

Acceleration of Convergence for Lattice Sums

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The lattice sums of nonbond interactions (electrostatic and dispersion) for computer simulations of periodic systems typically converge very slowly. Here, we examine the accelerated convergence of these sums based on Ewald procedures and derive equations for the energies, forces, stresses, and curvatures. A method is proposed and tested for selecting the convergence acceleration parameter η on the basis of minimum calculation time. As an illustration and check, the properties of argon and NaCl crystals are calculated by using these equations and compared with values obtained analytically.

I. Introduction

To carry out molecular mechanics and molecular dynamics calculations, it is necessary to sum various nonbonded interactions over all pairs of atoms. Thus, the electrostatic energy for a collection of point charges, $\{q_i\}$, is

$$E_Q = \frac{1}{2} \sum'_{ij} \frac{Q_{ij}}{R_{ij}} \quad (1)$$

where $Q_{ij} = (\text{Cunit}/\epsilon)q_iq_j$ and q_i is the charge of the atom i . Here the prime indicates that $i = j$ terms are excluded, ϵ is the dielectric constant (which we take as 1.0), and $\text{Cunit} = 332.0647$ puts the final energy in kcal/mol if distances are in angstroms ($\text{Cunit} = 14.400$ if the energy is in electronvolts). Similarly, the dispersion part of the vdw interaction has the form

$$E_{\text{disp}} = \frac{1}{2} \sum'_{ij} \frac{B_{ij}}{R_{ij}^6} \quad (2)$$

where B_{ij} is negative.

These sums are notoriously slow to converge. This is illustrated in Table I for NaCl and polyethylene (PE) crystals. To obtain an electrostatic energy good to 0.01 kcal/mol by this procedure would require calculating all terms larger than 0.001 kcal/mol, which for unit charges would require a cutoff distance of 332 000 Å! With a typical density of 10^{22} atoms/cm³ this would require 10^{15} atoms! Clearly such large cutoffs are untenable.

The convergence is speeded by grouping together all atoms of a cell and summing complete unit cells as illustrated in Table II. However, the convergence is still far too slow.

The general solution to this problem originated with Ewald in 1921 using convergence functions for $1/R$ interactions.¹ Nijboer and de Wette² generalized this approach to include all cases where the interactions are proportional to negative powers of distance for a single atom in a cell. Williams³ extended the formulas to allow multiple atoms in a cell.

Consider a general lattice sum of the type

$$S_m = \frac{1}{2} \sum'_{L,i,j} \frac{A_{ij}}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|^m} \quad (3)$$

where \mathbf{r}_i and \mathbf{r}_j are the basis vectors of atoms i and j in the cell and \mathbf{R}_L is the lattice translation vector. The sums over i and j each go over all atoms inside the cell except that $i \neq j$ when $L = 0$. The total electrostatic energy is given by S_1 , while the dispersion term is given by S_6 . Multiplying every term in (3) by the convergence function ϕ_m and then by $(1 - \phi_m)$, we obtain

$$S_m = \frac{1}{2} \sum'_{L,i,j} \frac{A_{ij}\phi_m(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|)}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|^m} + \frac{1}{2} \sum'_{L,i,j} \frac{A_{ij}[1 - \phi_m(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|)]}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|^m} \quad (4)$$

If $\phi_m(r)$ is a rapidly decreasing function, then the first term of

(4) converges much faster than (3). The second term converges slowly, but by taking the Fourier transform, the resulting sum (over the reciprocal lattice vectors) converges much faster. Following Nijboer and de Wette² and Williams,³ we choose ϕ_m as

$$\phi_m(r) = \frac{1}{\Gamma(m/2)} \int_{r^2/\eta^2}^{\infty} t^{m/2-1} e^{-t} dt \quad (5)$$

II. Coulomb Sums

For the Coulomb case (5) becomes

$$\phi_1(r) = \text{erfc}(r/\eta) = 1 - \text{erf}(r/\eta) \quad (6)$$

where erf is the error function. In this case, the Coulomb interaction with infinite range is replaced by an interaction of range η and summed in the real space, while the long range corrections are summed in the reciprocal space. The parameter η determines how much of the real space sum is converted to the reciprocal space sum (large η leads to a larger real space sum).

A. Total Energy. The energy sum is

$$S_1 = \frac{1}{2\eta} \sum'_{L,i,j} Q_{ij} \frac{\text{erfc}(a)}{a} + \frac{2\pi}{\Omega} \sum'_{\mathbf{h}} S(\mathbf{h})S(-\mathbf{h})h^{-2}e^{-b^2} - \frac{1}{\pi^{1/2}\eta} \sum_i Q_{ii} \quad (7)$$

where it is assumed that each cell is neutral

$$\sum_i q_i = 0 \quad (8)$$

and the prime indicates that the term at the origin is excluded. Here \mathbf{h} is the reciprocal lattice vector, Ω is the volume of the unit cell, $a = |\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|/\eta$, $b = 1/2h\eta$, and $h = |\mathbf{h}|$. The first term in (7) is just the first term of (4). The last term in (7) arises from the exclusion of $i = j$ terms when $L = 0$, since in the reciprocal space sum, these terms are included.

The second term of (7) arises from the expansion of the second term of (4) in terms of Fourier transforms of the point charge δ function distribution

$$\sum'_{i,j,L} Q_{ij}\delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_j + \mathbf{R}_L) = \frac{1}{\Omega} \sum'_{\mathbf{h}} S(\mathbf{h})S(-\mathbf{h})e^{i\mathbf{h}\cdot\mathbf{r}} \quad (9a)$$

where

$$S(\mathbf{h}) = \left(\frac{\text{Cunit}}{\epsilon}\right)^{1/2} \sum_j q_j e^{-i\mathbf{h}\cdot\mathbf{r}_j} \quad (9b)$$

is referred to as the structure factor. The quantity $S(\mathbf{h})S(-\mathbf{h})$ in (7) has the form

$$S(\mathbf{h})S(-\mathbf{h}) = \sum'_{i,j} Q_{ij} \cos[\mathbf{h}\cdot(\mathbf{r}_i - \mathbf{r}_j)] \quad (10)$$

which Cowley et al.⁴ have shown can be rewritten as

$$S(\mathbf{h})S(-\mathbf{h}) = \frac{\text{Cunit}}{\epsilon} \{[\sum_i q_i \cos(\mathbf{h}\cdot\mathbf{r}_i)]^2 + [\sum_i q_i \sin(\mathbf{h}\cdot\mathbf{r}_i)]^2\} \quad (11)$$

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(3) (a) Williams, D. E. *Acta Crystallogr., Sect. A* **1971**, *27*, 452. (b) Williams, D. E. In *Crystal Cohesion and Conformational Energies*; Metzger, R. M., Ed.; Springer-Verlag: Berlin-Heidelberg-New York, 1981; pp 3-40.

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TABLE I: Convergence of Nonbond Interactions Using Atom-Based Cutoffs^a

$R_{\text{outer}},^b \text{ \AA}$	$R_{\text{inner}},^b \text{ \AA}$	NaCl ^d			polyethylene		
		terms	E_Q	E_{disp}	terms	E_Q	E_{disp}
10	8	608	-981.65	-20.330	3072	-51.870	-797.687
10	9	608	-1556.20	-20.413	3072	-2.343	-797.798
10	10	608	-1492.67	-20.445	3072	-111.998	-797.863
15	14	2152	1446.83	-20.726	10394	-40.272	-798.184
15	15	2152	1281.61	-20.735	10394	-52.972	-798.198
20	19	5296	-1743.32	-20.794	24615	-79.905	-798.275
20	20	5296	1207.33	-20.800	24615	-63.080	-798.280
25	24	10320	1210.98	-20.821	48015	-107.974	-798.306
25	25	10320	109.11	-20.822	48015	-54.830	-798.308
Ewald ^c			-824.59	-20.846		-65.685	-798.338

^a Energies are in kcal/mol. ^b Each term of (1) or (2) is multiplied by the cubic cutoff function $S(R_{ij})$, where $S(R) = 1.0$ if $R < R_{\text{inner}}$, $S(R) = 0.0$ if $R > R_{\text{outer}}$, and $S(R) = [R_{\text{outer}}^2 - R^2]^2 [R_{\text{outer}}^2 + 2R^2 - 3R_{\text{inner}}^2] / [R_{\text{outer}}^2 - R_{\text{inner}}^2]^3$, otherwise. ^c $\eta = 2.5$ for NaCl and $\eta = 2.0$ for polyethylene. ^d Parameters used are $B_{\text{NaNa}} = -24.180$, $B_{\text{NaCl}} = -161.20$, $B_{\text{ClCl}} = -1669.58$ kcal \AA^6 mol⁻¹. $q_{\text{Na}} = e$, $q_{\text{Cl}} = -e$, $A = 5.63$ \AA .

TABLE II: Convergence of Nonbond Interactions Using Cell-Based Cutoffs^a

$r_{\text{cut}}, \text{ \AA}$	NaCl ^c			polyethylene		
	terms ^b	E_Q	E_{disp}	terms ^b	E_Q	E_{disp}
6	3500 (2 2 2)	-824.5563	-20.7615	6930 (1 3 2)	-65.6032	-798.0302
8	3500 (2 2 2)	-824.5563	-20.7615	14850 (2 4 2)	-65.6402	-798.1933
10	3500 (2 2 2)	-824.5563	-20.7615	20790 (2 4 3)	-65.6521	-798.2312
15	9604 (3 3 3)	-824.5768	-20.8161	54054 (3 6 4)	-65.6655	-798.3005
20	20412 (4 4 4)	-824.5836	-20.8323	86394 (3 8 5)	-65.6669	-798.3176
25	37268 (5 5 5)	-824.5852	-20.8387	162162 (4 10 6)	-65.6725	-798.3274
Ewald ^c	512 + 2240 ^d	-824.5861		1748 + 1584 ^d	-65.6836	
	296 + 2240 ^d		-20.8463	1044 + 6204 ^d		-798.3383

^a Energies are in kcal/mol. ^b The numbers in parentheses show the (a b c) index for the last shell considered. ^c $\eta = 2.5$ for NaCl and $\eta = 2.0$ for polyethylene. $\delta_Q = 0.001$ kcal/mol. $\delta_{\text{disp}} = 10^{-4}$ kcal/mol. ^d The number of terms in real space and reciprocal space sums, respectively (eq 10 is used). ^e Parameters are given in Table I.

Since the summation in (11) runs only over single atoms rather than pairs, the computations for the reciprocal space sum are significantly reduced.

B. Force and Stress. The force at atom p is given by

$$\mathbf{f}_{1,p} = -\frac{\partial S_1}{\partial \mathbf{r}_p} = \frac{1}{\eta^3} \sum_L \sum_i Q_{pi} (\mathbf{r}_p - \mathbf{r}_i - \mathbf{R}_L) \left[\frac{\text{erfc}(a_p)}{a_p^3} + \frac{2\pi^{-1/2} e^{-a_p^2}}{a_p^2} \right] + \frac{4\pi}{\Omega} \sum_{\mathbf{h}} \sum_i Q_{pi} \sin(\mathbf{h} \cdot (\mathbf{r}_p - \mathbf{r}_i)) h^{-2} e^{-b^2} \quad (12)$$

where $a_p = |\mathbf{r}_p - \mathbf{r}_i - \mathbf{R}_L|/\eta$. By use of (11), the second term can be rewritten as

$$\frac{C_{\text{unit}}}{\epsilon} \frac{4\pi}{\Omega} \sum_{\mathbf{h}} \sum_i q_i \sin(\mathbf{h} \cdot \mathbf{r}_p) [\sum_i q_i \cos(\mathbf{h} \cdot \mathbf{r}_i) - \cos(\mathbf{h} \cdot \mathbf{r}_p) \times [\sum_i q_i \sin(\mathbf{h} \cdot \mathbf{r}_i)]] h^{-2} e^{-b^2} \quad (13)$$

To calculate the stress, consider the matrix \mathbf{H} that contains the real space unit cell vectors in Cartesian coordinates, i.e., $\mathbf{H} = [\mathbf{a}, \mathbf{b}, \mathbf{c}]$, where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the unit cell vectors.⁵ Then we have

$$\Omega = \det(\mathbf{H}) \quad (14)$$

$$\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L = \mathbf{H}(\mathbf{s}_i - \mathbf{s}_j - \mathbf{L}) \quad (15)$$

and

$$\mathbf{h} = 2\pi \tilde{\mathbf{H}}^{-1} \mathbf{n} \quad (16)$$

where \mathbf{s}_i is the fractional coordinate vector of the atom i , and \mathbf{n} and \mathbf{L} are vectors whose elements are the integers specifying the

reciprocal lattice and real lattice vectors, and $\tilde{\mathbf{H}}$ is the transpose of \mathbf{H} . The stress $\Pi_{\alpha\beta}$ is given by the relation⁵

$$-\frac{\partial E}{\partial \mathbf{H}_{\alpha\gamma}} = \sum_{\beta} \Pi_{\alpha\beta} \Omega \mathbf{H}_{\gamma\beta}^{-1} \quad (17)$$

where E is the total (potential) energy of the system. For the electrostatic stress, we have

$$\Omega \Pi_{\alpha\beta} = \frac{1}{2\eta^3} \sum_{L,i,j} Q_{ij} \left[\frac{\text{erfc}(a)}{a^3} + \frac{2\pi^{-1/2} e^{-a^2}}{a^2} \right] (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_{\alpha} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_{\beta} + \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h}) S(-\mathbf{h}) \frac{e^{-b^2}}{h^2} \left[\delta_{\alpha\beta} - 2 \frac{(1+b^2)}{h^2} \mathbf{h}_{\alpha} \mathbf{h}_{\beta} \right] \quad (18)$$

The stresses can also be obtained by differentiating the energy with respect to strains. The strain tensor is defined by⁶

$$\epsilon = \frac{1}{2} (\tilde{\mathbf{H}}_0^{-1} \tilde{\mathbf{H}} \mathbf{H} \mathbf{H}_0^{-1} - 1) \quad (19)$$

where \mathbf{H}_0 contains the original cell vectors and \mathbf{H} contains the deformed cell vectors. ϵ is symmetric so we define six independent strain components e_i such that $e_1 = \epsilon_{11}$, $e_2 = \epsilon_{22}$, $e_3 = \epsilon_{33}$, $e_4 = 2\epsilon_{23}$, $e_5 = 2\epsilon_{31}$, and $e_6 = 2\epsilon_{12}$. Then we have

$$\Omega \Pi_k = - \left(\frac{\partial E}{\partial e_k} \right)_{e_i=0} \quad (k = 1, \dots, 6) \quad (20)$$

where $\Pi_1 = \Pi_{11}$, $\Pi_2 = \Pi_{22}$, $\Pi_3 = \Pi_{33}$, $\Pi_4 = \Pi_{23}$, $\Pi_5 = \Pi_{31}$, and $\Pi_6 = \Pi_{12}$. To derive this equation, we use the relations

$$\frac{\partial \mathbf{H}_{\alpha\gamma}}{\partial \epsilon_{ii}} = \sum_k \mathbf{H}_{k\alpha}^{-1} \mathbf{H}_{0i\gamma} \mathbf{H}_{0ik} = \delta_{i\alpha} \mathbf{H}_{i\gamma} \quad (e_i = 0) \quad (21a)$$

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(4) Cowley, E. R.; Jacucci, G.; Klein, M. L.; McDonald, I. R. *Phys. Rev. B* **1976**, *14*, 1758. In this paper, $A_n(\eta)$ in eq 3 must be multiplied by a factor $(1/\pi L)$.

(5) Nosé, S.; Klein, M. L. *Mol. Phys.* **1983**, *50*, 1055.

$$\frac{\partial \mathbf{H}_{\alpha\gamma}}{\partial \epsilon_{ij}} = \sum_k \mathbf{H}_{k\alpha}^{-1} (\mathbf{H}_{0i\gamma} \mathbf{H}_{0jk} + \mathbf{H}_{0j\gamma} \mathbf{H}_{0ik}) \\ = \delta_{ja} \mathbf{H}_{i\gamma} + \delta_{ia} \mathbf{H}_{j\gamma} \quad (e_i = 0) \quad (21b)$$

derived from (19).

C. *Curvatures.* The second derivatives with respect to XX and YY strains have the form

$$(i) \\ \frac{\partial^2 S_1}{\partial e_1 \partial e_1} = -\frac{1}{2\eta^3} \sum_{L,i,j} Q_{ij} \left[F' \frac{1}{a\eta^2} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^4 + 2F(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^2 \right] + \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h}) S(-\mathbf{h}) \left[\frac{1}{2} \eta^2 \mathbf{h}_1^4 \mathbf{H}' + 4\mathbf{H} \mathbf{h}_1^2 + G \right] \quad (22a)$$

$$(ii) \\ \frac{\partial^2 S_1}{\partial e_1 \partial e_2} = -\frac{1}{2\eta^3} \sum_{L,i,j} Q_{ij} \left[F' \frac{1}{a\eta^2} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^2 (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_2^2 \right] + \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h}) S(-\mathbf{h}) \left[\frac{1}{2} \eta^2 \mathbf{h}_1^2 \mathbf{h}_2^2 \mathbf{H}' + \mathbf{H}(\mathbf{h}_1^2 + \mathbf{h}_2^2) + G \right] \quad (22b)$$

where

$$F = [\operatorname{erfc}(a) + 2\pi^{-1/2} a e^{-a^2}] / a^3$$

$$G = \eta^2 e^{-b^2} / 4b^2$$

$$\mathbf{H} = -\eta^4 (1 + b^2) e^{-b^2} / 8b^4$$

$$F' = \frac{dF}{da}, \quad \mathbf{H}' = \frac{d\mathbf{H}}{db^2}$$

III. Dispersion Sums

For the dispersion sum with $m = 6$ in (3), the form for ϕ_6 is

$$\phi_6 = \left[1 + (r/\eta)^2 + \frac{1}{2} (r/\eta)^4 \right] e^{-(r/\eta)^2} \quad (23)$$

A. *Energy.* This leads to an energy of

$$S_6 = \frac{1}{2\eta^6} \sum_{L,i,j} B_{ij} \left(a^{-6} + a^{-4} + \frac{1}{2} a^{-2} \right) e^{-a^2} + \frac{\pi^{3/2}}{24\Omega} \sum_{\mathbf{h}} \sum_{i,j} B_{ij} \cos [\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] h^3 \left[\pi^{1/2} \operatorname{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right] + \frac{\pi^{3/2}}{6\Omega \eta^3} \sum_{i,j} B_{ij} - \frac{1}{12\eta^6} \sum_i B_{ii} \quad (24)$$

where $b = 1/2 h \eta$, $a = |\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L| / \eta$, and $h = |\mathbf{h}|$. The first term in (24) arises from the first term in (4) and can be written as

$$\frac{1}{\eta^6} \sum_L \left[\sum_{i,j>i} B_{ij} a^{-2} e^{-a^2} \left(a^{-4} + a^{-2} + \frac{1}{2} \right) + \frac{1}{2} a_L^{-2} e^{-a_L^2} \left(a_L^{-4} + a_L^{-2} + \frac{1}{2} \right) \sum_i B_{ii} \right] \quad (25)$$

where $a_L = |\mathbf{R}_L| / \eta$. The second term arises from the second term in (4) using (9) and (10). The third term is from $\mathbf{h} = 0$ in the second term, while the fourth term is from exclusion of $i = j$ terms when $L = 0$.

Often the dispersion terms are assumed to satisfy the geometric combination rules

$$-B_{ij} = (B_{ii} B_{jj})^{1/2} \quad (26)$$

and expressions similar to (24) are based on this form.³ However, in the above derivation, no such assumptions are made. When (26) is satisfied, we can use

$$\sum_{i,j} B_{ij} \cos [\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] = -\left[\sum_i (|B_{ii}|)^{1/2} \cos (\mathbf{h} \cdot \mathbf{r}_i) \right]^2 - \left[\sum_i (|B_{ii}|)^{1/2} \sin (\mathbf{h} \cdot \mathbf{r}_i) \right]^2 \quad (26')$$

in the reciprocal space sum of (24) to reduce the computing time.

B. *Force and Stress.* The force on atom p is

$$\mathbf{f}_{6,p} = -\frac{\partial S_6}{\partial \mathbf{r}_p} \\ = \frac{1}{\eta^8} \sum_L \sum_i B_{pi} (\mathbf{r}_p - \mathbf{r}_i - \mathbf{R}_L) \times \\ \left(6a_p^{-8} + 6a_p^{-6} + 3a_p^{-4} + a_p^{-2} \right) e^{-a_p^2} + \frac{\pi^{3/2}}{12\Omega} \sum_{\mathbf{h}} \mathbf{h} \left[\sum_i B_{pi} \times \right. \\ \left. \sin [\mathbf{h} \cdot (\mathbf{r}_p - \mathbf{r}_i)] \right] h^3 \left[\pi^{1/2} \operatorname{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right] \quad (27)$$

The stress term is

$$\Omega \Pi_{\alpha\beta} = \frac{1}{2\eta^8} \sum_L \sum_{i,j} B_{ij} (6a^{-8} + 6a^{-6} + 3a^{-4} + a^{-2}) e^{-a^2} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_\alpha \times \\ (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_\beta + \frac{\pi^{3/2}}{24\Omega} \sum_{\mathbf{h}} \sum_{i,j} B_{ij} \cos [\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \times \\ \left[h^3 \left\{ \pi^{1/2} \operatorname{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right\} \delta_{\alpha\beta} + \right. \\ \left. 3h \left(\pi^{1/2} \operatorname{erfc}(b) - \frac{e^{-b^2}}{b} \right) \mathbf{h}_\alpha \mathbf{h}_\beta \right] + \frac{\pi^{3/2}}{6\eta^3 \Omega} \sum_{i,j} B_{ij} \delta_{\alpha\beta} \quad (28)$$

Here we have used

$$\frac{\partial a}{\partial \mathbf{H}_{\alpha\beta}} = \frac{1}{\eta} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_\alpha (\mathbf{s}_i - \mathbf{s}_j - \mathbf{L})_\beta \quad (29)$$

where $\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L$ is given in (15) and

$$\frac{\partial b^2}{\partial \mathbf{H}_{\alpha\beta}} = -\frac{1}{2} \eta^2 \mathbf{h}_\alpha \sum_\gamma \mathbf{H}_{\beta\gamma}^{-1} \mathbf{h}_\gamma \quad (30)$$

C. *Curvatures.* The second derivatives with respect to XX and YY strains have the form

$$(i) \\ \frac{\partial^2 S_6}{\partial e_1 \partial e_1} = -\frac{1}{2\eta^8} \sum_{L,i,j} B_{ij} \left[F' \frac{1}{a\eta^2} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^4 + 2F(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^2 \right] + \frac{\pi^{3/2}}{24\Omega} \sum_{\mathbf{h}} \sum_{i,j} B_{ij} \cos [\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \times \\ \left[\frac{1}{2} \eta^2 \mathbf{h}_1^4 \mathbf{H}' + 4\mathbf{H} \mathbf{h}_1^2 + G \right] + \frac{\pi^{3/2}}{6\eta^3 \Omega} \sum_{i,j} B_{ij} \quad (31a)$$

(ii)

$$\frac{\partial^2 S_6}{\partial e_1 \partial e_2} = -\frac{1}{2\eta^8} \sum_{L,i,j} B_{ij} \left[F' \frac{1}{a\eta^2} (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_1^2 (\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L)_2^2 \right] + \frac{\pi^{3/2}}{24\Omega} \sum_{\mathbf{h}} \sum_{i,j} B_{ij} \cos [\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \times \\ \left[\frac{1}{2} \eta^2 \mathbf{h}_1^2 \mathbf{h}_2^2 \mathbf{H}' + \mathbf{H}(\mathbf{h}_1^2 + \mathbf{h}_2^2) + G \right] + \frac{\pi^{3/2}}{6\eta^3 \Omega} \sum_{i,j} B_{ij} \quad (31b)$$

where

$$F = (6a^{-8} + 6a^{-6} + 3a^{-4} + a^{-2}) e^{-a^2} \\ G = \frac{8b^3}{\eta^3} \left\{ \pi^{1/2} \operatorname{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right\} \\ \mathbf{H} = \frac{6b}{\eta} \left(\pi^{1/2} \operatorname{erfc}(b) - \frac{e^{-b^2}}{b} \right) \\ F' = \frac{dF}{da}, \quad \mathbf{H}' = \frac{d\mathbf{H}}{db^2}$$

TABLE III: Predicted Values of η_{opt} (Using (34))

crystal	$ R_{L,\text{min}} , \text{\AA}$	$ h_{\text{min}} , \text{\AA}^{-1}$	$\eta_{\text{opt}}, \text{\AA}$
NaCl (8 atoms/cell)	5.63	1.116	3.18
NaCl (2 atoms/cell)	3.98	1.933	2.03
Ar (4 atoms/cell)	5.31	1.183	3.00
Ar (1 atom/cell)	3.755	2.050	1.91
polyethylene (12 atoms/cell)	2.54	0.8656	2.42
orthorhombic poly(oxyethylene) (16 atoms/cell)	3.56	0.8212	2.94

IV. Selection of η

A. Choice of η from Cell Parameters. The parameter η should be chosen to optimize the convergence of both the real lattice and reciprocal lattice sums. If η is too small, the reciprocal lattice sum does not converge quickly since $b = 1/2h\eta$ remains small when h becomes large. Similarly, if η is too large, the real space sum does not converge quickly since $a = |r_i - r_j - \mathbf{R}_L|/\eta$ remains small for large $|\mathbf{R}_L|$.

Since both sums are multiplied by terms like e^{-x^2} or $\text{erfc}(x)$ (where $x = a$ for real space and $x = b$ for reciprocal space), a simple estimate of the optimum parameter η for rapid convergence of both sums can be obtained as follows. These terms decrease rapidly for large x , so that both sums converge similarly when $a = b$. This leads to

$$\eta_{\text{opt}}^2 = \frac{|r_i - r_j - \mathbf{R}_L|}{1/2h} \approx \frac{|\mathbf{R}_L|}{1/2h} \quad (32)$$

which determines η in terms of L and h . The simplest choice of η is to use the minimum length of \mathbf{R}_L and of h so that we have the same orders of magnitude of a and b when these have the minimum values (of course, $|\mathbf{R}_L| \neq 0$ and $h \neq 0$). Then

$$\eta_{\text{opt}}^2 = \frac{|\mathbf{R}_{L,\text{min}}|}{1/2h_{\text{min}}} \quad (33)$$

Assuming $a < b, c$ and $h_c < h_a, h_b$ (33) leads to

$$\eta_{\text{opt}}^2 = \frac{a\Omega}{\pi|\mathbf{a} \times \mathbf{b}|} = \frac{\Omega}{\pi b \sin \gamma} \quad (34)$$

This determines η_{opt} in terms of the crystal structure. The η_{opt} thus obtained may not be the optimum η for minimizing computation time, since we assumed that the computation time per each term is the same for both real and reciprocal space sums. Table III shows the calculated η_{opt} for various systems.

B. Accuracy Specified Cutoffs. With η specified there is still an infinite number of terms in the sums over the real space and reciprocal space lattices, and we use an accuracy criteria to specify limits on these sums. To this end we specify a tolerance δ and carry out the sums until the neglected terms have a total contribution smaller than this tolerance.

1. Electrostatic Sums. (a) Real Space Sum. Using a cutoff distance R_{cut} introduces an error in the total energy for the real space sum of

$$E_{Q,\text{real}} = \frac{1}{2} \sum_{L,ij} Q_{ij} \frac{\text{erfc}(R_{ijL}/\eta)}{R_{ijL}} \Theta(R_{ijL} - R_{\text{cut}}) \quad (35)$$

where $\Theta(x)$ is the step function [$\Theta(x) = 1$ when $x > 0$ and $\Theta(x) = 0$ when $x < 0$]. To estimate this error, we replace discrete sum (35) by a continuous integral. Defining the average interaction as $\langle q^2 \rangle = \sum_i q_i^2/N$, we obtain

$$E_{Q,\text{real}} \approx \frac{1}{2} \frac{N^2 \langle q^2 \rangle}{\epsilon} \frac{\text{Cunit}}{\Omega} \int_{R_{\text{cut}}}^{\infty} 4\pi R^2 \frac{\text{erfc}(R/\eta)}{R} dR$$

Since

$$\text{erfc}\left(\frac{R}{\eta}\right) = \frac{1}{\pi^{1/2}} \int_{R^2/\eta^2}^{\infty} \frac{1}{t^{1/2}} e^{-t} dt \leq \frac{1}{\pi^{1/2}} \int_{R^2/\eta^2}^{\infty} \frac{\eta}{R} e^{-t} dt = \frac{\eta}{\pi^{1/2} R} e^{-R^2/\eta^2}$$

we obtain

$$E_{Q,\text{real}} \leq \frac{1}{2} \frac{N^2 \langle q^2 \rangle}{\epsilon} \frac{\text{Cunit}}{\Omega} \int_{R_{\text{cut}}}^{\infty} 4\pi^{1/2} \eta e^{-R^2/\eta^2} dR = \pi \frac{N^2 \langle q^2 \rangle}{\epsilon \Omega} \text{Cunit} \eta^2 \text{erfc}\left(\frac{R_{\text{cut}}}{\eta}\right) \quad (36)$$

(b) Reciprocal Space Sum. The error in the reciprocal space sum due to a cutoff at H_{cut} is given by

$$E_{Q,\text{real}} = \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h})S(-\mathbf{h}) \frac{e^{-b^2}}{h^2} \Theta(h - H_{\text{cut}}) \quad (37)$$

Replacing the sum by an integral and replacing $S(\mathbf{h})S(-\mathbf{h})$ by $\text{Cunit} N^2 \langle q^2 \rangle / \epsilon$, we obtain

$$E_{Q,\text{recip}} \approx \frac{2\pi}{\Omega} \frac{N^2 \langle q^2 \rangle}{\epsilon} \text{Cunit} \frac{\Omega}{8\pi^3} \int_{H_{\text{cut}}}^{\infty} 4\pi h^2 \frac{e^{-(h\eta/2)^2}}{h^2} dh = \frac{N^2 \langle q^2 \rangle}{\epsilon \pi^{1/2}} \text{Cunit} \frac{1}{\eta} \text{erfc}\left(\eta \frac{H_{\text{cut}}}{2}\right) \quad (38)$$

Using (36) and (38), we can evaluate the cutoff distances R_{cut} and H_{cut} to obtain a given accuracy δ_Q (for given η). Because of the neutrality of the cell, there will be a great deal of cancellation in (35) and (37) that is ignored in (36) and (38). Consequently, eq (36) and (38) generally overestimate the error by a factor of 10 or so.

2. Dispersion Sums. (a) Real Space Sum. The total error in the real space dispersion sum is given by

$$E_{6,\text{real}} = \frac{1}{2} \sum_{L,ij} |B_{ij}| \left(\frac{1}{R_{ijL}^6} + \frac{1}{R_{ijL}^4 \eta^2} + \frac{1}{2R_{ijL}^2 \eta^4} \right) e^{-(R_{ijL}/\eta)^2} \Theta(R_{ijL} - R_{\text{cut}}) \quad (39)$$

Approximating this by an integral, we have

$$E_{6,\text{real}} \approx \frac{1}{2} N^2 \langle B \rangle \frac{1}{\Omega} \int_{R_{\text{cut}}}^{\infty} \left(\frac{1}{R^6} + \frac{1}{R^4 \eta^2} + \frac{1}{2R^2 \eta^4} \right) 4\pi R^2 e^{-(R/\eta)^2} dR = 2\pi \frac{N^2 \langle B \rangle}{\Omega} \int_{R_{\text{cut}}}^{\infty} \left(\frac{1}{R^4} + \frac{1}{R^2 \eta^2} + \frac{1}{2\eta^4} \right) e^{-(R/\eta)^2} dR$$

where $N^2 \langle B \rangle = \sum_{i,j} |B_{ij}|$ is the sum of coefficients of dispersion terms. We approximate the above equation as

$$E_{6,\text{real}} \leq 2\pi \frac{N^2 \langle B \rangle}{\Omega} \left(\frac{1}{R_{\text{cut}}^4} + \frac{1}{R_{\text{cut}}^2 \eta^2} + \frac{1}{2\eta^4} \right) \int_{R_{\text{cut}}}^{\infty} e^{-(R/\eta)^2} dR = \frac{\pi^{3/2} N^2 \langle B \rangle}{\Omega} \eta \left(\frac{1}{R_{\text{cut}}^4} + \frac{1}{R_{\text{cut}}^2 \eta^2} + \frac{1}{2\eta^4} \right) \text{erfc}\left(\frac{R_{\text{cut}}}{\eta}\right) \quad (40)$$

(b) Reciprocal Space Sum. The total error in the reciprocal space sum is given by

$$E_{6,\text{recip}} = \frac{\pi^{3/2}}{24\Omega} \sum_{\mathbf{h}} \sum_{ij} |B_{ij}| \cos[\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] h^3 \left[\pi^{1/2} \text{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right] \Theta(h - H_{\text{cut}}) \quad (41)$$

Approximating this sum as an integral leads to

$$E_{6,\text{recip}} \approx \frac{\pi^{3/2}}{24\Omega} N^2 \langle B \rangle \frac{\Omega}{8\pi^3} \int_{H_{\text{cut}}}^{\infty} h^3 \left[\pi^{1/2} \text{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right] 4\pi h^2 dh$$

By using $\pi^{1/2} \operatorname{erfc}(b) \leq (1/b)e^{-b^2}$, we have

$$E_{\delta, \text{recip}} \leq \frac{\pi^{3/2}}{24\Omega} N^2 \langle B \rangle \frac{\Omega}{8\pi^3} \int_{H_{\text{cut}}}^{\infty} 4\pi h^5 \frac{1}{2b^3} e^{-b^2} dh = \frac{2N^2 \langle B \rangle}{3\pi^{1/2}} \frac{1}{\eta^6} \int_{(H_{\text{cut}}\eta)/2}^{\infty} b^2 e^{-b^2} db = \frac{N^2 \langle B \rangle}{6\pi^{1/2}} \frac{1}{\eta^6} \left[H_{\text{cut}} \eta e^{-(H_{\text{cut}}\eta/2)^2} + \pi^{1/2} \operatorname{erfc} \left(\frac{H_{\text{cut}}\eta}{2} \right) \right] \quad (42)$$

Using (40) and (42), we can calculate the cutoff distances R_{cut} and H_{cut} that lead to a total error δ_v for given η .

3. *Repulsive Terms.* The repulsive terms in simulations generally have the form

$$E_{12} = \frac{1}{2} \sum_{ij} A_{ij} R_{ij}^{-12} \quad (43)$$

or

$$E_{\text{ex}} = \frac{1}{2} \sum_{ij} A_{ij} e^{-\lambda_{ij} R_{ij}} \quad (44)$$

We can estimate the R_{cut} for these cases in a similar way. The results are

$$E_{12, \text{real}} = \frac{2\pi N^2 \langle A \rangle}{9\Omega} \frac{1}{R_{\text{cut}}^9} \quad (45)$$

$$E_{\text{ex, real}} = \frac{2\pi N^2 \langle A \rangle}{\Omega} \frac{e^{-(\lambda)R_{\text{cut}}}}{\langle \lambda \rangle} \left(R_{\text{cut}}^2 + \frac{2R_{\text{cut}}}{\langle \lambda \rangle} + \frac{2}{\langle \lambda \rangle^2} \right) \quad (46)$$

where $N^2 \langle A \rangle = \sum_{ij} A_{ij}$ and $\langle \lambda \rangle$ is determined by the relation

$$N^2 \langle A \rangle e^{-(\lambda)R_{\text{cut}}} = \sum_{ij} A_{ij} e^{-\lambda_{ij} R_{\text{cut}}}$$

4. *Implementations of the Limits.* The limit on the real space sum, L , is chosen so that all cells containing any atoms within R_{cut} of any atom in the unit cell are included.⁹ This leads to

$$L_a = \frac{R_{\text{cut}} bc \sin \alpha}{\Omega} + 1$$

and similarly for L_b , L_c . The sum over the reciprocal lattice has limits of $H_a = (a/2\pi)H_{\text{cut}}$ and similarly for H_b and H_c . Within this set of cells, we eliminate any terms for which $R > R_{\text{cut}}$. This leads to a considerable reduction in effort, as indicated in Table IV.

C. *Time Minimized η .* Since the choice of η affects the R_{cut} and H_{cut} and thereby the number of terms in real and reciprocal space sums, we can choose η so as to minimize calculation time while retaining prespecified computational accuracy. This is illustrated in Table V for the case of poly(oxymethylene). In this table the electrostatic energy using (11) (a2) as well as those using (10) (a1) are shown. On the basis of several test calculations, we estimate that $t_{\text{real}}/t_{\text{recip}} \approx 4$ in (a1) and (b) and $t_{\text{real}}/t_{\text{recip}} \approx 10$ in (a2), where t_{real} is the time per term for the real space calculation, while t_{recip} is the time per term for the reciprocal space calculation. Of course, these values will depend on the actual program and computer used. The reason that the evaluation of the reciprocal space term is much faster than the real space term is that the reciprocal space lattice sum involves a factor that only depends on h , which is calculated only once, while in the real space sum, all factors depend on atomic distances and must be calculated for each pair.

Excluding the interactions between the same atoms in different cells (since there are easy to evaluate) and using (10), the number of terms in the real space and reciprocal space sums can be estimated as follows (assuming constant atomic density)

$$N_{\text{real}} = \frac{4\pi}{3} R_{\text{cut}}^3 \frac{N(N-1)}{2\Omega} \quad (47)$$

$$N_{\text{recip}} = \left(\frac{4\pi}{3} H_{\text{cut}}^3 \frac{\Omega}{(2\pi)^3} - 1 \right) \frac{N(N-1)}{2} \quad (48)$$

where N is the number of atoms in the unit cell. When (11) is used, $N(N-1)/2$ in (48) should be replaced by $2N$. Since there is a cancellation of terms in the electrostatic sum due to the charge neutrality in the unit cell, we use $\delta_Q = 10\delta_{\text{disp}}$ to obtain similar accuracy in both sums. By using the estimated number of terms and the values of $t_{\text{real}}/t_{\text{recip}}$, we select η so that $N_{\text{real}} + N_{\text{recip}}/m$ is minimized where m is the ratio $t_{\text{real}}/t_{\text{recip}}$.

In Table V we show the results for poly(oxymethylene). In this system, there are 24 centers of which 16 are charged. In (a1) and (b), the η leading to the fastest calculation is $\eta \approx 2.5 \text{ \AA}$, while in (a2), the η leading to the fastest calculation is $\eta \approx 2.0 \text{ \AA}$. The η predicted using (33) is 2.94 \AA , in reasonable agreement with (a1) and (b). In (a2), it is shown that the computing times are shorter than those in (a1) for any η due to the smaller number of terms in the reciprocal space sum. Also, the computing time for each term in the reciprocal space sum is shorter in (a2) than in (a1). Therefore, the time-minimized η in this case is smaller than for other cases. The accuracy here is 10^{-3} kcal/mol for electrostatic and 10^{-4} kcal/mol for dispersion. Note that the error in the energy is independent of η in these calculations, showing the effectiveness of accuracy-specified cutoffs.

V. Application to Ar Crystal

As a test case for the Ewald dispersion sum formulas, we will calculate the structure and properties of argon face-centered cubic (fcc) crystal analytically and compare with those obtained by using the lattice sums.

A. *Model.* We will describe the Ar–Ar interactions with the Lennard–Jones 12–6 form

$$U(R) = D_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right] \quad (49)$$

where $R_0 = 3.8666 \text{ \AA}$, and $D_0 = 0.2351$ kcal/mol are adjusted to reproduce the experimental lattice spacing and heat of vaporization. For an fcc crystal structure, the total energy E_{tot} is⁷

$$E_{\text{tot}}(R) = \frac{1}{2} N D_0 \left[p_{12} \left(\frac{R_0}{R} \right)^{12} - 2p_6 \left(\frac{R_0}{R} \right)^6 \right] \quad (50)$$

where, R is the nearest-neighbor distance, $N = 4$ is the number of atoms in the conventional fcc cell, $p_{12} = 12.13188$, and $p_6 = 14.45392$.

B. *Equilibrium Lattice Constants.* Requiring $\partial E_{\text{tot}}/\partial R = 0$ leads to the equilibrium nearest-neighbor distance

$$R_e = \left(\frac{p_{12}}{p_6} \right)^{1/6} R_0 = 0.97123 R_0 \quad (51a)$$

The lattice constant at equilibrium becomes

$$A_e = 2^{1/2} R_e = 1.37353 R_0 = 5.3109 \text{ \AA} \quad (51b)$$

the experimental value¹⁰ at 0 K.

C. *Cohesive Energy.* Substituting (51) into (50) leads to

$$U_{\text{tot}}(R_e) = -\frac{1}{2} N D_0 \frac{p_6^2}{p_{12}} \quad (52)$$

so that the cohesive energy (per atom) is

$$U_{\text{coh}} = 8.6102 D_0 \quad (53)$$

This leads to $U_{\text{coh}} = 2.0244$ kcal/mol (of atoms), the experimental heat of vaporization at 0 K (after correcting for zero point energy).¹¹

(10) Donohue, J. *Structures of the Elements*; R. E. Krieger Publishing Co.: Malabar, FL, 1982. For argon, $A = 5.3109 \text{ \AA}$ at 0 K.

(11) Hultgren, R.; et al. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973. For argon, $\Delta H_v = 1.848$ kcal/mol at 0 K. Estimating the zero point energy as 0.1764 kcal/mol (from our calculations) leads to $U_{\text{coh}} = 2.0244$ kcal/mol.

(9) Calculations optimizing the cell parameters and internal coordinates of crystals were carried out using the PolyGraf polymer simulation program from Molecular Simulations, Inc. (BioDesign Division), Pasadena, CA 91101.

TABLE IV: Number of Terms in the Sum for Given Ewald (η) and Accuracy (δ) Parameters

(a) Electrostatic Sum										
η , Å	δ_Q , kcal/mol	NaCl				polyethylene				
		R_{cut} , Å	H_{cut} , Å ⁻¹	real terms	recip terms ^a	R_{cut} , Å	H_{cut} , Å ⁻¹	real terms	recip terms ^a	
1.5	10 ⁻²	4.645	4.568	72	7168	4.226	4.090	212	7128	
1.5	10 ⁻³	5.152	4.983	104	10192	4.773	4.549	344	9372	
1.5	10 ⁻⁴	5.617	5.366	104	12880	5.269	4.964	468	11088	
2.5	10 ⁻²	8.127	2.683	296	1568	7.460	2.394	1264	924	
2.5	10 ⁻³	8.938	2.934	512	2240	8.332	2.670	1748	1584	
2.5	10 ⁻⁴	9.686	3.173	608	2576	9.126	2.922	2342	2904	
3.5	10 ⁻²	11.721	1.891	1088	504	10.814	1.678	3820	528	
3.5	10 ⁻³	12.828	2.073	1328	728	11.999	1.879	5322	660	
3.5	10 ⁻⁴	13.852	2.243	1616	896	13.084	2.061	6824	660	

(b) Dispersion Sum										
η , Å	δ_{disp} , kcal/(mol Å)	NaCl				polyethylene				
		R_{cut} , Å	H_{cut} , Å ⁻¹	real terms	recip terms ^a	R_{cut} , Å	H_{cut} , Å ⁻¹	real terms	recip terms ^a	
1.5	10 ⁻³	4.819	5.089	72	10864	4.867	5.001	372	11880	
1.5	10 ⁻⁴	5.304	5.485	104	13552	5.348	5.410	480	16104	
1.5	10 ⁻⁵	5.752	5.856	104	17304	5.793	5.787	628	20328	
2.5	10 ⁻³	7.453	2.695	296	1568	7.539	2.639	1302	1584	
2.5	10 ⁻⁴	8.310	2.966	296	2240	8.387	2.915	1816	2376	
2.5	10 ⁻⁵	9.096	3.217	512	2576	9.168	3.167	2390	3432	
3.5	10 ⁻³	9.872	1.740	608	504	9.997	1.690	3066	528	
3.5	10 ⁻⁴	11.122	1.954	896	728	11.235	1.910	4326	660	
3.5	10 ⁻⁵	12.262	2.143	1232	728	12.366	2.105	5854	660	

^aThe number of atom pairs in the sum.

D. Bulk Modulus. The bulk modulus, a measure of the stiffness of the crystal, is defined by

$$B = -V \frac{dP}{dV} = V \frac{d^2 U_{\text{tot}}}{dV^2} \quad (54)$$

Writing the volume of the crystal as $V = NR^3/2^{1/2}$, we have

$$U_{\text{tot}}(V) = \frac{b_{12}}{V^4} - \frac{b_6}{V^2} \quad (55)$$

where $b_{12} = (1/8)p_{12}N^5D_0R_0^{12}$ and $b_6 = (1/2)p_6N^3D_0R_0^6$. The equilibrium volume is $V_e = (1/2^{1/2})NR_0^3(p_{12}/p_6)^{1/2}$, leading to

$$B = \frac{20b_{12}}{V_e^5} - \frac{6b_6}{V_e^3} = 2^{1/2} \frac{b_6^{5/2}}{b_{12}^{3/2}} = 4(2^{1/2}) \left(\frac{p_6^{5/2}}{p_{12}^{3/2}} \right) \left(\frac{D_0}{R_0^3} \right) = 106.328 \left(\frac{D_0}{R_0^3} \right) \quad (56)$$

E. Elastic Constants. The elastic constants have the form⁸

$$C_{11} = \frac{2}{V_e} \sum_L \left[\frac{d^2 U}{d(R^2)^2} \right]_L x_L^4 \quad (57a)$$

and

$$C_{12} = \frac{2}{V_e} \sum_L \left[\frac{d^2 U}{d(R^2)^2} \right]_L x_L^2 y_L^2 \quad (57b)$$

(For a two-body potential such as (49), the shear constant C_{44} is equal to C_{12} .) This leads to

$$C_{11} = 96(2^{1/2}) \left(\frac{D_0}{R_0^3} \right) \left(\frac{p_6}{p_{12}} \right)^{3/2} \left[56 \left(\frac{p_6}{p_{12}} \right) s_{1,8} - 4s_{1,5} \right] \quad (58a)$$

$$C_{12} = 96(2^{1/2}) \left(\frac{D_0}{R_0^3} \right) \left(\frac{p_6}{p_{12}} \right)^{3/2} \left[56 \left(\frac{p_6}{p_{12}} \right) s_{2,8} - 4s_{2,5} \right] \quad (58b)$$

where lattice sum constants $s_{1,m}$ and $s_{2,m}$ are given by

$$s_{1,m} = \sum_l \frac{l_1^4}{(l_1^2 + l_2^2 + l_3^2)^m} \quad (59)$$

$$s_{2,m} = \sum_l \frac{l_1^2 l_2^2}{(l_1^2 + l_2^2 + l_3^2)^m} \quad (60)$$

Here the sum is over all integer values of l_1, l_2, l_3 where $l_1 + l_2 + l_3$ must be even. The constants $s_{1,8} = 0.03184001$, $s_{2,8} = 0.01567332$, $s_{1,5} = 0.320449$, and $s_{2,5} = 0.140899$ were obtained by numerical computations. The result is

$$C_{11} = 148.762 \left(\frac{D_0}{R_0^3} \right)$$

$$C_{12} = C_{44} = 85.123 \left(\frac{D_0}{R_0^3} \right)$$

The Poisson ratio σ for this cubic system

$$\sigma = -\frac{e_2}{e_1} = \frac{C_{12}}{C_{11} + C_{12}} = 0.3640 \quad (61)$$

is independent of R_0 and D_0 .

If D_0 is expressed in kcal/mol and R_0 is expressed in Å, then a conversion factor of 6.94780 is needed to obtain pressures in GPa. Thus the above expressions lead to

$$C_{11} = 4.2031 \text{ GPa}$$

$$C_{12} = 2.4051 \text{ GPa}$$

and

$$B = \frac{1}{3}(C_{11} + 2C_{12}) = 3.0044 \text{ GPa}$$

These can be compared to the experimental values at 0 K of¹²

$$C_{11} = 4.0 \text{ GPa}$$

$$C_{12} = 2.0 \text{ GPa}$$

$$C_{44} = 2.0 \text{ GPa}$$

F. Results. In Table VI we compare the results of optimizing the unit cell parameters of Ar with various ways of carrying out the lattice sums (all of which used periodic boundary conditions). In these calculations we used conjugate gradient minimization to optimize both cell parameters and atomic coordinates inside

TABLE V: Dependence of Timing on Choice of η for Orthorhombic Poly(oxymethylene)^a(a1) Electrostatic Sum. $\delta_Q = 0.001$ kcal/mol. Equation 10 is used. Use of $\delta_Q = 10^{-5}$ kcal/mol leads to $E = -51.19144$ kcal/mol.

η , Å	E , kcal/mol	N_{real}	N_{rec}	$t_{\text{real}}/t_{\text{recip}}$	t_{est}	t_{calc} , s
1.0	-51.1916	116	92160	8.3	23156	7.38
1.5	-51.1914	443	27360	6.9	7283	2.25
2.0	-51.1916	1154	10320	4.4	3734	1.08
2.25	-51.1915	1656	6720	5.9	3336	1.11
2.5	-51.1915	2306	4800	5.1	3506	1.13
3.0	-51.1914	4232	2880	4.6	4952	1.47
3.5	-51.1915	6928	1440	4.3	7288	2.02
4.0	-51.1914	10830	960	3.9	11070	2.67
4.5	-51.1914	15795	480	4.4	15915	4.35
5.0	-51.1914	22136	480	4.0	22256	5.55

(a2) Electrostatic Sum. $\delta_Q = 0.001$ kcal/mol. Equation 11 is used.

η , Å	E , kcal/mol	N_{real}	N_{rec}	$t_{\text{real}}/t_{\text{recip}}$	t_{est}	t_{calc} , s
0.75	-51.1919	36	61312	35.3	6168	3.10
1.0	-51.1916	116	24576	13.6	2573	1.32
1.25	-51.1915	234	12608	12.7	1494	0.74
1.5	-51.1914	443	7296	12.1	1172	0.57
1.75	-51.1914	741	4160	8.5	1157	0.49
2.0	-51.1916	1154	2752	7.3	1429	0.50
2.25	-51.1915	1656	1792	9.4	1835	0.75
2.5	-51.1915	2306	1280	7.8	2434	0.86
3.0	-51.1914	4232	768	7.8	4308	1.32

(b) Dispersion Sum. $\delta_{\text{disp}} = 10^{-4}$ kcal/mol. Use of $\delta_{\text{disp}} = 10^{-5}$ kcal/mol leads to $E = -8085.19405$ kcal/mol.

η , Å	E , kcal/mol	N_{real}	N_{rec}	$t_{\text{real}}/t_{\text{recip}}$	t_{est}	t_{calc} , s
1.0	-8085.1939	440	416760	6.6	104630	33.93
1.5	-8085.1939	1479	104880	4.0	27699	8.39
2.0	-8085.1940	3209	35880	2.6	12179	3.17
2.25	-8085.1940	4261	23736	3.8	10195	1.78
2.5	-8085.1939	5656	15456	3.2	9520	2.29
3.0	-8085.1940	9136	8832	3.1	11344	2.41
3.5	-8085.1940	13741	4416	2.8	14845	2.83
4.0	-8085.1940	19501	2208	2.5	20053	3.15
4.5	-8085.1940	26581	1104	2.5	26857	4.04
5.0	-8085.1940	34738	552	2.7	34876	6.03

^a E is the energy, N_{real} and N_{rec} are the numbers of terms in the real space and reciprocal space sums, $t_{\text{real}}/t_{\text{recip}}$ is the actual ratio of calculation time per term for real and reciprocal space, t_{est} is the estimated relative time, and t_{calc} is the actual calculation time. The estimated relative time is calculated from $N_{\text{real}} + N_{\text{rec}}/m$, where $m = 4$ in (a1) and (b) and $m = 10$ in (a2).

the cell.⁹ In each case the final root mean square (RMS) force per atomic degree of freedom is less than 0.001 kcal/mol, and the RMS stress for the six cell parameters is less than 0.0001 kcal/mol.

Using traditional distance cutoffs with $R_{\text{cut}} = 9$ Å leads to an error in the lattice constant of 0.006 Å or 0.1%, an error in the cohesive energy of 0.68 kcal/mol (of cells) or 8.4%, and an error in the bulk modulus of 0.09 GPa or 3.0%.

In the Ewald calculations, we evaluated the repulsive terms by using direct sums and used the error bounding procedures of section IV.B with several energy criteria, where $\delta_Q = 10\delta_v$. We also carried out calculations as a function of strain by introducing a finite strain to the system, optimizing the atomic coordinates, and calculating the stresses.⁹ The highly repulsive nature of the atomic interactions for short R (due to the Pauli principle that requires orthogonalization of the overlapping atomic orbitals) leads to a quite nonlinear stress-strain relation. Using the stress versus strain results for small strains (± 0.005 , ± 0.01), we obtained numerical estimates of C_{11} and C_{12} to compare with the analytic values. The results agreed to two decimal places in each case.

VI. Application to NaCl Crystal

As a test case for the Ewald Coulomb sum formula, we will calculate the structure and properties of NaCl crystal analytically and compare with those obtained by using the lattice sums.

A. Model. For the atom-atom interactions, we use the form

$$U_{ij} = \lambda e^{-R/\rho} - \frac{q^2}{R} \quad (\text{nearest neighbors}) \quad (62)$$

$$\pm \frac{q^2}{P_{ij}R} \quad (\text{otherwise})$$

The total energy E_{tot} (relative to free ions) is given by⁷

$$E_{\text{tot}}(R) = N \left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right) \quad (63)$$

Here R is the nearest neighbor distance, $N = 4$ is the number of pairs of NaCl atoms in the unit cell, and $z = 6$ is the number of nearest neighbors. The Madelung constant is $\alpha = 1.747565$, while unit charges on each ion lead to $q^2 = 332.0647$ Å kcal/mol (allowing R to be in Å and E in kcal/mol).

B. Parameters. We will choose the parameters λ and ρ in (62) to obtain the experimental lattice constant¹³

$$A = 5.578 \text{ Å}$$

and cohesive energy¹³

$$E_{\text{tot}}(R_e) = -740.0 \text{ kcal/mol}$$

at 0 K.

The equilibrium nearest neighbor distance $R_e = (1/2)A_e$ is obtained by requiring that $\partial E_{\text{tot}}/\partial R = 0$, leading to

$$R_e^2 e^{-R_e/\rho} = \frac{\rho \alpha q^2}{z\lambda} \quad (64)$$

Substituting R_e into (63) leads to

$$E_{\text{tot}}(R_e) = -\frac{N\alpha q^2}{R_e} \left(1 - \frac{\rho}{R_e} \right) \quad (65)$$

Using these results leads to

$$\rho = 0.309223 \text{ Å}$$

$$\lambda = 3.84485e^{R_e/\rho} = 31765.8 \text{ kcal/mol}$$

C. Bulk Modulus and Elastic Constants. The volume of the crystal V is given by $V = 2NR_e^3$; hence

$$E_{\text{tot}}(V) = N \left(z\lambda \exp \left[-\left(\frac{V}{2N} \right)^{1/3} / \rho \right] - \left(\frac{2N}{V} \right)^{1/3} \alpha q^2 \right) \quad (66)$$

Using eq 54, we have

$$B = \left(V \frac{d^2 E_{\text{tot}}}{dV^2} \right)_{V_e} = \frac{\alpha q^2}{18R_e^3} \left(\frac{1}{\rho} - \frac{2}{R_e} \right) = 25.9858 \text{ GPa} \quad (67)$$

where the equilibrium volume V_e is $2NR_e^3$ and the conversion factor $1 \text{ kcal}/(\text{mol Å}^3) = 6.94780 \text{ GPa}$ was used. This can be compared with the experimental value of¹³ 26.60 GPa.

Since each atom in the NaCl crystal is at a point of inversion symmetry, no internal strain is induced when external stress is applied. Hence, the two independent elastic constants are given by

$$C_{11} = \frac{\alpha q^2}{zR_e^4} \left(\frac{R_e}{\rho} - 1 \right) + \frac{1}{V_e} \frac{\partial^2 S_1}{\partial e_1 \partial e_1} \quad (68)$$

$$C_{12} = \frac{1}{V_e} \frac{\partial^2 S_1}{\partial e_1 \partial e_2} \quad (69)$$

where e_1 and e_2 are strains (XX and YY components) and the first term in C_{11} arises from the repulsive part of the potential. The lattice sums for the second partial derivatives of the elec-

(13) (a) Sangster, M. J. L.; Schröder, U.; Atwood, R. M. *J. Phys. C* **1978**, *11*, 1523. (b) Sangster, M. J. L.; Atwood, R. M. *J. Phys. C* **1978**, *11*, 1541.

TABLE VI: Equilibrium Properties of Argon Crystal (Using Four Atoms per Cell)

	exper ^a	exact	Ewald			direct summation		
			0.00001 ^b	0.001 ^b	0.01 ^b	9 Å ^c	15 Å ^c	30 Å ^c
<i>A</i> , Å	5.3109	5.3109	5.3109	5.3108	5.3090	5.3172	5.3176	5.3111
<i>U</i> , kcal/mol	-8.0975	-8.0976	-8.0970	-8.0981	-8.1171	-7.4202	-7.9756	-8.0830
<i>B</i> , GPa	2.67	3.0044	3.0044	3.0054	3.0164	3.0940	2.9482	3.0050
<i>C</i> ₁₁ , GPa	4.0	4.2031	4.2031	4.2048	4.2216	4.4123	4.1309	4.2052
<i>C</i> ₁₂ , GPa	2.0	2.4051	2.4051	2.4057	2.4138	2.4348	2.3569	2.4049
<i>C</i> ₄₄ , GPa	2.0	2.4051	2.4051	2.4057	2.4138	2.4348	2.3569	2.4049
σ	0.32	0.364	0.3640	0.3639	0.3638	0.3556	0.3633	0.3638
time, ^d s			0.171	0.143	0.084	0.045	0.124	0.866
pairs R space ^d			120	72	24	120	480	4320
pairs K space ^d			480	336	156			

^aSee ref 10 (*A*), 11 (*U*), and 12 (*C*₁₁, *C*₁₂, and *C*₄₄). ^bAccuracy parameters in kcal/mol. ^cCutoff distances (*R*_{cut}). Using a cubic spline function to decrease the potential from full value at *R*_{cut} -1 Å to zero at *R*_{cut} -0.5 Å. ^dOnly attractive terms are considered.

trostatic energy with respect to the strain components converge very slowly, requiring Ewald sums. By using (22), we have

$$\frac{\partial^2 S_1}{\partial e_1 \partial e_1} = \frac{1}{2\eta^5} \sum_{L,i,j} Q_{ij} \left\{ \left[\frac{3 \operatorname{erfc}(a)}{a^5} + \frac{6\pi^{-1/2}e^{-a^2}}{a^4} + \frac{4\pi^{-1/2}e^{-a^2}}{a^2} \right] \times \right. \\ \left. (r_i - r_j - \mathbf{R}_L)_1^4 - 2\eta^2 \left[\frac{\operatorname{erfc}(a)}{a^3} + \frac{2\pi^{-1/2}e^{-a^2}}{a^2} \right] \times \right. \\ \left. (r_i - r_j - \mathbf{R}_L)_1^2 \right\} + \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h})S(-\mathbf{h}) \times \\ \left[\frac{e^{-b^2}}{h^2} \left(1 - 8 \frac{(1+b^2)}{h^2} h_1^2 \right) + \frac{4h_1^4 e^{-b^2}}{h^6} \left(2 + \frac{h^2 \eta^2}{2} + \frac{h^4 \eta^4}{16} \right) \right] \quad (70)$$

$$\frac{\partial^2 S_1}{\partial e_1 \partial e_2} = \frac{1}{2\eta^5} \sum_{L,i,j} Q_{ij} \left[\frac{3 \operatorname{erfc}(a)}{a^5} + \frac{6\pi^{-1/2}e^{-a^2}}{a^4} + \frac{4\pi^{-1/2}e^{-a^2}}{a^2} \right] \times \\ (r_i - r_j - \mathbf{R}_L)_1^2 (r_i - r_j - \mathbf{R}_L)_2^2 + \frac{2\pi}{\Omega} \sum_{\mathbf{h}} S(\mathbf{h})S(-\mathbf{h}) \left[\frac{e^{-b^2}}{h^2} \left(1 - \right. \right. \\ \left. \left. 2 \frac{(1+b^2)}{h^2} (h_1^2 + h_2^2) \right) + \frac{4h_1^2 h_2^2 e^{-b^2}}{h^6} \left(2 + \frac{h^2 \eta^2}{2} + \frac{h^4 \eta^4}{16} \right) \right] \quad (71)$$

In this model, *C*₄₄ = *C*₁₂. The calculations of these sums give

$$C_{11} = 51.4366 \text{ GPa}$$

$$C_{12} = C_{44} = 13.2598 \text{ GPa}$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}) = 25.9854 \text{ GPa}$$

while the Poisson ratio (61) is

$$\sigma = 0.2050$$

D. Result. In Table VII, we show the results of optimizing the unit cell parameters of NaCl with three different accuracy parameters.

TABLE VII: Equilibrium Properties of NaCl Crystal (Using Four Molecules per Cell)

	exper ^a	exact	Ewald		
			0.1 ^b	0.01 ^b	0.001 ^b
<i>A</i> , Å	5.578	5.5780	5.5776	5.5776	5.5780
<i>U</i> , kcal/mol	-740.0	-740.00	-739.9938	-740.0184	-739.9985
<i>B</i> , GPa	26.60	25.9858	25.97	25.963	25.9854
<i>C</i> ₁₁ , GPa	57.33		51.46	51.433	51.4366
<i>C</i> ₁₂ , GPa	11.23		13.23	13.228	13.2598
<i>C</i> ₄₄ , GPa	13.31		13.23	13.228	13.2598
σ	0.164		0.205	0.205	0.2050

^aSee ref 13. ^bAccuracy parameters in kcal/mol.

VII. Summary and Discussion

Using Ewald-inspired approximations for accelerated convergence of lattice sums, we developed and tested equations for the energies, forces, stresses, and second derivatives for both electrostatic (1/*R*) and dispersion (1/*R*⁶) lattice sums. In addition, we developed an approach for estimating the convergence parameter η in order to minimize the computation time while retaining a fixed level of accuracy.

With these accuracy specification procedures, the costs of carrying out accurate lattice sums is less than that for normal direct sums (at the same level of accuracy) despite the more complicated formulas for accelerated convergence.

We suggest that these procedures may also prove equally valuable for biological systems. A molecule such as hemoglobin with ~6000 atoms would lead to 18 000 000 pairwise interactions, which are truncated to ~500 000 by using energy cutoffs of 9 Å. We suspect that such cutoffs lead to errors in the Coulomb interactions similar to those shown for NaCl. By considering the hemoglobin to be in a unit cell sufficiently large that interactions between cells is small, one could use the Ewald procedures to generate a given level of accuracy. This approach would be especially valuable for including explicit solvent (water) in the calculation. Water has large charges (0.4 *e* on each H and -0.8 *e* on O) so that use of a finite solvent shell leads to very large surface effects. With a periodic cell containing Hb and H₂O, one could eliminate surface effects while obtaining accurate energies.

Acknowledgment. This work was partially supported by a grant from Imperial Chemical Industries, Cleveland, England, and by a grant from the Air Force Office of Scientific Research (No. AFOSR-88-0051). We thank Molecular Simulation, Inc. (Biodesign, Inc.), Pasadena, CA for use of the PolyGraf polymer simulation program.

Registry No. NaCl, 7647-14-5.