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Prediction of Polymer Crystal Structures and Properties. A Method Utilizing Simultaneous *Inter*- and *Intra*molecular Energy Minimization

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ABSTRACT: A method is described for using molecular mechanics to calculate in a unified manner, from transferable conformational energy functions, the packing parameters and energy, vibrational dispersion curves, heat capacity and thermodynamic functions, elastic constants, and refractive indices of polymer crystals. The *inter*- and *intra*molecular conformational energies are simultaneously minimized. This allows assessment of the effect of packing forces on the polymer helix parameters and the intramolecular geometry. In addition, the converged Newton–Raphson coefficient matrix used in minimization allows convenient vibrational analysis and calculation of the elastic constants of the crystal.

Molecular mechanics calculations have proven very useful in accounting for the conformational energetics and properties of polymer molecules. The method is based on the premise that a molecule can be simulated by empirical transferable energy functions that represent bond stretching, bending, and twisting as well as more distant nonbonded or steric interactions. Electrostatic forces are included when appropriate. Stable conformations are found as minima in the total energy function. When applied to a segment of an isolated polymer molecule, the most stable local conformation, when repeated, often can be indentified as the conformation of the helix obtaining in the crystalline state. The molecular mechanics calculations on a variety of local conformations often can be summarized by association of local conformations with structurally motivated energy parameters (e.g., gauche trans energy differences, four-bond pentane interferences, etc.). These parameters then lead to statistical weight matrices that may be utilized as input to statistical calculations of the average properties of disordered long chains.[1] This process has reached a high state of development and had many successes. In bulk systems, defects and energy paths for molecular motion in polymer crystals have been successfully described via conformational energy calculations.[2–4]

There has also been interest in predicting the packing and structure of polymer crystals.[5,6] It is this subject that is the concern of the present work. Most past effort in this area has proceeded via a reasonable two-step process. A conformation of the polymer helix is adopted. It is determined either from molecular mechanics calculations on the isolated molecule or from other sources. Then the packing is analyzed by assembling the polymer helices, assuming no further change in conformation. Thus, *inter*molecular nonbonded and polar energy functions are the only participants in the total energy function optimized. In the present work we generalize the packing analysis by describing a method where both the *intra*molecular and intermolecular degrees of freedom are permitted to participate simultaneously in the optimization. The motivation for this is twofold. First, although the rigid molecule analysis is no doubt viable in numerous cases, there are also important ones known where there

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are important distortions of the intramolecular geometry occasioned by the packing forces. As an example, Kusanagi et al.[7] treated the case of poly(ethylene oxybenzoate) and found that a calculated isolated chain structure was far from one allowing solution of the X-ray structure. They introduced a step of minimizing the packing energy with chain torsional angles included and were able to solve the X-ray structure. The packing forces can be sufficient to lead to polymorphism as a result of intramolecular distortions. An important such case, that of polyoxymethylene, is analyzed in the companion paper. Our second reason for undertaking the implementation of this procedure is based on the desire to be able to calculate a variety of useful crystal properties in accompaniment with the packing prediction. These properties include vibrational analysis to determine dispersion curves, infrared and Raman spectra and thermodynamic functions (heat capacity, entropy, enthalpy, and free energy), and calculation of elastic constants. These calculations require the participation of all of the internal degrees of freedom in their execution.

It has been demonstrated previously that the Newton–Raphson method provides an effective procedure for conformational energy minimization with respect to the internal degrees of freedom of molecules and that the second-derivative coefficient matrix of the converged molecule conveniently provides the dynamical matrix for input into harmonic vibrational analysis.[8] We utilize this convenience in the present work. In addition, since this matrix contains the second derivatives of the crystal energy with respect to the cell parameters, it forms the basis for elastic constant calculation. Therefore a major task is to formulate a Newton–Raphson coefficient matrix that includes the crystal packing parameters as well as the molecular internal coordinates. The strategy is described in the next section.

Crystal Energy Minimization with Molecular Internal Coordinate Participation

The packing of polymer molecules presupposes the existence of an extended rodlike conformation describable as a helix. The latter is best represented in terms of cylindrical coordinates and by a repeat unit that rotates through a helical advance angle, σ, and a translational advance, d, in replicating itself (see Figure 1). In what follows, the helix is oriented with respect to a Cartesian coordinate system such that the helix axis is along the z axis and the first atom of the repeat unit is on the x axis at $z = 0$. The Cartesian coordinates of the repeat unit in this orientation are called the "unrotated coordinates". They are represented by $\mathbf{v}$, a $3N$ dimensional vector made up of vectors $\mathbf{v}(i)$, $i = 1, N$ with components $v(i)_x$, $v(i)_y$, and $v(i)_z$ that are the coordinates of the N atoms of the helical repeat unit. The crystal lattice is represented by nonorthogonal basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ that are oriented with $\mathbf{c}$ along the Cartesian z axis and with the projection of $\mathbf{a}$ in the x,y plane along x. The position vector, $\mathbf{x}_n(i)$, of the ith atom in the nth repeat unit along a central chain located at $x,y = 0$ is expressible in terms of $\mathbf{v}(i)$, the helical advance angle, σ, and translation, d, as

$$\mathbf{x}_n(i) = \boldsymbol{R}\{\sigma,\theta_x\}\mathbf{v}(i) + \mathbf{T} \tag{1}$$

where $\mathbf{R}\{\sigma,\theta_x\}$ is a rotation matrix,

$$\mathbf{R}\{\sigma,\theta_x\} = \begin{bmatrix} \cos((n-1)\sigma + \theta_x) & -\sin((n-1)\sigma + \theta_x & 0 \\ \sin((n-1)\sigma + \theta_x) & \cos((n-1)\sigma + \theta_x) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

that is a function of a possible chain setting angle, θ_x, as well as the advance angle, σ, and where $\mathbf{T}$ is the translation vector,

$$\mathbf{T} = [0, 0, (n-1)d]^{t}$$

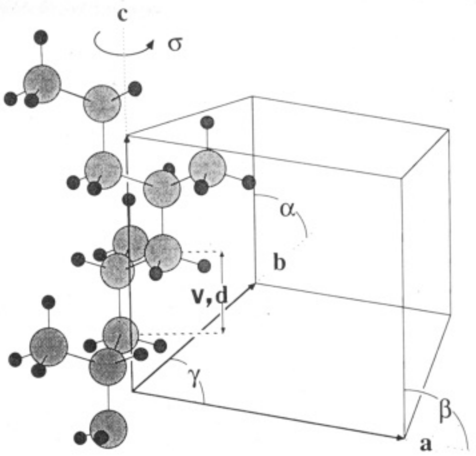

Figure 1. Schematic depiction of the parameters involved in simultaneous inter- and intramolecular energy minimization of a polymer crystal. The repeat unit internal coordinates are designated by $\mathbf{v}$, the helix advance angle and distance by σ and d, the chain setting angle by θ_x, and the lattice parameters by a, b, α, β, γ.

The position vector, $\mathbf{x}_{n,k}(i)$, of the ith atom in the nth repeat unit in a distant chain, k, located at a', b', ($c = 0$), (where the primes on a,b indicate the possibility of fractional values of a,b in lattices with more than one chain per cell) is obtained by adding a lattice translation to eq 1 and can be expressed as

$$\mathbf{x}_{n,k}(i) = \mathbf{R}\{\sigma,\theta_{x(k)}\}\mathbf{v}(i) + \mathbf{R}\{\alpha,\beta,\gamma\}\mathbf{T}_k \tag{2}$$

using the above helix rotation matrix (but with a k subscript on θ_x to indicate the possibility of $a \pm$ dependence on k) and where, in nonorthogonal basis vector lattices, the lattice translation can be written as the product of a rotation-like matrix $\mathbf{R}\{\alpha,\beta,\gamma\}$,

$$\mathbf{R}\{\alpha,\beta,\gamma\} = \begin{bmatrix} \sin\beta & C_2/\sin\beta & 0 \\ 0 & C_1/\sin\beta & 0 \\ \cos\beta & \cos\alpha & 1 \end{bmatrix}$$

in which α, β, and γ are the unit cell angles (γ between a, b, etc.) and

$$C_1 = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$$

$$C_2 = \cos\gamma - \cos\alpha\cos\beta$$

and a translation vector $\mathbf{T}_k$,

$$\mathbf{T}_k = [A_k a, B_k b, (n-1)d]^{t}$$

in which A_k, B_k are appropriate (possibly nonintegral) multiples of a and b required to place the chain at a', b'. The helix d translation in eq 1 has been absorbed into $\mathbf{T}_k$. A chain translational offset along c, $= Z_{0(k)}$, a possibility when more than one chain per cell is present, can be incorporated as a parameter into each $v_z(i)$ as $v_z(i) + Z_{0(k)}$.

Since the crystal energy is expressed as a function of the position vectors $\mathbf{x}_{n,k}(i)$, it follows that the independent basis parameters to be optimized in energy minimization are the unrotated repeat unit coordinates, v, the helix parameters, σ and d, a chain setting angle, θ_x, chain c-axis offset, Z_0, and the lattice parameters, a, b, α, β, γ. We collect the basis parameters into a vector, $\mathbf{P}$,

$$\mathbf{P} = [\mathbf{v}, \sigma, d, \theta_x, Z_0, a, b, \alpha, \beta, \gamma]^{t} \tag{3}$$

In the Newton–Raphson method the energy is expressed as a quadratic function of the parameter displacements. In molecular mechanics the explicit energy functions are expressed in terms of "valence coordinates" that are two-center interatom distances, r, three-center valence angles, Θ, four-center torsional angles, ϕ, etc. These functions are easily expanded as quadratics in r, Θ, ϕ, but then transformations to the basis parameters must be provided. This proceeds as follows. Let q,q' be generalized valence coordinates expressing an interaction between a set of atoms i, j, k, ... and a set i', j', k', ... Then the explicit interaction energy expression, $U(q,q')$, may be expanded,

$$U(q,q') = U^0(q,q') + \partial U/\partial q \Delta q + \partial V/\partial q' \Delta q' + \tfrac{1}{2}\sum \partial^2 U/\partial q \partial q' \Delta q \Delta q' + \ldots \quad (4)$$

As an example, in the case of a simple bond stretching function, where $U = {}^1/_2 k(r_{ij} - R^0{}_{ij})^2$, $q,q' = r_{i,j}$ and

$$U_r = U^0(r^0{}_{ij}) + k(r^0{}_{ij} - R^0{}_{ij})\Delta r_{ij} + \tfrac{1}{2}k\Delta r_{ij}{}^2$$

The coordinate q is then transformed to the Cartesian basis, $\mathbf{x}$. Let

$$\mathbf{D}_1(s) = [\partial q/\partial x_s, \partial q/\partial y_s, \partial q/\partial z_s]^t \qquad s = k, j, k, \ldots$$

be the vector containing the first derivatives of q with respect to the Cartesian coordinate, $\mathbf{x}(s)$, let $\mathbf{D}_2(s,s')$ be the 3×3 matrix of second derivatives of q with respect to x_s, y_s, $z_s x_{s'}$, $y_{s'}$, $z_{s'}$ and let $\Delta\mathbf{x}(s)$ be the vector $= [\Delta x_s, \Delta y_s, \Delta z_s]^t$. Then

$$\Delta q = \sum_{s=i,j,k,\ldots} \mathbf{D}_1(\mathrm{s})\Delta\mathbf{x}(s) + \tfrac{1}{2}\sum_{s,s'} \Delta\mathbf{x}(s)^t \mathbf{D}_2(s,s')\Delta\mathbf{x}(s') + \ldots \quad (5)$$

Use of eq 5 in eq 4 then expresses a potential energy interaction term as a quadratic in Cartesian coordinates, $\Delta\mathbf{x}(s)$. It remains to transform the $\Delta\mathbf{x}(s)$ coordinates to the basis parameter set as

$$\Delta x^\alpha(s) = \mathbf{B}_1\Delta\mathbf{P} + \tfrac{1}{2}\Delta\mathbf{P}^t\mathbf{B}_2\Delta\mathbf{P} + \ldots \quad (6)$$

where $\Delta x^\alpha(s)$ is a component, $\alpha = x, y, z$, of $\Delta\mathbf{x}(s)$, $\mathbf{B}_1$ is the vector of first derivatives of $x^\alpha(s)$ with respect to the basis parameters in $\mathbf{P}$ (eq 3), $\mathbf{B}_2$ is the matrix of second derivatives and from eq 3,

$$\Delta\mathbf{P} = [\Delta\mathbf{v}, \Delta\sigma, \Delta d, \Delta\theta_x, \Delta Z_0, \Delta a, \Delta b, \Delta\alpha, \Delta\beta, \Delta\gamma]^t$$

Substitution of eq 6 into eq 5 and then eq 5 into eq 4 results in a quadratic expansion in terms of the independent basis parameters for a single potential energy interaction expression. When this process is repeated for all the potential energy terms considered and the results accumulated, a quadratic expression for the total energy is obtained that may be expressed as

$$U = U^0 + \mathbf{A}\Delta\mathbf{P} + \tfrac{1}{2}\Delta\mathbf{P}^t\mathbf{C}\Delta\mathbf{P} + \ldots \quad (7)$$

where all of the first-order terms are accumulated into $\mathbf{A}$ and the second-order ones into $\mathbf{C}$. The condition for stationary energy, $\delta U = 0$, since the elements of $\Delta\mathbf{P}$ are independent, leads, on differentiation of U with respect to each of the parameters in $\Delta\mathbf{P}$ and setting the result equal to zero, to a set of linear algebraic equations

$$\mathbf{C}\Delta\mathbf{P} = -\mathbf{A} \quad (8)$$

On solving the $\Delta\mathbf{P}$ the parameters may be updated $\mathbf{P}' = \mathbf{P} + \Delta\mathbf{P}$ and the process repeated until convergence, $\mathbf{A} \rightarrow 0$, $\Delta\mathbf{P} \rightarrow 0$.

It is appropriate to comment on some considerations in implementing these equations in practice. The total energy should be a sum over sufficient potential energy interactions to represent the energy of the crystal. Because of the lattice periodicity only the interactions within a suitably chosen reference unit and between the reference unit and external units need be considered. The reference unit at the maximum is the unit cell but could be a smaller if a crystal symmetry operation permitted. The energy per reference unit is thus regarded as the total energy

$$U = \sum{}' U(q,q') \quad (9)$$

where $\sum'$ indicates the above type of summation. It is very convenient to divide the summation in eq 9 into terms internal to the reference unit and those external. All of the intramolecular valence coordinate contributions (bond stretching (r), bending (θ), torsion (ϕ)) will lie in the internal sum and the external one will contain only two-center, r-type atom–atom interactions. Thus,

$$U = \sum{}'' U(q,q') + \tfrac{1}{2}\sum_{i,j} U_{\mathrm{ext}}(r_{ij}) \quad (10)$$

where the sum $\sum''$ is over the valence interactions internal to the reference unit (including the internal nonbonded interactions) and the external ("ext") interaction sum over i is over the reference unit atoms and j over external atoms.

In terms of computer coding, the transformation derivatives $\mathbf{D}_1$, $\mathbf{D}_2$, eq 5, and $\mathbf{B}_1$, $\mathbf{B}_2$, eq 6, are the programming intensive parts. However, the task is somewhat simplified by the fact that in the first sum above, $\sum''$, where the $\mathbf{D}_1$ and $\mathbf{D}_2$ transformations are fairly complicated, the accompanying $\mathbf{B}_1$ and $\mathbf{B}_2$ transformations are truncated in that the lattice parameters (a, b, α, β, γ) do not appear. In the second sum, $\sum_{i,j}$, the $\mathbf{D}_1$ and $\mathbf{D}_2$ transformations are simplified since r is the only type of valence coordinate to appear. This is the result of the nonbonded functions or Coulombic interactions being functions of r only. Formulas for the elements of $\mathbf{D}_1$ for valence coordinates for two-center interatom distances, r, three-center valence angles, Θ, four center torsional angles, ϕ, and a four-center out-of-plane bending, δ, have previously been presented as have formulas of $\mathbf{D}_2$ for r.[8] For the other valence coordinates, $\mathbf{D}_2$ is calculated by numerical differentiation from $\mathbf{D}_1$. The list of formulas for the elements of both $\mathbf{B}_1$ and $\mathbf{B}_2$ is quite extensive but one may be found in the Ph.D. Dissertation of R.A.S.[9]

Generation of Starting Structures. As the Newton–Raphson method is an iterative one, a trial structure must be generated and discussion of this task is appropriate. This involves setting up a trial helix and a trial packing grid. The latter is straightforward as an operation and requires little elaboration in that sense. However, from a computational result point of view it is very important, as the choice of grid and starting lattice parameters may greatly influence the structure obtained. That is to say, it is very probable that a number of packing arrangements are possible and lead to energy minima. The number and choices of starting packings will obviously greatly influence the number and nature of optimized structures obtained.

Setting up a trial helix does require elaboration from the operational point of view as there are two ways to approach it. The first is more directly connected to the formalism of energy minimization above but is less directly connected with the useful and familiar conformational and structural concepts already developed. That is, it is possible to start by defining a helix in terms of the advance angle and distance σ and d values and then to construct the atom coordinates $\mathbf{v}$ by geometric constructions based on standard bond lengths and valence angles. For example, polyethylene can be generated by $\sigma = 180°$, $d = 1.27$ Å, $\mathbf{v}(\mathrm{C}) = (0.866, 0.0, 0.0)$, and $\mathbf{v}(\mathrm{H}_1)$ and $\mathbf{v}(\mathrm{H}_2)$ generated by geometric construction.

The above is not always a convenient approach. Another useful method is to generate the starting helix in terms of the internal torsional angles of the repeat unit and derive the helix σ and d values from this information. Thus polyethylene is described as having a skeletal torsional angle of $\phi = 180°$, valence angle $\theta = 112°$, bond length $R = 1.54$ Å, and the hydrogens placed by geometric construction. The helix σ and d values are then computed. A general method for deriving helix parameters from the coordinates of an arbitrary repeat unit has been given by Sugeta and Miyazawa[10] and the relation between helix parameters and internal coordinates is also discussed by Tadokoro.[11] In practice, we can construct the repeat unit using a general structure-building method[12] that uses structural valence information as input and gives Cartesian coordinates as output. In addition to the minimum atoms in the repeat unit, three extra skeletal atoms are included as well. These are necessary to define the skeleton of the helix. In polyethylene, for example, there is only one skeletal atom in the repeat unit, but four are required to define the torsional angle, three to define the valence angle, and two for the bond distance. The three extra atoms serve this purpose. From the Cartesian coordinates of the repeat unit plus the three extra atoms, a transformation to the helical coordinate system ($\mathbf{v}$, σ, d) is computed by a modification of the Sugeta and Miyazawa method.[10] Further details may be found in the Ph.D. dissertation of R.A.S.[9]

Vibrational Analysis

In order to analyze the vibrations we use the converged quadratic energy where the linear terms now vanish. In order to introduce the phase differences for the periodic lattice it is necessary to work with the individual Cartesian displacements (eq 1 and 2). When, on convergence of the Newton–Raphson iteration process, eq 5 is substituted into eq 4 the result for the total energy/reference unit in Cartesian basis may be summarized by

$$U = {}^1\!/_2 \textstyle\sum_{i=1,N} \sum_j \sum_{\alpha,\beta} \Delta x^{\alpha}(i) g^{\alpha,\beta}(i,j) \Delta x(j)^{\beta} \tag{11}$$

where $\Delta x^{\alpha}(i)$, $\Delta x(j)^{\beta}$ are the α, β, $= x, y, z$ components of (vibrational) displacements of atoms i, j and $g^{\alpha,\beta}(i,j)$ are the elements of the matrix resulting from the above substitution. The summation over i is over the N atoms in the reference unit and that over j is unrestricted. The equation of motion of the atom i in the reference unit is

$$-m_i \Delta \ddot{x}^{\alpha}(i) = \textstyle\sum_j \sum_{\beta} g^{\alpha,\beta}(i,j) \Delta x(j)^{\beta} \tag{12}$$

In the usual manner we let the displacement of atom j differ from its counterpart, j', in the reference cell, by a cell-dependent phase and write solutions to eq 12 as

$$\Delta x^{\alpha}(j) = \Delta x^{\alpha}{}_0(j') e^{i*(\omega t - \mathbf{k}\cdot\delta)} \tag{13}$$

where $\Delta x^{\alpha}{}_0(j)$ is a displacement amplitude, $\mathbf{k}$, is a wave vector

$$\mathbf{k} = k_a \vec{i} + k_b \vec{j} + k_c \vec{k}$$

and δ the phase shift

$$\delta = \delta_a \vec{i} + \delta_b \vec{j} + \delta_c \vec{k}$$

From the equation of motion of atom, i, there results

$$m_i \omega^2 \Delta x^{\alpha}{}_0(i) = \sum_{j'=1,N} \sum_{\beta} G^{\alpha,\beta}(i,j') \Delta x^{\beta}{}_0(j') \tag{14}$$

where

$$G^{\alpha,\beta}(i,j') = \sum_{\mathbf{k}} g^{\alpha,\beta}(i,j) e^{-i*(\mathbf{k}\cdot\delta)}$$

and the sum over j equivalent to j' to distant cells is now expressed as a sum over $\mathbf{k}$. The sum over atom j' is restricted to the reference cell. The above equations can then be reduced by standard methods to the eigenvalues and vectors as functions of the phases, δ_a, δ_b, δ_c.

The dispersion curves that result from the above can be sampled at appropriate intervals in δ_a, δ_b, δ_c to construct a vibrational partition function from which the thermodynamic functions can be calculated. Three-dimensional dispersion curves, as opposed to a single-chain dispersion curve, are essential in obtaining a representation of the low-frequency lattice vibrations that in turn permits an accurate low-temperature heat capacity to be calculated.

Elastic Constants

The elastic constants are the second derivatives of the energy (per unit volume) with respect to the lattice strains. The converged energy of the lattice has been expressed (eq 7, $\mathbf{A} = 0$) as quadratic in the basis parameters, $\Delta\mathbf{P}$. However, because there are more parameters in $\mathbf{P}$ than the six strains, the elements of eq 7 are not directly the elastic constants. Another complication is that strains are conventionally cast as Cartesian strains. However, the parameter list contains the lattice parameters, Δa, Δb, Δd, $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$. These are strains (a, b, d scaled by a_0, b_0, d_0) only in the orthorhombic, tetragonal, and cubic crystal systems. Thus two tasks are required, elimination of the extra parameters in $\mathbf{P}$ and the transformation of the resultant energy quadratic to a Cartesian system.

Elimination of Internal Parameters. Let the parameter vector, eq 3, be divided into two parts. One containing the six lattice parameters a, b, d, α, β, γ has elements subscripted l or k, the rest of the parameters are subscripted m or n. Thus $\Delta\mathbf{P}$ is partitioned as $\Delta\mathbf{P}_k = \Delta\mathbf{P}_l = \Delta[a, b, d, \alpha, \beta, \gamma]$ and $\Delta\mathbf{P}_m = \Delta\mathbf{P}_n = \Delta[\sigma, \theta_x, Z_0, \mathbf{v}]$. The energy, eq 7, when partitioned this way is

$$U = {}^1\!/_2 \textstyle\sum_{k,l} C_{k,l} \Delta P_k \Delta P_l + \sum_{k,m} C_{k,m} \Delta P_k \Delta P_m + {}^1\!/_2 \sum_{m,n} C_{m,n} \Delta P_m \Delta P_n \tag{15}$$

The extra parameters are eliminated by requiring the energy to be stationary with respect to internal parameters, ΔP_m, for arbitrary variations in lattice parameters, ΔP_k. Differentiating eq 15 with respect to one of the internal parameters, ΔP_m, and setting the result to zero give

$$\partial U / \partial \Delta P_{\mathrm{m}} = \textstyle\sum_l C_{m,l} \Delta P_l + \sum_n C_{m,n} \Delta P_n = 0 \tag{16}$$

Requiring the above condition for arbitrary $\Delta P_{l=L}$ leads to a set of simultaneous equations over $m, n = \sigma, \theta_x, Z_0, \mathbf{v}$,

$$C_{m,L} + \textstyle\sum_n C_{m,n} \partial \Delta P_n / \partial \Delta P_L = 0 \tag{17}$$

that may be solved for the derivatives of the dependent internal parameters, ΔP_n, with respect to the independent lattice parameter, ΔP_L, i.e., $\Delta P_n / \partial \Delta P_L$. Repeating this process for $L = 1, 6$ results in all of the derivatives of the dependent internal parameters with respect to the lattice parameters. The second derivatives of the energy with respect to the lattice parameters are, from eq 15,

$$\partial^2 U / \partial \Delta p_k \partial \Delta p_l = C_{k,l} + \textstyle\sum_n C_{k,n} \partial \Delta P_n / \partial \Delta P_l + \sum_n C_{l,n} \partial \Delta P_n / \partial \Delta P_k + \sum_{m,n} C_{m,n} (\partial \Delta P_m / \partial \Delta P_k)(\partial \Delta P_n / \partial \Delta P_l) \tag{18}$$

Since the derivatives of the internal parameters with respect to the lattice parameters that appear on the right-hand side of eq 18 are known through the above process, the desired second derivatives of the energy with respect to lattice parameters are now known.

Transformation of the Energy Derivatives to a Cartesian Basis. The transformation proceeds from expressing the Cartesian system in terms of the crystallographic system. First the following definitions are made:

$$A = (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2} \tag{19a}$$

$$B_1 = \cos \alpha - \cos \beta \cos \gamma \tag{19b}$$

$$B_2 = \cos \beta - \cos \alpha \cos \gamma \tag{19c}$$

$$B_3 = \cos \gamma - \cos \alpha \cos \beta \tag{19d}$$

In the axes orientation described earlier,

$$x = k_a a \sin \beta + k_b b B_3 / \sin \beta \tag{20a}$$

$$y = k_b b A / \sin \beta \tag{20b}$$

$$z = k_a a \cos \beta + k_b b \cos \alpha + k_d d \tag{20c}$$

Displacements Δx, Δy, Δz may be found in terms of Δa, Δb, Δd, $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$ by differentiating eq 20. Then k_a, k_b, k_d may be eliminated from the result in favor of x, y, z by solving eq 20 for the former in terms of the latter. The result of these two operations gives

$$u \equiv \Delta x = (x - yB_3/A)\Delta a/a + y(B_3/A)\Delta b/b + y(\sin \alpha \cos \beta/A)\Delta\alpha + [x \cos \beta/\sin \beta + y(B_1 - B_3 \cos \beta)/(A \sin \beta)]\Delta\beta - y(\sin \gamma/A)\Delta\gamma \tag{21a}$$

$$v \equiv \Delta y = y\Delta b/b + y(B_1 \sin \alpha/A^2)\Delta\alpha + y[(B_2 \sin \beta/A^2) - \cos \beta/\sin \beta]\Delta\beta + y(B_3 \sin \gamma/A^2)\Delta\gamma \tag{21b}$$

$$w \equiv \Delta z = (x - yB_3/A)(\cos \beta/\sin \beta)\Delta a/a + (y \sin \beta \cos \alpha/A)\Delta b/b + [z - x \cos \beta/\sin \beta + yB_3 \cos \beta/(A \sin \beta) - (y \sin \beta \cos \alpha/A)]\Delta d/d - (x - yB_3/A)\Delta\beta - (y \sin \alpha \sin \beta/A)\Delta\alpha \tag{21c}$$

The strains arranged as the six components of the vector ϵ may now be found as

$$\epsilon_1 = \partial u/\partial x = \Delta a/a + (\cos \beta/\sin \beta)\Delta\beta \tag{22a}$$

$$\epsilon_2 = \partial v/\partial y = \Delta b/b + (B_1 \sin \alpha/A^2)\Delta\alpha + (B_2 \sin \beta/A^2 - \cos \beta/\sin \beta)\Delta\beta + (B_3 \sin \gamma/A^2)\Delta\gamma \tag{22b}$$

$$\epsilon_3 = \partial w/\partial z = \Delta d/d \tag{22c}$$

$$\epsilon_4 = \partial w/\partial y + \partial v/\partial z = -(\cos \beta/\sin \beta)(B_3/A)\Delta a/a + (\sin \beta \cos \alpha/A)\Delta b/b + [(\cos \beta/\sin \beta)(B_3/A) - (\sin \beta \times \cos \alpha/A)]\Delta d/d + (B_3/A)\Delta\beta - (\sin \alpha \sin \beta/A)\Delta\alpha \tag{22d}$$

$$\epsilon_5 = \partial u/\partial z + \partial w/\partial x = (\cos \beta/\sin \beta)\Delta a/a - (\cos \beta/\sin \beta)\Delta d/d - \Delta\beta \tag{22e}$$

$$\epsilon_6 = \partial u/\partial y + \partial v/\partial x = -(B_3/A)\Delta a/a + (B_3/A)\Delta b/b + (\sin \alpha \cos \beta/A)\Delta\alpha + (B_1 - \cos \beta\, B_3)/(A \sin \beta)\Delta\beta - (\sin \gamma/A)\Delta\gamma \tag{22f}$$

Equation 22 thus provides the elements of a 6 × 6 matrix, $\mathbf{T}_l$, that transforms the lattice parameter vector, $\Delta\mathbf{P}_l = \Delta[a,b,d,\alpha,\beta,\gamma]$, to the strains, ϵ,

$$\epsilon = \mathbf{T}_l \Delta\mathbf{P}_l \tag{23}$$

If we let the energy derivatives in eq 18 be represented by a matrix, $\mathbf{C}_L$, with elements

$$C_L(k,l) = \partial^2 U/\partial\Delta p_k \partial\Delta p_l$$

the energy is

$$U = \tfrac{1}{2}\Delta\mathbf{P}_l{}^t C_L \Delta\mathbf{P}_l$$

Since the elastic constant matrix, $\mathbf{C}_e$, represents the energy (per reference unit volume, V_0) in terms of the strains, ϵ,

$$U/V_0 = \tfrac{1}{2}\epsilon^t \mathbf{C}_e \epsilon$$

we need the inverse of the transformation above (eq 23), or $\mathbf{T}_e = \mathbf{T}_l^{-1}$, in order to find the elastic constants,

$$\mathbf{C}_e = (\mathbf{T}_e{}^t \mathbf{C}_L \boldsymbol{T}_e)/V_0 \tag{24}$$

The elements of $\mathbf{T}_e = \mathbf{T}_l^{-1} = t_{ij}$ found from $\mathbf{T}_l$ are given below:

$$t_{11} = \sin^2 \beta \qquad t_{12} = 0 \qquad t_{13} = \cos^2 \beta$$

$$t_{14} = 0 \qquad t_{15} = \cos \beta \sin \beta \qquad t_{16} = 0$$

$$t_{21} = B_3{}^2/\sin^2 \beta \qquad t_{15} = A^2/\sin^2 \beta \qquad t_{23} = \cos^2 \alpha$$

$$t_{24} = A \cos \alpha/\sin \beta \qquad t_{25} = B_3 \cos \alpha/\sin \beta$$

$$t_{26} = AB_3/\sin^2 \beta$$

$$t_{31} = 0 \qquad t_{32} = 0 \qquad t_{33} = 1$$

$$t_{34} = 0 \qquad t_{35} = 0 \qquad t_{36} = 0$$

$$t_{41} = B_3{}^2 \cos \alpha/(\sin \alpha \sin^2 \beta)$$

$$t_{42} = A^2 \cos \alpha/(\sin \alpha \sin^2 \beta) \qquad t_{43} = -\sin \alpha \cos \alpha$$

$$t_{44} = -A \sin \alpha/\sin \beta \qquad t_{45} = -B_3 \sin \alpha/\sin \beta$$

$$t_{46} = AB_3 \cos \alpha/(\sin \alpha \sin^2 \beta)$$

$$t_{51} = \cos \beta \sin \beta \qquad t_{52} = 0 \qquad t_{53} = -\cos \beta \sin \beta$$

$$t_{54} = 0 \qquad t_{55} = -\sin^2 \beta \qquad t_{56} = 0$$

$$t_{61} = A^3/(\sin \beta \sin \gamma)[-B_3 \sin \beta/A + \cos \alpha \cos^3 \beta/(A \sin \beta) - (B_1/A)\{B_3 \cos \alpha/(A^2 \sin \beta) - \cos \beta/\sin \beta\} - B_2 \cos \gamma \cos \beta \sin \beta/A^3 + B_1{}^2 \cos \alpha \cos \beta/(A^3 \sin \beta)]$$

$$t_{62} = A^2 \cos \gamma/(\sin^2 \beta \sin \gamma)$$

$$t_{63} = (-B_1 \cos \beta - B_2 \cos \alpha)/\sin \gamma$$

$$t_{64} = -(A^3 \cos \beta - AB_1B_3)/(\sin^3 \beta \sin \gamma)$$

$$t_{65} = -(B_1 \sin^2 \beta + B_2B_3)/(\sin \beta \sin \gamma)$$

$$t_{66} = -A(A^2 + B_1 \cos \alpha)/(\sin^2 \beta \sin \gamma)$$

Compressibility for Heat Capacity Correction. The molecular mechanics energy minimization results in a fixed volume structure and the heat capacity obtained from vibrational analysis is at constant volume. If the standard thermodynamic formulation for computing C_p from C_v by utilizing the isothermal compressibility and thermal expansion is invoked, we point out that the compressibility is available from the methods discussed here. As developed above, the elastic constant matrix, $\mathbf{C}_e$, is available. The latter can be inverted to the compliance matrix, $\mathbf{S}$, where the stresses, arranged as a vector, are σ and $\epsilon = \mathbf{S}\sigma$. The sum of the tensile strains under uniform applied tensile stress gives the fractional change in volume under applied pressure, or, since $\sigma_{11} = \sigma_{22} = \sigma_{33} = -\Delta P$,

$$\beta_c = -(\Delta V/\Delta P)/V = -(\epsilon_{11} + \epsilon_{22} + \epsilon_{33})/\Delta P = \textstyle\sum_{i,j=1,3} S_{ij} \tag{25}$$

Electrostatics and Polar Bond Energetics

The treatment of electrostatics and polarity utilized in our methodology requires some special comments. We have advocated representing electrostatic and polar effects via bond-centered dipoles and polarizability centers.[13] The dipoles can thus interact with each other via mutual induction. Since this is a microscopic calculation of the induced polarization and internal field, no assumption about an "effective" macroscopic dielectric constant mediating the interaction between distant dipoles is required.

The method has been applied to isolated molecules[13–15] and more recently to the calculation of the high-frequency dielectric constant or refractive index of polymer crystals.[16] In the latter case, the utilization of the lattice periodicity and the evaluation of the resulting lattice sums in calculating the internal field was discussed and a procedure for it developed. This procedure for determining the internal field is followed here and does not need great elaboration. However, in the previous work the response to an external field only was considered and no treatment of the electrostatic energy of interaction between polar bonds was given. The opportunity is taken here to describe evaluation of the electrostatic energy contribution to the crystal energy on the basis of the mutual induction model.

In the case of an applied static field, $\mathbf{E}^0$, with components E^0_x, E^0_y, E^0_z it was shown previously[16] (eq 11, of ref 16) that the internal field component, $E_p(m)$ in the direction, $p = x, y, z$ at bond m, is given by

$$E_p(m) = E^0{}_j\delta_{i,p} + 4\pi V^{-1}\textstyle\sum_k\sum_l\sum_q L_{p,l}(m,k)\alpha_{l,q}(k)E_q(k) \tag{26}$$

where V is the unit cell volume, $E_q(k)$ is the $q = x, y, z$ component of the field at a another bond, k, and $\alpha_{l,q}(k)$ is the l, $q = x, y, z$ component of the bond polarizability tensor at bond k. The summation over k is over the bonds in one cell. The Lorentz tensor, $L_{p,l}(m,k)$ is evaluated by the methods described by Colpa.[17,18] In the extension considered here, where there is no applied field $E^0{}_j$ but where there is a permanent dipole moment, $\mu^0(k)$, located at each polarizability center, each term $\sum_q\alpha_{l,a}(k)E_q(k)$ is replaced by $\mu^0{}_l(k) + \sum_q\alpha_{l,q}(k)E_q(k)$. This follows because a total moment is the sum of the induced plus permanent. Thus, the internal field in the absence of an external field is

$$E_p(m) = 4\pi V^{-1}\textstyle\sum_k\sum_l\sum_q L_{p,l}(m,k)\alpha_{l,q}(k)E_q(k) + 4\pi V^{-1}\sum_k\sum_l L_{p,l}(m,k)\mu^0{}_l(k) \tag{27}$$

where k is summed over the bonds in a cell and $p, q = x, y, z$. Equation 27 with m varying over the bonds in a cell forms a complete set of linear algebraic equations for the field components, $E_p(m)$, which may be solved simultaneously. With the internal field, $E_p(m)$, now known the electrostatic energy of the lattice may now be calculated. This is computed as

$$U_{\mathrm{ES}} = -\tfrac{1}{2}\textstyle\sum_m\sum_p\mu^0{}_p(m)E_p(m) \tag{28}$$

This expression results from the conceptual process of placing real charges by charging all the bonds uniformly by $\mu^0{}_p(m)\,d\lambda$ from $\lambda = 0$–1, with the field responding in proportion to λ. Notice that only the permanent moment, μ^0, appears in the energy expression and not the total moment, permanent and induced.

Because of the cooperative nature of the interactions between the induced moments as expressed in eq 27, the mutual induction model does not lend itself to direct inclusion of the electostatic energy, eq 28, as part of the total energy in the energy minimization process. We have circumvented this difficulty in previous work[13–15] by the following method. The electrostatic dipole energy can make a significant contribution to the total energy and it is important to include it on the basis of a physically realistic model. However, its role in determining geometry is relatively minor. The electrostatic forces are "soft" in competition with the "harder" intramolecular valence bond stretching, bending, and twisting forces and with the intermolecular nonbonded forces. The geometry of conformation and packing is largely determined by these nonelectrostatic forces. Thus we simulate the electrical forces during minimization by atom-centered fixed charges but calculate the electrostatic contribution to the total energy after minimization using the mutual induction model. The fixed charges are parameterized, as are the mutual induction model parameters, to fit dipole moment data on model compounds.

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