Structure and Properties of Polymeric Glasses by Energy Minimization

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ABSTRACT: A method is described for using molecular mechanics in determining the structure of minimum energy and the elastic constants of a polymeric glass. The periodic box dimensions are allowed to participate in the minimization. Hence, the volume change from the starting state, which is presumed to be a liquid, and the inter- and intramolecular rearrangements accompanying the densification can be addressed. The mechanical elastic properties associated with the compliance constants are determined also. The latter are calculated for infinitesimal deformation directly from the second derivatives associated with the converged molecular geometry. Calculation of finite deformations is considered also.

Introduction

As more or less rigid structural materials, both the crystalline and glassy states of polymers are important. Molecular mechanics has proven effective in computing the structures and a variety of properties of polymeric crystals.[1-3] There is also great interest in atomistic simulations of polymeric amorphous glasses. Since a glass implies vitrification from the liquid state, there are two aspects to this endeavor. One is the simulation of the preexisting liquid, and the other is the generation of the glass from it. Molecular dynamics (MD), the direct integration of the classical equations of motion, has been used for both aspects.[4-6] That is, the temperature of a material that is liquid over the time scale of a simulation is lowered to where the materials appear to be glassy over a similar time scale. Molecular mechanics, which implies the invocation of energy minimization alone without explicit temperature inclusion, has been used to study glasses that are prepared from a state that has correct intramolecular chain statistics but is intermolecularly poorly packed.[7-9] In the present work we address another circumstance, one in which the liquid structure is presumed to have been prepared by a realistic simulation, either by MD or by Monte Carlo methods.[10] Then the structural and property changes on vitrification are studied by application of molecular mechanics, i.e., energy minimization. In doing so, it is very valuable to allow volume changes to take place. Densification is one of the central features of glass formation, and the molecular level rearrangements accompanying it are of considerable interest. Thus, we have formulated the minimization method so that the system dimensions participate simultaneously with atom coordinate displacements.

The mechanical properties of the glass are of interest as well. The molecular mechanics energy function on convergence to the minimized structure contains the information necessary for the determination of the elastic or compliance constants. In the present instance we determine the latter for infinitesimal deformation directly from the quadratic energy function expansion by eliminating the atom displacements.

The Energy Function

The energy minimization is carried out with the usual periodic boundary conditions. That is, a chain is considered to have its start at an end chain atom that lies in the central box. When succeeding atoms in that chain fall outside the box, they reenter it by virtue of a translation across the box. The interaction between a selected chain atom in the box and any other atom is based on the distance between the selected atom and the nearest periodic image of the second one. The coordinates of the set of *connected* atoms that comprise a single chain and start in the central box are the "unwrapped" coordinates[11] of the chain.

The array of periodic boxes is assumed to be orthorhombic and therefore specified by three box edge dimensions, a–c. Consideration of a general triclinic system with angles α, β, and γ while desirable does not seem to warrant the complication. The simulated systems are hopefully large enough to be effectively isotropic, and separate a–c variations allow the determination of volume changes as well as the tensile moduli and Poisson's ratios. The shear moduli can be determined by invoking isotropy.

The energy is considered to be a sum of two terms. One is the intramolecular energy and is a function of the valence coordinates and the intramolecular nonbonded distances (or Coulombic charge interaction distances). The other is the intermolecular nonbonded energy. The valence coordinates are bond distances, R_{ij}, valence angles, θ_{ijk}, and torsional angles, ϕ_{ijkl}. Thus, the total valence interaction energy, U_{intra}, is

$$U_{\text{intra}} = \sum_{R_{ij}} u_{\text{R}}(R_{ij}) + \sum_{\theta_{ijk}} u_{\theta}(\theta_{ijk}) + \sum_{\phi_{ijkl}} u_{\phi}(\phi_{ijkl}) + \sum_{R_{ij}} u_{\text{nb}}(R_{ij}) \quad (1)$$

and the sums are over the bond stretching, valence angle bending, torsions, and intramolecular nonbonded interactions present. The total intermolecular energy, U_{inter}, is a function only of intermolecular $R_{i'j'}$ nonbonded (or Coulombic) distances

$$U_{\text{inter}} = \sum_{R_{i'j'}} u_{\text{nb}}(R_{i'j'}) \quad (2)$$

The introduction of the box dimensions as a variable in the energy function comes through the application of the periodic boundary conditions. Because the intramolecular valence coordinate energy is "hard" compared to the relatively "soft" intermolecular nonbonded energy, the application of periodic boundary conditions has to be carefully considered. In the usual methodology the conformational energy is transformed to Cartesian coordinates by an expansion of the valence coordinates in the latter basis. If the periodic boundary conditions are applied directly to the Cartesian coordinates, the valence *coor-*

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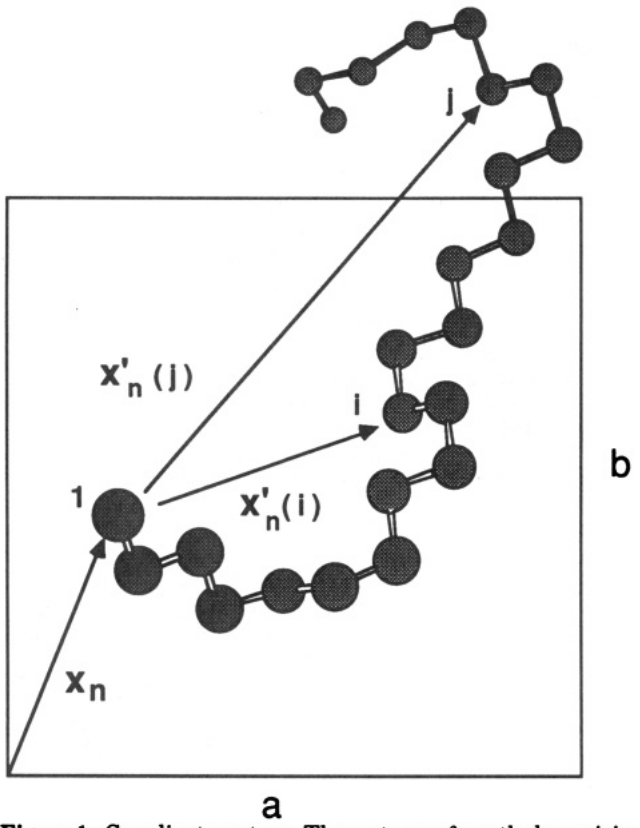

Figure 1. Coordinate system. The vectors $\mathbf{x}_n$ from the box origin to the first atom of each chain, n, define the chain location. The rest of the chain atom positions (i) in chain n are defined relative to the chain origin as "unwrapped" coordinates, $\mathbf{x}'_n(i)$, the connected progression of atoms for the entire chain.

dinate terms from pairs spanning a boundary give rise to large derivatives that can cause numerical instabilities. It is found that by the proper choice of independent variables this problem can be avoided.

The origin of each chain is considered to be in the central box, with $\mathbf{x}_n$ being the vector from the origin to atom number 1 of the nth chain (Figure 1). Then the coordinates of the rest of the atoms i for the nth chain are the *unwrapped coordinates relative to origin of the chain* and are designated $\mathbf{x}'_n(i)$; see Figure 1. The chain origins, $\mathbf{x}_n$, and the relative unwrapped atom coordinates, $\mathbf{x}'_n(i)$, along with the box dimensions a–c are taken as the independent variables.

Valence Coordinates. The intramolecular valence-coordinate energy can be formulated entirely in terms of the $\mathbf{x}'_n(i)$ directly. Following Sorensen et al.,[1] let q be a generalized valence coordinate standing for a R_{ij}, θ_{ijk}, or ϕ_{ijkl} coordinate. A specific energy term, $U(q)$, involving this coordinate, q, may be expanded

$$U(q) = U^0 + \partial U/\partial q\, \Delta q + (1/2)\partial^2 U/\partial q^2\, \Delta q^2 + \dots \quad (3)$$

The coordinate q is then transformed to the relative unwrapped Cartesian basis, $\mathbf{x}'_n(i)$. Let

$$\mathbf{D}_1(s) = [\partial q/\partial x'_n(s), \partial q/\partial y'_n(s), \partial q/\partial z'_n(s)]^t, \quad s = i, j, k, \dots \quad (4)$$

be the vector containing the first derivatives of q with respect to the coordinate $\mathbf{x}'_n(s)$. Vectors are considered here to be $(n \times 1)$ column matrices so that the superscript "t" on the square bracket denotes the transpose of the row notation. Let $\mathbf{D}_2(s|s')$ be the 3×3 matrix of second derivatives of q with respect to $x'_n(s)$, $y'_n(s)$, and $z'_n(s)$ and $x'_n(s')$, $y'_n(s')$, and $z'_n(s')$ and let $\Delta\mathbf{x}'_n(s)$ be the vector = $[\Delta x_n(s), \Delta y_n(s), \Delta z_n(s)]^t$. Then

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

Since intramolecular coordinates, $\mathbf{x}'_n$, do not involve the periodic boundary conditions, the transformation derivatives $\mathbf{D}_1(s)$, for s of the types R_{ij}, θ_{ijk}, or ϕ_{ijkl} can be taken from previous exposition for isolated molecule minimization[12] as can formulas for $\mathbf{D}_2(s|s')$ for $s = R_{ij}$. For the θ_{ijk} or ϕ_{ijkl} types $\mathbf{D}_2(s|s')$ can be calculated by numerical differentiation of $\mathbf{D}_1(s)$.

Intermolecular Coordinates. Turning to the nonbonded energies, consider the centers i' and j' for which a nonbonded energy interaction arises. The center i' is associated with atom i in chain n but is *taken to lie in the central box* rather than as an unwrapped center. The center j' is associated with atom j in chain m and is also taken to lie in the central box. Let $\mathbf{x}(i')$ and $\mathbf{x}(j')$ be the position vectors of i' and j' relative to the central box origin. Let $\mathbf{T}(i)$ be a translation vector

$$\mathbf{T}(i) = [\delta_x(i)\, a, \delta_y(i)\, b, \delta_z(i)\, c]^t \quad (6)$$

such that it brings the unwrapped coordinate image of i into the central box or

$$\mathbf{x}(i') = \mathbf{x}'_n(i) + \mathbf{x}_n + \mathbf{T}(i) \quad (7)$$

where $\delta_x(i)$, $\delta_y(i)$, and $\delta_z(i)$ thus take on the appropriate values among 0 and ± 1 to accomplish the shift for a box of dimensions a–c. Similarly

$$\mathbf{x}(j') = \mathbf{x}'_m(j) + \mathbf{x}_m + \mathbf{T}(j) \quad (8)$$

where

$$\mathbf{T}(j) = [\delta_x(j)\, a, \delta_y(j)\, b, \delta_z(j)\, c]^t \quad (9)$$

the values of $\delta_x(j)$, $\delta_y(j)$, and $\delta_z(j)$ are those required to place j' in the central box. Let $\mathbf{R}_{i'j'}$ be the vector joining i' and j' but with the minimum distance image convention so that it expresses the desired nonbonded interaction distance. Let $\mathbf{T}(i',j')$ be the translation vector that brings i' and j' into the minimum image distance or

$$\mathbf{T}(i',j') = [\delta_x(i'j')\, a, \delta_y(i'j')\, b, \delta_z(i'j')\, c]^t \quad (10)$$

where $\delta_x(i'j')$, $\delta_y(i'j')$, and $\delta_z(i'j')$ are the required translation integers. Then the vector $\mathbf{R}_{i'j'}$ may be expressed in terms of the independent variable set as

$$\mathbf{R}_{i'j'} = \mathbf{x}(j') - \mathbf{x}(i') + \mathbf{T}(i',j') = \mathbf{x}'_m(j) - \mathbf{x}'_n(i) + \mathbf{x}_m - \mathbf{x}_n + \mathbf{T} \quad (11)$$

where

$$\begin{aligned}\mathbf{T} &= \mathbf{T}(i',j') + \mathbf{T}(j) - \mathbf{T}(i) \\ &= [(\delta_x(i'j') + \delta_x(j) - \delta_x(i))\, a, (\delta_y(i'j') + \\ &\qquad \delta_y(j) - \delta_y(i))\, b, (\delta_z(i'j') + \delta_z(j) - \delta_z(i))\, c]^t \quad (12)\end{aligned}$$

In the above equation, the translation integers $\delta_x(i)$, $\delta_y(i)$, and $\delta_z(i)$ and $\delta_x(j)$, $\delta_y(j)$, and $\delta_z(j)$ exist for each atom coordinate independently of the pair being considered. Thus only $\delta_x(i'j')$, $\delta_y(i'j')$, and $\delta_z(i'j')$ need be computed for a specific i',j' pair, and standard algorithms[13] for the nearest image location can be used.

The nonbonded energy function, $U(R_{i'j'})$, associated with i',j' can be expanded as in eq 5 by the identification $q = R_{i'j'}$. Letting $\mathbf{l} = [a, b, c]^t$, a vector containing the three box dimensions, and $\Delta l = [\Delta a, \Delta b, \Delta c]^t$, then the following

expansion of $\Delta q = \Delta R_{i'j'}$ through second order can be carried out

$$\Delta R_{i'j'} = \sum_{(p,s)} \mathbf{D}_1(p,s)\,\Delta\mathbf{x'}_p(s) + \sum_{(p)} \mathbf{D}_1(p)\,\Delta\mathbf{x}_p + \mathbf{D}_1(l)\,\Delta\mathbf{l} + (1/2)\sum_{(p,s),(p',s')} \Delta\mathbf{x'}_p(s)^t\,\mathbf{D}_2(p,s|p',s')\,\Delta\mathbf{x'}_{p'}(s') + (1/2)\sum_{(p),(p')} \Delta\mathbf{x}_p{}^t\mathbf{D}_2(p|p')\Delta\mathbf{x}_{p'} + \sum_{(p,s),(p')} \Delta\mathbf{x'}_p(s)^t\,\mathbf{D}_2(p,s|p')\,\Delta\mathbf{x}_{p'} + \sum_{(p,s)} \Delta\mathbf{x'}_p(s)^t\,\mathbf{D}_2(p,s|l)\,\Delta\mathbf{l} + \sum_{(p)} \Delta\mathbf{x}_p{}^t\mathbf{D}_2(p|l)\,\Delta\mathbf{l} + (1/2)\Delta\mathbf{l}^t\mathbf{D}_2(l|l)\,\Delta\mathbf{l} + \ldots \quad (13)$$

where $\mathbf{D}_1(p,s)$ is the vector of first derivatives of R with respect to $x'_p(s)$, $y'_p(s)$, and $z'_p(s)$, and (p,s) in the sum can take on the values (n,i) or (m,j); $\mathbf{D}_1(p)$ is the vector of first derivatives of R with respect to x_p, y_p, and z_p, and (p) in the sum can take on the values n or m; $\mathbf{D}_1(l)$ is the vector of first derivatives with respect to a–c; $\mathbf{D}_2(p,s|p',s')$ is the 3×3 matrix of second derivatives of R with respect to $x'_p(s)$, $y'_p(s)$, and $z'_p(s)$ and to $x'_{p'}(s')$, $y'_{p'}(s')$, and $z'_{p'}(s')$, and $(p,s),(p',s')$ in the sum can each take on the values (n,i) or (m,j); $\mathbf{D}_2(p|p')$ is the 3×3 second derivative matrix with respect to x_p, y_p, and z_p and to $x_{p'}$, $y_{p'}$, and $z_{p'}$, and $(p),(p')$ in the sum can each take on the values n or m; the remaining 3×3 second derivative matrices have meanings consistent with the preceding.

The formulas for the transformation derivatives $\mathbf{D}_1$ and $\mathbf{D}_2$, which include lattice translations on a–c, have been previously considered by Sorensen.[14]

Total Energy. Substitution of the Δq expansions of eq 5 for the intramolecular valence coordinates and eq 13 for the nonbonded terms into their respective appropriate expanded potential functions as represented by eq 3 and accumulating all such terms for the total energy result in a second-order expansion of the total energy in the chosen independent variables, i.e., the set of chain origin displacements, $\Delta\mathbf{x}_n$, and relative unwrapped chain atom displacements, $\Delta\mathbf{x'}_n(i)$, for $n = 1$, N_{chains}, and $i = 2$, $N_{\text{atoms/chain}}$, and the box size displacements, $\Delta\mathbf{l}$. If $\mathbf{P}$ is a parameter vector containing these independent variables, then

$$\Delta\mathbf{P} = [\Delta\mathbf{x}_1, \ldots\Delta\mathbf{x}_n\ldots, \Delta\mathbf{x}_{N_{\text{chains}}}, \mathbf{x'}_1(2), \ldots\Delta\mathbf{x'}_n(i)\ldots, \Delta\mathbf{x'}_{N_{\text{chains}}}(N_{\text{atoms/chain}}), \Delta a, \Delta b, \Delta c]^t \quad (14)$$

The total energy may be expressed as

$$U = U^0 + \mathbf{A}^t\Delta\mathbf{P} + (1/2)\Delta\mathbf{P}^t\mathbf{C}\Delta\mathbf{P} + \ldots \quad (15)$$

where all of the first-order terms are accumulated into a $(N_{\text{chains}} \times N_{\text{atoms/chain}} + 3)$ vector, $\mathbf{A}$, and the second-order ones into a $(N_{\text{chains}} \times N_{\text{atoms/chain}} + 3) \times (N_{\text{chains}} \times N_{\text{atoms/chain}} + 3)$ matrix, $\mathbf{C}$.

In energy minimization, eq 15 can be used directly via Newton–Raphson methods. That is, differentiation with respect to the parameters $\Delta\mathbf{P}$ leads to a set of linear equations for the displacements

$$\mathbf{C}\Delta\mathbf{P} = -\mathbf{A} \quad (16)$$

that can be iteratively solved until the gradient $\mathbf{A}$ vanishes. Alternatively, it can be truncated at the linear term, $U = U^0 + \mathbf{A}^t\Delta\mathbf{P} + \ldots$, and used as the basis for gradient minimization methods. The Hessian matrix $\mathbf{C}$ is still useful, however, in that instance. On convergence, it can be calculated for determining the elastic or compliance constants as discussed below.

Energy Minimization

Although the primary purpose of the present paper is to outline methodology, it is appropriate to present some observations we have made regarding computations using several minimization methods. Methods can be classified as "first order" when only the gradient, $\mathbf{A}$, in eq 15 is used and "second order" or Newton–Raphson when the Hessian, $\mathbf{C}$, is used as in eq 16. There are also "quasi-Newton" methods where the inverse of $\mathbf{C}$ is approximated numerically from gradient information as the minimization proceeds. In the present work we have compared, via computations on a system of appropriate characteristics, the conjugate gradient version[15] of first-order methods, the Newton–Raphson second-order method, as developed here, and the quasi-Newton method.[16]

The system chosen is the same one as for which detailed simulation results are reported separately.[17] It contains 32 chains of 24 atom centers each or a total of $32 \times 24 \times 3 + 3 = 2307$ variables. It is necessary to constrain translation of the system as a whole by fixing one of the chain origin coordinates, so that there are actually 2304 degrees of freedom. For the Newton–Raphson method, eq 16 leads therefore to a set of 2304×2304 linear equations. The computation time for direct solution of $N \times N$ linear equations in the second-order method increases as $O(N^3)$ whereas gradient methods are effectively $O(N^2)$. The second-order method generally requires far fewer iterations to reach the minimum. For smaller systems, the trade-off favors fewer iterations and the second-order method is invariably faster. Thus the question is where the crossover occurs for the advantage of fewer iterations being outweighed by the computation time of a single iteration. For a 2304×2304 system, tradition would indicate that the crossover had already occurred. Further a linear equation system of this size could well have memory storage problems. However, the advent of large memory vector processor machines alters the situation significantly. The linear equation solution, unlike much of the overhead in gradient and Hessian determination, is *highly* vectorizable and usually has highly optimized machine-specific routines available. Thus the question of method efficiency would appear to be open. In the present work it was found that the above considerations were greatly complicated by another factor and that was the way in which the methods responded to inclusion of volume as a variable.

In general, it was found that the Newton–Raphson method converged well. It was implemented in nearly straightforward fashion based on iteratively solving eq 16. A departure was included that altered the updates, $\Delta\mathbf{P}$, found from the linear equation solution to the one, $\Delta\mathbf{P}'$, actually used in recalculating $\mathbf{A}$ and $\mathbf{C}$, via the relation

$$\Delta\mathbf{P}' = \Delta\mathbf{P}/(1 + D\sigma) \quad (17)$$

where σ is the root-mean-square deviation of the parameter updates, $\sigma = (\sum_k \Delta P_k{}^2/n)^{1/2}$, and D is a suitably chosen constant. The $D\sigma$ term mitigates toward large parameter excursions that the Newton method is prone to at the start of minimization but has negligible effect near convergence.

Some results are shown in Figure 2 for the energy and Figure 3 for the volume. The effect of two values of the damping parameter, $D = 5$ and 10, in eq 17 is illustrated. After an initial period of uncertainty, which is due to the invocation of the $D\sigma$ term through eq 17 and which we have found is typical of the method even in isolated molecule minimization, the system tracks to minimum energy well. It is apparent that the value chosen for "D"

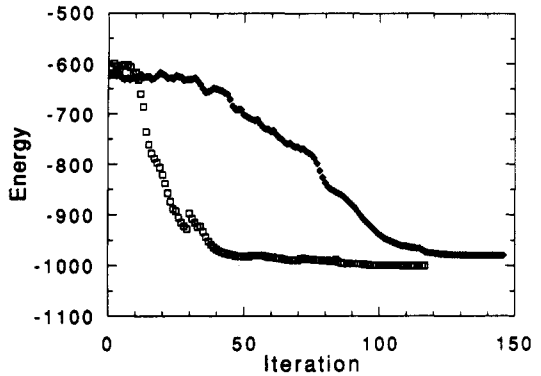

Figure 2. System energy [(kJ/mol)/periodic box] versus iteration number in a Newton–Raphson minimization where the box dimensions participate along with the atom coordinates in optimization. The two curves are for different values of the damping parameter D, eq 17: (□) $D = 5$, (◆) $D = 10$.

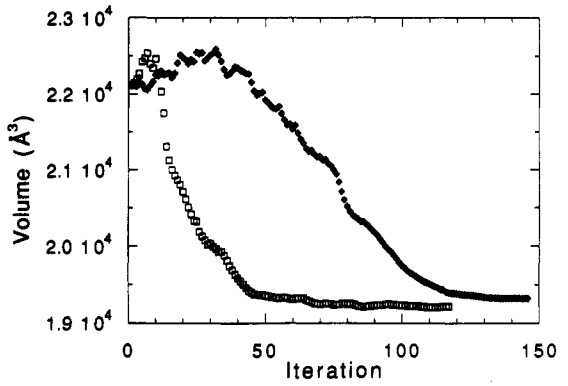

Figure 3. System volume versus iteration number in the Newton–Raphson minimization of Figure 2 where the box dimensions participate along with the atom coordinates in optimization.

is important as the convergence is several times more rapid for $D = 5$ even though an upward energy step occurs. For smaller values of D the energy versus iteration becomes rather erratic with more up steps.

Most importantly the above Newton–Raphson minimization is under the condition of box dimensions and therefore volume participation. This participation makes little difference in the energy convergence, and the volume converges well also (Figure 3). In contrast, in the conjugate gradient method, it was found that convergence was difficult or impossible when box dimensions participated directly in the gradient. To obtain good convergence, it was necessary to constrain box dimensions and minimize at fixed volume. In principle, the optimum volume could then be found by optimizing atom coordinates at a series of box volumes. However, at each step of the box size variation, the atom coordinates must be rescaled. We effected this by an affine movement of all atom centers. The number of fixed box size atom coordinate minimizations must be limited if an efficient method is to result. Hence, the magnitude of the box size steps must be fairly large. This means the atom center rescaling is a significant perturbation. The reminimization after repositioning particle coordinates resulted in considerable noise in the energy versus box size curve near the minimum. The noise could probably be reduced by very small box size steps, but this greatly increases the overall computation time. These considerations bias the overall optimization in favor of the second-order Newton technique as the latter does not require explicit particle rescaling with box size or, rather, accomplishes it alongside and simultaneously with the atom displacements arising from the interparticle forces. Some results are summarized in Table I.

Table I
Computation Time (s) for Conjugate Gradient and Newton–Raphson Minimizations[a]

conjugate gradients:[b] convergence at one fixed volume	Newton–Raphson[c]			
	Hessian compute	linear equation solution	per iteration subtotal	convergence with variable volume total
400	5	83	88	4400

[a] CPU times for indicated computations on a system of 768 atom centers and 2304 degrees of freedom, using the Utah Supercomputing Institute IBM 3090-600S computer. The linear equation solution used vectorized ESSL library. [b] Typical time at one fixed volume. [c] Periodic box a–c dimensions participating along with atom coordinates; 50 iterations were assumed (see Figures 2 and 3).

The quasi-Newton method[16] was found to have many of the same problems with respect to the volume variations as did the conjugate gradient method. That is, with variable volume it had trouble converging to a stable volume.

Elastic Constants

After energy minimization, the total energy, U, eq 15, is stationary with respect to the parameters **P**, and the linear term **A** vanishes. The Hessian matrix, **C**, contains the second derivatives of the energy with respect to the parameters. The elastic constants are the second derivatives of the energy (per unit volume) with respect to the box strains, $\Delta a/a_0$, $\Delta b/b_0$, and $\Delta c/c_0$. However, the energy function also contains the atom coordinates, and they must be eliminated to obtain the energy as a function of Δa, Δb, and Δc alone. This is accomplished through the condition that the atoms remain at minimum energy positions under box distortions. The formalism for carrying this out for the elastic constants has already been presented.[1] It is also useful to compute the compliance matrix. The latter is more directly connected with the engineering constants of interest such as the tensile modulus and Poisson's ratio. Obviously the elastic constant matrix can be inverted to find the compliance matrix. However, the latter can also be found directly from the energy function by eliminating the atom coordinates. We present the formalism for that here.

Let the parameter vector, eq 14, be numbered so that ΔP_k is an element that is one of the atom coordinates, either a chain origin or a relative unwrapped atom coordinate, and let the remaining elements be written explicitly as the box size displacements Δa, Δb, and Δc. Then derivatives of the total energy, eq 15, with respect to the p_k and Δa, Δb, and Δc lead to a set of linear equations

$$\partial U/\partial a = \sum_k C_{a,k}\Delta P_k + C_{a,a}\Delta a + C_{a,b}\Delta b + C_{a,c}\Delta c$$

$$\partial U/\partial b = \sum_k C_{b,k}\Delta P_k + C_{b,a}\Delta a + C_{b,b}\Delta b + C_{b,c}\Delta c$$

$$\partial U/\partial c = \sum_k C_{c,k}\Delta P_k + C_{c,a}\Delta a + C_{c,b}\Delta b + C_{c,c}\Delta c$$

$$\partial U/\partial p_{k'} = \sum_k C_{k',k}\Delta P_k + C_{k',a}\Delta a + C_{k',b}\Delta b + C_{k',c}\Delta c \quad (18)$$

The derivative $\partial U/\partial a$ corresponds to an applied tensile force in the "a" direction. If it is given the value F_a and the other parameters, ΔP_k, Δb, Δc, are allowed to relax to values that give zero forces, i.e., ...$\partial U/\partial p_{k'}$..., $\partial U/\partial b$, $\partial U/$

$\partial c = 0$, then the set of equations can be written as

$$\mathbf{C}\Delta\mathbf{P} = \mathbf{F}_a \tag{19}$$

where $\mathbf{C}$ and $\Delta\mathbf{P}$ are the matrix and full parameter vector of eq 15 and the applied force vector $\mathbf{F}_a = [...0...F_a, 0, 0]^t$ has zeros except for the element for "a". On solving the set of equations, $...\Delta P_k...$, Δa, Δb, and Δc are found. The compliance matrix element S_{aa} is therefore $=(\Delta a/a_0)/(F_a/b_0c_0) = V_0\Delta a/(F_a a_0^2)$ and $S_{a,b} = V_0\Delta b/(F_a a_0 b_0)$ and $S_{a,c} = V_0\Delta c/(F_a a_0 c_0)$, where V_0 is the box volume $= a_0b_0c_0$. Repeating the process for $\mathbf{F}_b$, a force applied in the "b" direction and for $\mathbf{F}_c$ in the "c" direction gives $S_{b,a}$, $S_{b,b}$, and $S_{b,c}$ and $S_{c,a}$, $S_{c,b}$, and $S_{c,c}$. The tensile moduli E are given by $E_a = S_{aa}^{-1}$, $E_b = S_{bb}^{-1}$, and $E_c = S_{cc}^{-1}$ and the Poisson's ratios by $\nu_{ba} = -S_{ab}/S_{aa}$, $\nu_{ca} = -S_{ac}/S_{aa}$, and $\nu_{bc} = -S_{bc}/S_{cc}$, etc. Since shears were not explicitly considered, the shear moduli are found from the condition of isotropy that is expected to result from simulation of a system large enough to represent an amorphous glass. That is, the shear modulus, G, is given in terms of the isotropic tensile modulus and Poisson's ratio by $G = (1/2)E/(1 + \nu)$.

Calculations of Finite Deformation

In the calculation of the elastic or compliance constants, it is not necessary to impose real deformations; the results follow from the energy function as a quadratic in the atom and box dimension variables. However, the formalism used in the compliance calculations can be used for constant stress calculations of finite deformations. The system of equations, eq 18 or 19, is actually the same as that used in minimum location, cf. eq 16. In the latter event, *all* of the elements of the force vector $\mathbf{F}$ in eq 19 are set to zero, or $\mathbf{F} = 0$. Solution of eq 19 with nonzero elements for a–c in $\mathbf{F}$ corresponds to the effect of an applied force. In the case of true harmonic potentials, there is no difference between finite and infinitesimal deformations. In the actual case of anharmonic potentials, with nonzero elements in $\mathbf{F}$ in eq 19 to represent the applied stress, when the parameters are updated from the solution $\mathbf{P} = \mathbf{P}_0 + \Delta\mathbf{P}$, the updated Hessian, $\mathbf{C}$, will change. The process can be continued iteratively with $\mathbf{A} + \mathbf{C}\Delta\mathbf{P} = \mathbf{F}$ rather than $\mathbf{A} + \mathbf{C}\Delta\mathbf{P} = 0$, as in ordinary minimization, eq 16. Thus iterative solution of

$$\mathbf{C}\Delta\mathbf{P} = -\mathbf{A} + \mathbf{F} \tag{20}$$

for $\Delta\mathbf{P}$ until $-\mathbf{A} + \mathbf{F}$ and thus $\Delta\mathbf{P}$ have approached zero leads to finding the atom positions and box dimensions under the condition of constant $\mathbf{F}$.

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