, 0) + C_{gg}(0, L_y, 0) + \\
 &\quad C_{gg}(0, 0, L_z) - C_{gg}(0, 0, 0)]/(L_x L_y L_z) \quad (29)
 \end{aligned}$$

Likewise, the surface contribution to the energy of the center cell can be written as

$$S_{\text{center}} = \frac{1}{V} \sum_g b_g p_g^2 \quad (30)$$

with b_g from substitution of $\mathbf{R}_i = (\mathbf{R}_1 + \mathbf{R}_2)/2$ into eq 23:

$$b_g = 4B_{gg}(L_x/2, L_y/2, L_z/2) \quad (31)$$

We have tabulated some numerical results for b_z and c_z in Table 1; values for the other components can be obtained by cyclic permutations. Of course, only the relative values of the crystal dimensions are relevant. A few special cases (needles, cubes, platelets) have already been discussed above; those results are the same as found by Smith.² It is interesting to note that

the disputed relation $S_{\text{center}} = U_2^{\text{outer}}$, or $c_g = b_g$, is valid for these special cases but not for more general crystal forms. The sum rule discovered by Smith can be shown to hold also for c_g :

$$\sum_g b_g = \sum_g c_g = 2\pi \quad (32)$$

It is of interest to compare our formulas with the results of Smith for a rectangular crystal. In his first paper² the relevant equation is (3.25):

$$b_g = \frac{2}{\pi^2} \int_0^\infty \int_{-\infty}^\infty w_g^2 \left[\prod_{\eta=1}^3 \exp(-tw_\eta^2) \frac{\sin(L_\eta w_\eta)}{w_\eta} \right] d^3 \mathbf{w} dt \quad (33)$$

which follows from eqs 15 and 17 for the rectangular crystal. Smith worked out the three integrals over \mathbf{w} , but with the subsequent integral over t he could make no analytic progress. Neither could we, but our eqs 31 and 26 show that b_z must be simply equal to 4 times $\arctan(L_x L_y / (L_z D))$, where D is the diagonal of the crystal. Since the derivation of this equality is rather roundabout, we have verified numerically for several values of L_x , L_y , L_z that eq 33 gives the same result as eq 31.

To calculate c_g , Smith's eq 4.20 should be used. As stated before, we distrust the discussion following that equation, which leads to the conclusion $b_g = c_g$. Rather, we start with the equivalent form of eq 2.4 from the subsequent paper,⁷ our eq 16. For a rectangular crystal this formula can also be developed using eq 17, with the result

$$c_g = \frac{2}{\pi^2} \int_0^\infty \int_{-\infty}^\infty w_g^2 \left[\prod_{\eta=1}^3 \exp(-tw_\eta^2) \frac{\sin^2(L_\eta w_\eta)}{L_\eta w_\eta^2} \right] d^3 \mathbf{w} dt \quad (34)$$

Again, using the MATHEMATICA¹⁴ program for partial analytical development followed by numerical integration over t for the examples in Table 1, we found the same values as from eq 29.

References and Notes

- (1) de Leeuw, S. W.; Perram, J. W.; Smith, E. R. *Proc. R. Soc. London* **1980**, A373, 27.
- (2) Smith, E. R. *Proc. R. Soc. London* **1981**, A375, 475.
- (3) Hansen, J.-P. In *Molecular-Dynamics Simulation of Statistical-Mechanical Systems*; Ciccotti, G., Hoover, W. G., Eds.; North-Holland: Amsterdam, 1986; p 89.
- (4) Deem, M. W.; Newsam, J. M.; Sinha, S. K. *J. Phys. Chem.* **1990**, 94, 8356.
- (5) Karasawa, N.; Goddard, W. A. III. *J. Phys. Chem.* **1989**, 93, 7320.
- (6) Roberts, J. E.; Schnitker, J. *J. Phys. Chem.* **1995**, 99, 1322.
- (7) Smith, E. R. *Proc. R. Soc. London* **1982**, A381, 241.
- (8) Gibson, K. D.; Scheraga, H. A. *J. Phys. Chem.* **1995**, 99, 3752.
- (9) Derissen, J. L.; Smit, P. H.; Voogd, J. *J. Phys. Chem.* **1977**, 81, 1474.
- (10) Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1985**, 107, 8239.
- (11) Shekunov, B. Y.; Shepherd, E. E. A.; Sherwood, J. N.; Simpson, G. S. *J. Phys. Chem.* **1995**, 99, 7130.
- (12) Whitesell, J. K.; Davis, R. E.; Saunders, L. L.; Wilson, R. J.; Feagins, J. P. *J. Am. Chem. Soc.* **1991**, 113, 3267.
- (13) Munn, R. W.; Hurst, M. *Chem. Phys.* **1990**, 147, 35.
- (14) Wolfram, S. *Mathematica—A System for Doing Mathematics by Computer*; Addison-Wesley: Reading, MA, 1993.