Voronoi space division of a polymer: Topological effects, free volume, and surface end segregation

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In order to investigate the topological effects of chain molecules, united-atom molecular dynamics simulations of a 500-mer polyethylene linked by 50 hexyl groups (a grafted polymer having 52 ends) are carried out and analyzed in terms of Voronoi space division. We find that the volume of a Voronoi polyhedron for a chain end is larger than that for an internal or junction atom, and that it is the most sensitive to temperature, both of which suggest higher mobility of chain ends. Moreover, chain ends dominantly localize at the surface of the globule: The striking evidence is that while the ratio of surface atoms is only 24% of all atoms, the ratio of ends at the surface is 91% out of all ends. The shape of Voronoi polyhedra for internal atoms is prolate even in the bulk, and near the surface it becomes more prolate. We propose the concept of bonding faces, which play a significant role in the Voronoi space division of covalently bonding polymers. Two bonding faces occupy 38% of the total surface area of a Voronoi polyhedron and determine the prolate shape.

I. INTRODUCTION

Voronoi analysis has been applied to study simple liquids and noncrystalline metallic solids to characterize the distributions of atoms.1-7 It consists of partitioning a space into a set of polyhedra and analyzing their volume and shape. In polymer science, the analysis has been used for bulk8 and isolated9 polymer chains. A fundamental question arises concerning the volume and shape of Voronoi polyhedra: In contrast to simple liquids or metallic glasses, are there any specific features of polymers?: Does chain connectivity have an influence upon the volume and the shape of Voronoi polyhedra? In this article, we show that the existence of bonds definitely affects Voronoi space division.

Here, we deal with a simplified simulational polymer model called the united-atom model, in which an atom represents one of CH3, CH2, and CH groups. Hydrogens are not explicitly modeled as distinct atoms, and an atom signifies one of the united atoms hereafter. A chain is thus represented by united atoms and bonds between neighboring united atoms. In the present study a model chain is a 500-mer polyethylene linked by 50 hexyl groups (-C6H13) per 10 repeating units as side chains (Fig. 1). Notice that in the united-atom scheme, there are three kinds of topologically different atoms with respect to the number of bonds: end atoms with one bond, internal atoms with two bonds, and junction atoms with three bonds. We will show that the number of bonds from an atom has a great influence on the volume of a Voronoi polyhedron and its temperature dependence. Our concern is the space partitioning of the united atoms of three types and the term topological effect here renders the effect of the number of bonds.

The so-called free volume argument relates to the topological effect. More than five decades ago, Fox and Flory10 found that the specific volume and the glass transition temperature (Tg) of polystyrene depend on the molecular weight (Mn) as a linear function of M−1/2n, and they explained that the phenomena are caused by the larger free volume of end groups; the number density of end groups is proportional to M−1/2n. In this direction, Rigby and Roe8 have shown in their simulation of amorphous polymers that the volume of a Voronoi polyhedron containing an end is much larger than that containing an internal atom.

Furthermore, the Voronoi analysis is not only applicable to bulk, but also to surfaces. Soyer et al.9 recently reported a Voronoi analysis of packing geometry of amino acids in folded proteins, and used the method to distinguish the bulk and the surface. We also use the method to distinguish the bulk and the surface of our chain and find that end groups segregate at the surface, implying that the topological effect appears at the surface as well.

Though our model is just an isolated chain in a vacuum, this end segregation effect reminds us of recent studies on surfaces of bulk polymers. The dependence of surface tension upon M−1/2n has been interpreted on one hand by the free volume argument of chain ends,11,12 and on the other hand, by the end segregation effect to reduce conformational en-
II. METHOD

A. Model

The model molecule is a 500-mer polyethylene linked by 50 hexyl groups: \([(-\text{CH}_2\text{CH}_2\text{-})_5(-\text{CH}_2\text{CH}(	ext{C}_6\text{H}_{13})\text{-})(-\text{CH}_2\text{CH}_2\text{-})_5]_{50}\). We choose a simple and typical polymer, polyethylene as a main chain. To gain meaningful statistics, we employ the following energy terms for an arbitrary geometry of molecules. Valence interactions consist of bond stretching \(E_b\), bond angle bending \(E_a\), and dihedral angle torsion \(E_t\) terms. Nonbond interaction is the van der Waals \(E_{\text{vdw}}\) potential. Each term is defined in the following equations:

\[
\begin{align*}
E_b & = \frac{1}{2} K_b (R - R_0)^2, \\
E_a & = \frac{1}{2} K_a (\Theta - \Theta_0)^2, \\
E_t & = \frac{1}{2} V [1 - \cos(n(\phi - \phi_0))], \\
E_{\text{vdw}} & = D_0 \left[ \frac{R_0}{R} \right]^{12} - 2 \left[ \frac{R_0}{R} \right]^6.
\end{align*}
\]

\(K_b\) and \(K_a\) are valence force constants for a single bond and for all angle bends, \(R\) is the bond distance, \(\Theta\) is the angle bend between two bonds, and \(\phi\) is the dihedral angle. \(R_0\), \(\Theta_0\), and \(\phi_0\) give potential minima. \(V\) is the total rotational barrier and \(n=3\) is the periodicity of the potential, that is the number of potential local minima.

The van der Waals interactions between atoms separated by more than three bonds are given according to Lennard-Jones 12-6 potential. The length \(R_0\) is the van der Waals bond length (Å), and the coefficient \(D_0\) is the van der Waals well depth (kcal/mol). For two different kinds of atoms, these values are calculated by \((R_0)_{ij} = 1/2((R_0)_{ii} + (R_0)_{jj})\) and \((D_0)_{ij} = \sqrt{(D_0)_{ii}(D_0)_{jj}}\). Nonbond interactions are handled by the spline switching method in which on–off parameters are defined and nonbond interactions are attenuated smoothly by a spline function between them. In this work, on–off parameters are 10.0 Å and 10.5 Å, respectively; nonbond interactions are considered exactly within 10.0 Å and ignored beyond 10.5 Å.

B. Force field

According to the Dreiding force field (Tables I and II),\(^{29}\) we employ the following energy terms for an arbitrary geometry of molecules. Valence interactions consist of bond stretching \(E_b\), bond angle bending \(E_a\), and dihedral angle torsion \(E_t\) terms. Nonbond interaction is the van der Waals \(E_{\text{vdw}}\) potential. Each term is defined in the following equations:

\[
\begin{align*}
E_b & = \frac{1}{2} K_b (R - R_0)^2, \\
E_a & = \frac{1}{2} K_a (\Theta - \Theta_0)^2, \\
E_t & = \frac{1}{2} V [1 - \cos(n(\phi - \phi_0))], \\
E_{\text{vdw}} & = D_0 \left[ \frac{R_0}{R} \right]^{12} - 2 \left[ \frac{R_0}{R} \right]^6.
\end{align*}
\]

\(K_b\) and \(K_a\) are valence force constants for a single bond and for all angle bends, \(R\) is the bond distance, \(\Theta\) is the angle bend between two bonds, and \(\phi\) is the dihedral angle. \(R_0\), \(\Theta_0\), and \(\phi_0\) give potential minima. \(V\) is the total rotational barrier and \(n=3\) is the periodicity of the potential, that is the number of potential local minima.

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C. Dynamics, initial conditions, and sample preparation

We used a program package CERIUS2 (Accelrys Inc., San Diego, California) in molecular modeling and molecular dynamics simulations. We use the Verlet’s leapfrog algorithm to solve the equations of motion. The molecular dynamics simulations are carried out under constant temperature which is controlled by the Nosé–Hoover thermostat.\(^{30,31}\) The integration time step and the relaxation time of heat bath are 1.0 fs and 0.1 ps, respectively.

At first, we constructed the model whose torsional angles are all-trans conformation. To start the dynamics, velocities are given according to the Maxwell–Boltzmann distribution at a specified temperature (800 K). Only during the first run, we save structures every 2 ps for the first 18 ps calculations, to prepare nine other samples whose coordinates are different for each other. At this stage, these samples are not folded or a globule, and thus they are totally different in shape far from equilibrium. Calculations over ten runs are performed at the temperature from 800 K to 50 K.
TABLE II. Masses and constants used for the van der Waals parameters.

<table>
<thead>
<tr>
<th></th>
<th>Mass (g/mol)</th>
<th>Rg (Å)</th>
<th>D0 (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{33}</td>
<td>15</td>
<td>4.15</td>
<td>0.250</td>
</tr>
<tr>
<td>C_{32}</td>
<td>14</td>
<td>4.07</td>
<td>0.198</td>
</tr>
<tr>
<td>C_{31}</td>
<td>13</td>
<td>3.98</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Simulations are carried out for durations up to 15 ns from 800 K to 50 K with a stepwise lowering of the temperature 50 K every interval of 1 ns; the data of the first 900 ps at each temperature are discarded for equilibration; in the last 100 ps, coordinates at every 10 ps (ten configurations) are used for analyses.

Our average $\langle A(T) \rangle$ of a physical quantity $A(T)$ is evaluated first by taking an average over ten configurations of a single run, and second by taking a further average over the ten starting structures described above. The error bar is estimated by the values of the ten starting structures.

III. STATE OF THE ISOLATED CHAIN

In this section, before embarking upon the Voronoi analysis, we take a look at the shape and the state of the isolated chain at various temperatures. The shape of isolated polymer is intriguing and has been investigated theoretically\textsuperscript{32–35} and numerically for a variety of chains generated by means of Monte Carlo simulations.\textsuperscript{36–40}

Let $X$ be the radius of gyration tensor for each configuration of chains, which is a symmetric matrix with elements defined by

$$X_{\alpha,\beta} = \frac{1}{N} \sum_{i=1}^{N} s_{\alpha i} s_{\beta i}, \quad \alpha,\beta = x,y,z,$$

where $s_{\alpha i}$ and $s_{\beta i}$ are the coordinates of a vector $s_i$ from the center of gravity of the chain to an $i$th atom. Since rotationally invariant quantity is required, the matrix $X$ is diagonalized to yield eigenvalues, $L_1^2$, $L_2^2$, and $L_3^2$, which are moments along the principal axes of the chain,\textsuperscript{32} and then the radius of gyration is expressed as

$$S^2 = \text{tr}X = L_1^2 + L_2^2 + L_3^2.$$  \hspace{1cm} (6)

The asphericity $A$ defined by Rudnick and Gaspari\textsuperscript{33} is given by

$$A = \frac{\|(L_1^2 - L_2^2)^2 + (L_2^2 - L_3^2)^2 + (L_3^2 - L_1^2)^2\|}{2\|(L_1^2 + L_2^2 + L_3^2)^2\|},$$  \hspace{1cm} (7)

where $\| \cdot \|$ denotes an average for a single run. It provides a generalized quantitative measure of the departure from spherical symmetry of the whole shape of a polymer chain. The value of $A$ varies as $0 \leq A \leq 1$: $A = 0$ corresponds to an exact sphere and $A = 1$ represents an extremely aspherical rodlike shape.

We plot $S^2$ and $A$ as functions of temperature in Figs. 2 and 3, respectively. The radius of gyration becomes shorter with decreasing temperature during the process of stepwise cooling run. The tendency is pronounced above 500 K and modest below 450 K. The asphericity decreases from 800 K to 500 K, while it appears to be an approximately constant value 0.016 below 450 K. The increase of the radius of gyration above 500 K corresponds to the deviation from a sphere.

The structure changes into a globule near 500 K. To show that the state in the low-temperature region is globular, we have checked the number distribution function $h(r)$ as a function of their distance from the center of gravity. Figure 4 illustrates an example at 300 K. The data can be fitted up to 15 Å with a squared function, we hence confirm the uniform bulk property. Beyond this bulk region, the function decreases because of the surface (and the asphericity). In the following section, we apply the Voronoi analysis to the low-temperature region where the chain forms a globular structure.

FIG. 2. Squared radius of gyration ($S^2$) against temperature. Error bars come from 10 starting structures. The coarse dashed and the fine dashed lines represent least-squares linear fittings to the data above 500 K and below 450 K, respectively.

FIG. 3. Asphericity ($A$) against temperature. The asphericity at each temperature was averaged over ten configurations. The asphericity decreases upon lowering the temperature from 800 K to 500 K, while from 450 K to 200 K, it is approximately 0.016 indicated by the dashed line.
have modified Tanaka’s algorithm. To distinguish surface atoms from bulk atoms, we use the sufficient information to describe neighborhood associated with the central atom. When an atom is near a surface, surface atoms have fewer neighbors than bulk atoms, or no neighbors. To judge whether bisecting planes form a closed polyhedron or an open structure, we take advantage of the Euler’s relation. The Euler’s relation for an arbitrary polyhedron is expressed as

$$v - e + f = 2,$$

where $v$, $e$, and $f$ are the numbers of vertices, edges, and faces, respectively. If the equation is satisfied for a set of three numbers for an atom, then we calculate the volume. Otherwise, we assume that the region is open, and set the volume of the Voronoi polyhedron infinite.

The procedure for the analysis is as follows: The first step is the construction of a Voronoi polyhedron ($1–5$). The second step is to test whether or not the Euler’s relation is fulfilled ($6$ and $7$). The last step is the calculation of the volume. Details of each procedure are given below.

1. Select atoms $P_i (i=1,2,3,...,M)$ within the sphere of radius $r_0=8 \AA$ centered at a central atom $P_0$. (The radius $r_0$ has been chosen by the economical reason in computation, and we have checked that the choice has no influence on the volume of any polyhedron.)
2. Generate $M$ perpendicularly bisecting planes between $P_0$ and $P_i (i=1,2,3,...,M)$.
3. Select three arbitrary planes out of $M$ bisecting planes, and find an intersection of these planes. The point is a trial vertex of the polyhedron.
4. Check whether the trial vertex is placed inside all $M$ planes, or not. If so, the vertex becomes a valid vertex of the polyhedron. To check, we have used the inner product of normal vector of a bisecting plane and the vector between the trial vertex and an arbitrary point in the bisecting plane.
5. Repeat the procedures (3 and 4) for all combinations of three planes out of $M$, and find all vertices of the Voronoi polyhedron surrounding $P_0$.
6. In practice, for every vertex of the polyhedron, a set of triplets $(j, k, l)$ indicating bisecting planes is assigned. Using the indices, we have computed the numbers of faces and edges of the polyhedron.
7. Check whether or not the Euler’s relation is satisfied. If not, the volume is assumed to be infinite.

Figure 6 displays some examples of Voronoi polyhedra: [Fig. 6(a)] An open polyhedron of $1/V=0$ at the surface of the globule and [Fig. 6(b)] a rodlike polyhedron of $1/V\approx0$ near the surface. In the bulk, [Fig. 6(c)] an end atom, [Fig. 6(d)] an internal atom, and [Fig. 6(e)] a junction atom being more like a sphere are displayed.

### IV. VORONOI ANALYSIS

#### A. Voronoi division

Several algorithms for Voronoi division have been proposed in the literature.$^1$–$^6$ We will demonstrate that the traditional Voronoi analysis serves as a systematic approach to distinguish surface atoms from bulk atoms. To do so, we have modified Tanaka’s algorithm.$^5$

Given the positions of atoms, Voronoi division is uniquely defined as the closer regions of space to be constructed with bisecting planes between neighboring atoms. A two-dimensional analog is illustrated in Fig. 5. When an atom is in a bulk, the atom is surrounded by a convex polyhedron. The volume and the shape of each polyhedron give us the sufficient information to describe neighborhood associated with the central atom. When an atom is near a surface, the volume of the polyhedron is much larger than those of bulk atoms, or the polyhedron may fail to form, because surface atoms have fewer neighbors than bulk atoms, or no neighbors outward.

To judge whether bisecting planes form a closed polyhedron or an open structure, we take advantage of the Euler’s relation. The Euler’s relation for an arbitrary polyhedron is expressed as
above definition are indicated by dark gray. One can notice that the circumference of the globule is occupied by dark gray atoms. Therefore, we think that the definition is reasonable.

For bulk atoms, as is seen in the peak shift in sequential Figs. 8–8, the volume of a polyhedron has clear dependence upon the number of bonds; the volume becomes smaller with increasing number of bonds. The volume of polyhedra for ends is larger than that for internal atoms and junction atoms. From Fig. 8, it is evident that peak III in Fig. 7 is attributed to junction atoms, while the peak in Fig. 8(a) is not clearly seen in the left-hand side envelope of the peak in Fig. 7.

C. Temperature effect on the distribution

The distributions of $1/\nu$ for all atoms at various temperatures are shown in Fig. 10. With increasing temperature, the distribution for bulk atoms becomes broader due to volume fluctuations and the peak shifts to smaller values due to thermal expansions. The bulk atom regions for ends I and for junction atom III exhibit the same tendency as shown in Fig. 11. In the surface atom regions, the temperature effect seems to be little, in contrast to what occurs in the bulk atom regions.

To see the temperature dependence of thermal expansion and volume fluctuations more clearly, assuming the distributions I, II, and III in Figs. 10 and 11 to be Gaussian, we have obtained the mean values $\mu$ and the standard deviations $\sigma$.
through curve fitting. Although envelopes for the smaller \(1/V\) values are almost constant and not the Gaussian distributions, we ignore the envelopes.

The meaning of these two values \(m\) and \(s\) are evident, since when we define

\[
\begin{align*}
\mu &= \left\langle \frac{1}{V} \right\rangle, \\
\sigma^2 &= \left\langle \frac{1}{V^2} \right\rangle - \mu^2,
\end{align*}
\]

\[
\begin{align*}
\bar{V} &= \langle V \rangle, \\
\sigma_v^2 &= \langle V^2 \rangle - \bar{V}^2,
\end{align*}
\]

a brief calculation yields

\[
\begin{align*}
\mu &= \frac{1}{V} + \frac{\sigma_v^2}{V^3} - \frac{1}{\sqrt{V}}, \\
\sigma^2 &= \frac{\sigma_v^2}{V^4} + O \left( \frac{1}{V^5} \right).
\end{align*}
\]

Therefore, we reasonably assume that

\[
\begin{align*}
\mu &\approx \frac{1}{V}, \\
\sigma &\approx \frac{\sigma_v}{\sqrt{V}}, \\
\frac{\sigma}{\mu} &\approx \frac{1}{V}.
\end{align*}
\]

The temperature dependence of \(\mu\) and \(\sigma\) is plotted in Fig. 12. It is evident that the polyhedron volume of each atom and the fluctuations become larger with increasing temperature.

In addition, the dimensionless value \(\mu(T)/\mu(T = 250\,\text{K})\) against temperature is plotted in Fig. 13. Notice that the slope \(-\Delta\mu/(\mu\Delta T)\) corresponds to the thermal expansion coefficient:

\[
\kappa = -\frac{1}{\mu} \left( \frac{\partial(1/V)}{\partial T} \right)_p = -\mu \left( \frac{\delta S}{\delta p} \right)_T.
\]

Based on Fig. 13, we conclude that the Voronoi volume concerning ends exhibits the largest thermal expansion and that for junction atoms shows the smallest thermal expansion.

D. Surface segregation of chain ends

In Fig. 14, end atoms are depicted by dark gray spheres. At the surface of the globule, we can see a number of chain ends and the side chain ends. In fact, from 50 K to 450 K, surface atoms are 24% of all atoms, while ends at the surface are 91% of all ends. The temperature dependence has been found to be quite small, because in the cooling run the vast change of conformations does not happen. The data were averaged over ten samples.

Two reasons have been argued in literature for why ends favor surfaces. On the one hand, a purely entropic reason has been argued that ends do not suffer from the loss of conformational entropy due to the imposed reflection at a surface,\(^{13,14}\) therefore the segregation arises [Fig. 15(a)]. One the other hand, there is a free volume contribution to reduce...
the surface free energy, namely, entropy gain by using larger free volume\textsuperscript{12} associated with ends [Fig. 15(b)].

It is very hard to discriminate these two mechanisms, because the energy scale is the same, however, our elucidation suggests that the end localization to the surface arises from the free volume contribution. Since the boundary of our chain is not a hard wall but a free surface, ends take advantage of free volume. Furthermore, not only end atoms appear on the surface, but also ends pull up some connected atoms to gain entropy in the free space regardless of energy reduction. About 60\% of the next to end are surface atoms as shown in Fig. 16. As expected, the closer to the end, the higher the probability of the surface atoms. We call this the pull mechanism [Fig. 15(c)]. See some popped end parts in Fig. 14. This mechanism is the extension of the free volume mechanism and the force for pulling is the entropic force. If the zigzag move due to covalent bonding in Fig. 16 is ignored, the percentage becomes smaller as atoms get closer to junctions.

E. Shapes of Voronoi polyhedra

Below, we describe detailed shape analysis at 300 K.

![FIG. 13. Normalized mean value of 1/V µ/µ(250 K) against temperature for bulk atoms. Slopes correspond to the “microscopic” thermal expansion coefficients. The slope for end atoms is the steepest downward implying that the microscopic thermal expansion for the ends are the largest.](image)

![FIG. 14. Instantaneous snapshot at 300 K. 52 end atoms are represented by dark gray spheres. It reveals a considerable degree of roughness at the surface and shows that ends are favorably near the surface.](image)

1. Shape factors

In analogy with the method described in the previous section, we clarify whether a polyhedron is oblate (disklike) or prolate (rodlike). The tensor $X$ in Eq. (5) is now calculated by using coordinates of vertices of a polyhedron and is diagonalized to yield eigenvalues $L_1^2$, $L_2^2$, and $L_3^2$ which are principal moments. They are divided by $S^2$ in order to compare configurations of the different sizes. We then obtain the dimensionless shape factors\textsuperscript{36} $g_n$:

$$g_n = \frac{L_n^2}{S^2}, \quad n = 1, 2, 3,$$

where $S^2 = \text{tr} X = L_1^2 + L_2^2 + L_3^2$.

A sphere is characterized by $g_1 = g_2 = g_3 = \frac{1}{3}$,

while for an extremely prolate (rodlike) shape, they become $g_1 = g_2 \approx 0, \quad g_3 \approx 1$,

and for an extremely oblate (disklike) shape, they are

![FIG. 15. Schematic illustration of entropic contributions to the surface free energy. (a) No-reflection mechanism: There is entropy loss for internal atoms (I) by imposed reflection at a surface, while there is no entropy loss for ends (E). Black positions are disallowed positions for I’s. (b) Free volume mechanism: There is entropy gain by larger free volume. E’s are less restrictive and thus gain more entropy than I’s. (c) Pull mechanism: E’s pull up connected atoms by entropic force. This mechanism is the extension of (b).](image)

![FIG. 16. Probability of surface atoms at 300 K vs the number from a junction atom in a side chain: $i = 0$, junction; $i = 6$, end. The dashed line indicates the probability of surface atoms for all atoms, 23.9%. Error bars come from ten starting structures.](image)
of atoms in each peak region between atoms more carefully, averaged shape factors for each kind large, is prolate or rodlike. The shape of a polyhedron for surface atoms whose volume is little asymmetry of approximation zero, while \( g_1 \) and \( g_2 \) approach zero, while \( g_3 \) approaches 1.0, indicating that the shape of a polyhedron is prolate, with a characteristic feature of polymers: In space, there are not only atoms but also covalent bonds between atoms. We call the face and the second closest face is bisected with the next neighbor atom from the end atom. The angles between these two faces are about 70° for an internal atom and 145° for an end (see Fig. 18). In the case of the internal atom, the atom is well surrounded by bonding faces due to the acute angle, while in the case of ends, the front space is relatively open.

Correspondingly, the number of faces per polyhedron reflects the circumstance, narrow or open space caused by bonding faces. Here, we consider typical bulk atoms in peak regions between \( \mu \pm \sigma \) in Figs. 8(a)–8(c) are listed in Table III. From Table III, we find that polyhedra containing internal atoms are more prolate compared to other types of atoms.

2. Bonding faces

We have seen that the polyhedra containing bulk atoms are not spherical. To clarify the reason, we consider the characteristic feature of polymers: In space, there are not only atoms but also covalent bonds between atoms. We call the face of a Voronoi polyhedron that bisects a covalent bond, a bonding face.

For an internal atom in the united-atom model, there are two bonding faces, which are the closest (or the second closest due to thermal vibrations) to the atom. On the other hand, for an end atom, the closest plane is the only one bonding face and the second closest face is bisected with the next neighbor atom from the end atom. Figure 17 displays the plot of the shape factors against \( 1/V \). The plot illustrates basically that \( g_1 \approx 0, \quad g_2 \approx g_3 \approx 0.5 \).

The curves in Fig. 17 are not smooth. To look into bulk atoms more carefully, averaged shape factors for each kind of atoms in each peak region between \( \mu \pm \sigma \) in Figs. 8(a)–8(c) are listed in Table III. From Table III, we find that polyhedra containing internal atoms are more prolate compared to other types of atoms.

![Image](https://via.placeholder.com/150)

**FIG. 17.** Shape factors of a Voronoi polyhedron vs \( 1/V \) at 300 K. The range of \( 1/V \) was divided into \( \Delta 1/V = 0.001 \, \text{Å}^{-3} \) intervals. For bulk atoms, the shape of polyhedra is prolate, because \( g_3 \) is larger than the others. At the surface, the shape is more prolate, because \( g_1 \) and \( g_2 \) approach zero and \( g_3 \) approaches 1 as the volume of a polyhedron becomes large.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( g_1 )</th>
<th>( g_2 )</th>
<th>( g_3 )</th>
<th>( \mu - \sigma )</th>
<th>( \mu + \sigma )</th>
<th>in ( \text{Å}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>End</td>
<td>0.181</td>
<td>0.332</td>
<td>0.487</td>
<td>0.023</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td>Internal</td>
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<td>0.248</td>
<td>0.592</td>
<td>0.044</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>Junction</td>
<td>0.207</td>
<td>0.296</td>
<td>0.497</td>
<td>0.075</td>
<td>0.087</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE III.** Averaged shape factors \( g_i \) of polyhedra for typical bulk atoms in peak regions between \( \mu \pm \sigma \) in Fig. 8.

**FIG. 18.** Relation between a central atom \( P_0 \) and the closest neighboring atom \( P_1 \) and the next closer atom \( P_2 \). They are along the chain. (a) \( P_1 \): end atom, (b) \( P_0 \): internal atom. The angle \( \phi \) between the bonding face and the second closest face is 145° in (a) and that between two bonding faces is 70° in (b).

**FIG. 19.** Histogram for the number of faces per polyhedron for typical bulk atoms at 300 K. The more the number of bonds, the fewer the number of faces of a polyhedron.
where $u$ is the angle between the principal axis and the edge of the polyhedron.

For internal and junction atoms, only two bonding face areas out of 15.3 faces (average) amounts to 38.2% of the total area for internal atoms.

Figure 21 shows that the principal direction for $g_3$ and that of the edge are nearly parallel.

To get a quantitative estimation of the orientational correlation, we use an order parameter $Q$ defined by

$$Q = \frac{1}{2} \{3(\cos^2 \theta) - 1\},$$

where $\theta$ is the angle between the principal axis and the edge as shown in Fig. 21. For a perfect correlation, $Q$ becomes 1, implying always parallel between the principal axis and the edge for each polyhedron, and for uniformly random orientations it takes 0. In our simulations, we have obtained $Q = 0.970$ for internal atoms. For ends, by taking a bonding face and the next nearest one, $Q = 0.738$.

V. CONCLUSION

The Voronoi analysis is of greatest utility for investigating the spatial structure of polymeric materials. We have seen from the $1/V$ histograms that the Voronoi polyhedron volume is related to the topology of atoms: The volume associated with end atoms is larger than that associated with internal and junction atoms. Clearly, the motion of internal atoms is restricted by the connection on both sides, while ends are less restrictive and move easily. The largest volume and the prominent microscopic thermal expansion of ends reflect the highest mobility. We note here that the capability to define microscopic (local) thermal expansion is the advantage of the Voronoi analysis.

The $1/V$ histogram is also useful to distinguish between surface and bulk parts. Then, we have obtained remarkable evidence that end atoms favor the surface. It is quite reasonable that side chain ends are usually functional parts, whose structure takes advantage of the mobility of the ends, leading to the increase of reactivity at a surface and in a bulk region.

In terms of shape factors that contain information of three principal directions representing whether the shape of Voronoi polyhedra is prolate or oblate, we have found that the shape of Voronoi polyhedra is prolate even in the bulk region and become more prolate near the surface region, thereby they finally break up and become open polyhedra. The factors provide more information than the one parameter that has been used in the preceding studies.

We have introduced the concept of bonding faces that allow us to understand why the polyhedra of internal atoms are prolate. We have evaluated that although the number of faces per polyhedron is 15.3, two bonding faces occupy close to 40% of the total surface area of a polyhedron. In addition, it is intriguing that the principal direction corresponding to the largest shape factor, i.e., the direction of a rod is parallel to the edge between two bonding faces. Therefore, we can say that two bonding faces play a significant role to determine the shape of a polyhedron.

In contrast to Ref. 9, pointing out the close relation to random packings of hard spheres, we emphasize the importance of bonding faces which represent the characteristic feature of the Voronoi space division of covalent bonded polymers, namely, the very existence of bonds; that is why a material is polymeric.

Finally, we anticipate that the Voronoi analysis will shed light on the understanding of microscopic structures of polymers concerning physical properties, chemical reactivity, and biological functions. The notion of microscopic thermal expansion and that of bonding faces are such insights which the Voronoi analysis of polymers allows us to put forward.

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7Voronoi analysis has been used not only in condensed matter physics, but also in a wide variety of fields such as mathematics, computational geometry, biology, and city planning, which are inherently geometrical. See, for example, F. Aurenhammer, ACM Comput. Surv. 23, 345 (1991), and references therein.