THE ATOMIC STRAIN TENSOR

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INTRODUCTION

Computer modelling provides coordinates of all atoms of model systems at any time. One fundamental property of interest is how the local atomic structure changes in response to applied global forces. While atomic displacements show the distance and direction of the movement for each atom, it gives no information on the change in position of an atom with respect to its neighbors. In order to study this local rearrangement in a thermodynamically meaningful way, we must define an "atomic strain tensor".

FOCUS OF STUDY

This work is concerned with studying the change in structure of a static, atomistic model of polypropylene, developed by Theodorou and Suter[1,2]. The polymer is modelled as a single chain of atoms, with fixed bond lengths and bond angles, packed into a periodic parallelpiped, initially an 18.15 Å cube (total number of atoms = 455, degree of polymerization = 76, density = 0.892 g/cm³). Molecular movement can occur only by rotation around the skeletal C-C bonds. Van der Waals interaction is modelled by the Lenard-Jones potential energy function; backbone skeletal rotation is modelled by a three-fold rotational potential energy barrier. An initial guess structure is generated by a modified rotational isomeric state (RIS) theory; the total energy of the system as a function of the bond rotation angles is then minimized using analytical derivatives.

Starting with a structure that is at a minimum energy, a small strain step is imposed on the periodic box continuation condition, which changes the position of the atoms in the parent chain to the positions of the atoms in the image chains. The energy of the system is then re-minimized, causing the polymer to seek a new conformation. Repeatedly straining the box and then minimizing the energy simulates large deformations, at an arbitrarily slow strain rate. The local environment of each atom was characterized by finding the Voronoi polyhedra, and the Delauney tetrahedra (DT).[3]

BACKGROUND

In the macroscopic, continuum sense, strain is defined by the change in length and orientation of an infinitesimal line segment, and is a function of position in the body. On the atomic level, only the change in the relative position of the neighboring atoms is important; in interstitial regions, the strain is constant. The empty regions inside the Delauney tetrahedra define a unique form of tessellation of the entire system. Consider the region in space between the atoms in a Delaunay tetrahedron shown in Figure 1. Take atom 0 to be the atom of interest, and place its original position at the origin. The displacement of each atom is si, where i is the atom number. The relative displacement u_i of atom i is then $s_i - s_0$. We define the deformation gradient tensor $\underline{D}$ inside a DT by interpolating the relative displacements u of

the four corner atoms of a DT, with respect to the three directions of the cartesian coordinate system, **x**:

$$\underline{D} = \frac{\partial \mathbf{u}}{\partial \mathbf{x}} \quad .$$

The displacement of positions so defined is piecewise continuous along the faces and edges of each DT, and the displacement *gradient* inside the DT is constant.

To find the deformation gradient of an atom, it is necessary to identify all the DTs sampled by the Voronoi polyhedron. Symbolically, we find the deformation gradient for atom i, $\underline{D}_i$, by the weighted sum over all DTs that the Voronoi polyhedron intersects:

$$\underline{D}_i = \sum_{j}^{DT's} \kappa_{i,j} \, \underline{D}_j$$

where $\kappa_{i,j}$ is the volume fraction of the Voronoi polyhedron that sits inside the jth DT. The atomic strain tensor is then found from the deformation gradient by subtracting out the rigid-body rotations in the usual way.

THE APPROACH TO THE PROBLEM

We chose to attack the problem using the original structure as the "ground state", and the strained structure is compared to the original. The number of atoms must be conserved between the original and the strained structure. Also required for the original structure is the neighbor list for each atom (atoms are neighbors when they share a face of their Voronoi polyhedron), the volume of the Voronoi polyhedra, and the set of Delaunnay tetrahedra for the structure.

The bulk of the algorithm is to calculate the intersection of the DTs with the Voronoi polyhedra. It can be shown that the center of a sphere that passes through the atoms of a DT define a corner shared by each of the Voronoi polyhedra about the four atoms of the DT. The main difficulty is that the center of the circumscribing sphere does not have to lie within the four planes of the DT, or even a neighboring DT.

Figure 2 is a stereo projection of the Voronoi face between atoms M1 and H3, which are the first and third atoms of a minimized structure (M and H indicate "methyl group" and "hydrogen atom", respectively). The Voronoi face between the atoms is the perpendicular bisector of the thick, bond-like line segment joining the two atoms, and all other features of the figure beside the atoms lie in this face plane. The corners of the face are denoted by the points F1 through F7; note that the face plane does not touch the line segment joining the atoms. The intersection of all DTs with the face plane that have some portion inside the face are shown as dashed lines. A pyramid may be formed by using the Voronoi face enclosed by the corners F1-F7 as the base and atom H3 as the summit, and pyramids so formed tesselate the Voronoi polyhedron. This pyramid may be further divided into sub-pyramids, using the dashed DT intersections as the base and H3 as the summit. Scrutinizing one such sub-pyramid, if the intersecting DT that forms the base happens to contain atom H3 as a member, then all of the volume of the sub-pyramid is inside the DT; fortunately, this is usually the case. If H3 is not a member of the DT, then the sub-pyramid must be further divided into volumes contained by different DTs.

ALGORITHM

I. Initialization. Input {i}, the set of atoms, and {j}, the set of DTs for the structure.

A. For each DT in {j}, find:

1. The position of the center of the sphere that passes through the atoms C_j, which correspond to a corner of a Voronoi polyhedron.

2. The volume fraction of the system Φ_j, and the displacement gradient D_j.

B. Check that $\Sigma \, \Phi_j = 1$ and $\Sigma \, \Phi_j \, \underline{D}_j = \underline{D}_{system}$

C. For each DT {j}, find the DT that contains the circumcenter C_j.

II. Main part of algorithm. For every atom in {i}:

A. Obtain the list of Voronoi face planes {k}.

B. Obtain the corners of the Voronoi faces from {C_j}, and the DTs that contain these corners. The corners must be ordered around the face along a single closed path.

C. For all Voronoi face planes in {k}:

1. Obtain the area of the face A_k and the volume fraction of the pyramid Ω_k formed by using the face as the base and the atom i as the summit.

2. Obtain the list of DTs {m} that intersect the face, and find the area of the face contained by each DT in {m}, α_m. Check that $\Sigma \, \alpha_m = A_k$.

3. For each DT in {m}, find the volume fraction of the sub-pyramid ω_m that has the intersecting area α_m as the base and the atom i as the summit.

4. For each DT in {m},

   a. Check if it has atom i as a member. If so, then add the volume fraction ω_m is the intersecting volume fraction $\kappa_{i,m}$. If not, then

   b. Further sub-divide the sub-pyramid into parts intersected by other DTs, starting at the base. Add the pertinent volume fractions to κ.

5. Add the DTs {m} to the list of DTs {n} sampled by all the faces of atom i.

D. Check that $\Sigma_n \, \kappa_{i,n} = V_i$, where V_i is the volume fraction of the Voronoi polyhedron of atom i. Calculate the atomic deformation gradient $\underline{D}_i = \Sigma_n \, \kappa_{i,n} \, \underline{D}_n$.

III. Finally, check that $\Sigma \, \underline{D}_i \, V_i = \underline{D}_{system}$, and that for all DTs in {j} $\Sigma_i \, \kappa_{i,j} = \Phi_j$.

REFERENCES

(1) Theodorou, D. N., and U. W. Suter, *Macromolecules*, **18**, 1467 (1985).

(2) Theodorou, D. N., and U. W. Suter, *Macromolecules*, **19**, 379, (1986).

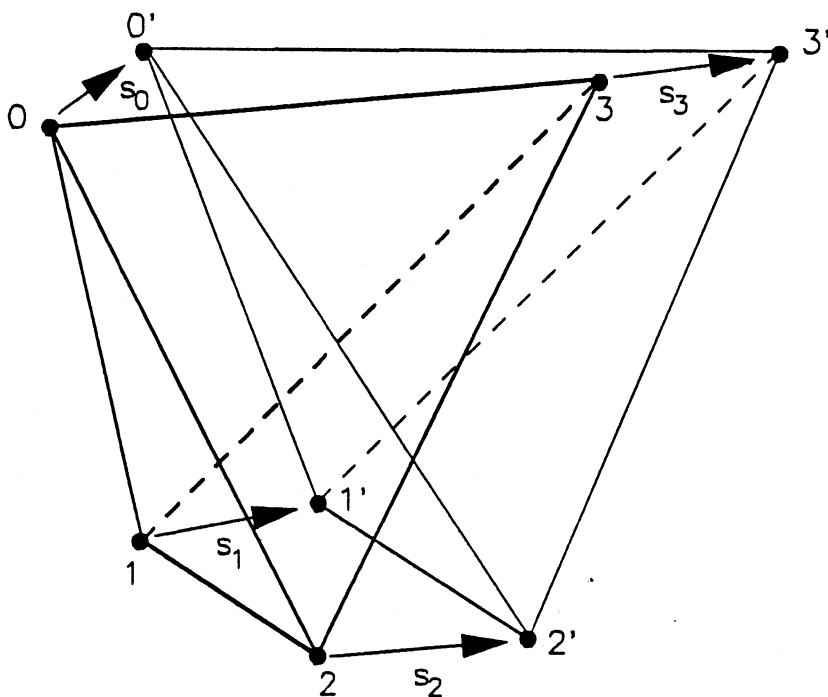(3) Tanemura, M., T. Ogawa and N. Ogita, *J. Comput. Phys.*, **51**, 191, (1983).

Figure 1: Displacement and distortion of a Delaunay tetrahedon.
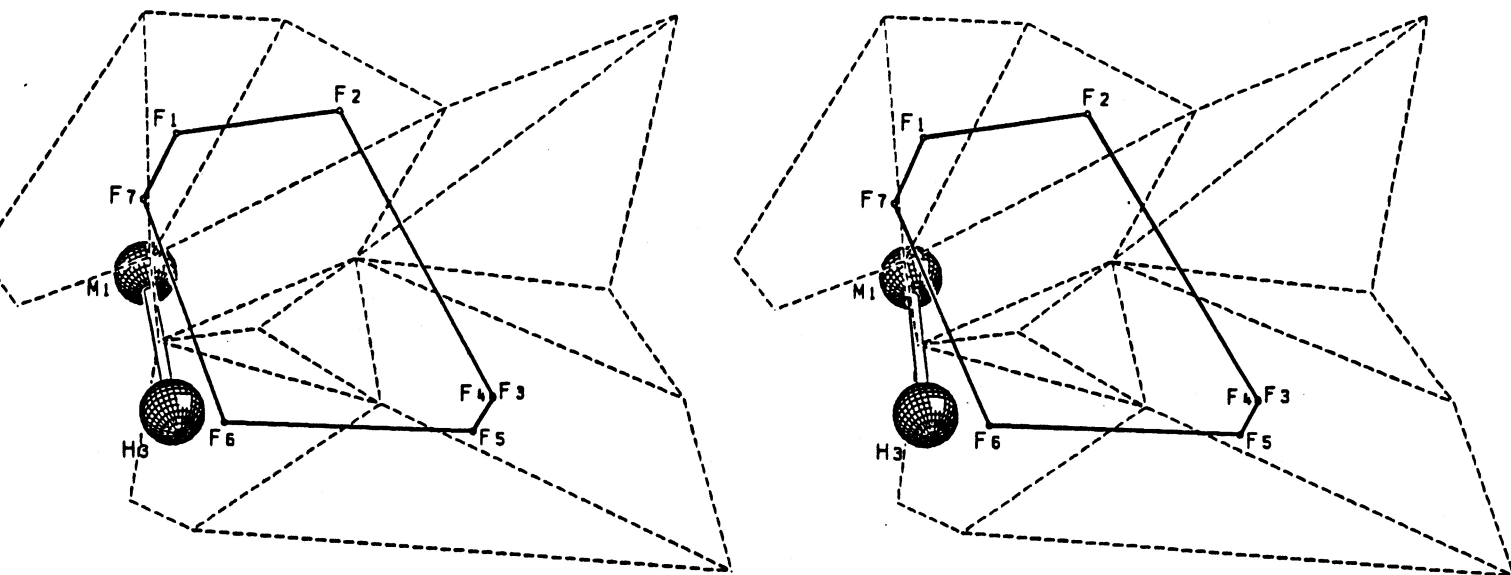

Figure 2: Stereo projection of the Voronoi face between atoms M1 and H3. See text for details.