

# Voronoi Space Division of a Polymer

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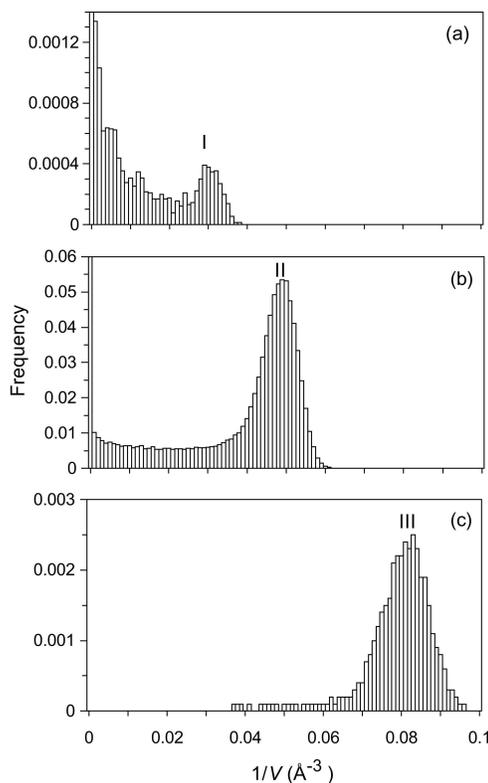
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**Abstract.** In terms of Voronoi division we study the local geometry of a grafted polymer having 52 ends in united-atom molecular dynamics simulations. The volume of a Voronoi polyhedron for a chain end is larger than that for an internal or junction atom, and that it is the most sensitive to temperature. Chain ends dominantly localize at the surface of the globule: 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. We find that two specific faces 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.

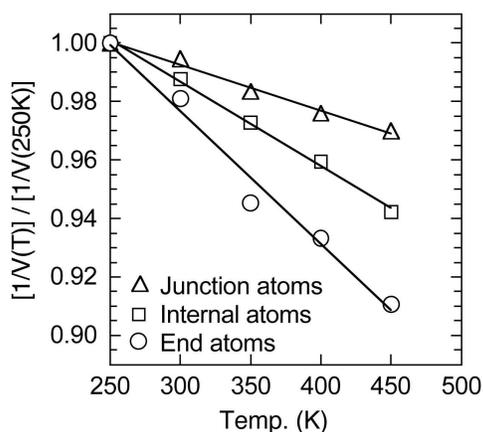
Voronoi analysis has been applied to study the distribution of atoms in simple liquids and non-crystalline metallic solids. Recently, the analysis has been employed to study local geometry of a protein [1] and a glass-forming melt [2]. When it is applied to polymers, a fundamental question arises concerning the volume and the shape of Voronoi polyhedra: Are there any specific features of polymers in contrast to simple liquids or metallic glasses? Does chain connectivity have influence upon the volume and the shape of Voronoi polyhedra? In this paper, we show that the existence of bonds affects Voronoi space division.

Here, united-atom molecular dynamics simulations of a single 500-mer polyethylene linked by 50 hexyl groups ( $-C_6H_{13}$ ), *i.e.* a grafted polymer with 52 ends, are carried out. In the molecule 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 find that the volume of a polyhedron strongly depends on the number of bonds: Polyhedra associated with ends have the largest volume [Fig.1] with the largest local thermal expansion [Fig.2].

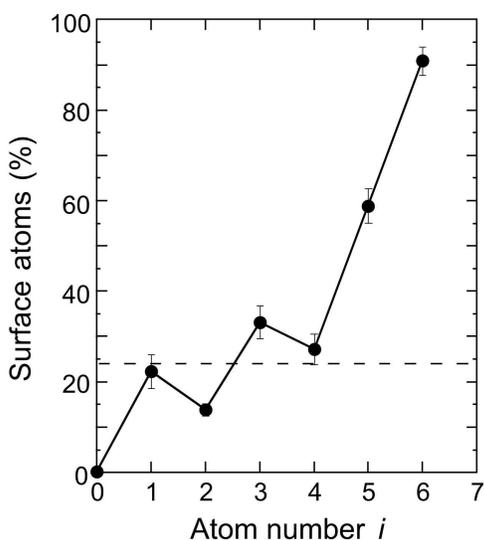
We assign atoms whose inverse volume is smaller than  $0.02 \text{ \AA}^{-3}$  to surface atoms. Then we find that the chain ends dominantly localize at the surface of the globule. In fact, from 50 K to 450 K surface atoms are 24% of all atoms, while ends at the surface are 91% of all ends. Furthermore, not only end atoms appear on the surface, but also ends pull up some connected atoms. About 60% of the next to ends are surface atoms [Fig.3]. As expected, the closer to ends, the higher the probability of surface atoms is, although there is a zigzag move due



**FIGURE 1.** Histograms of the frequency distribution of the inverse polyhedron volume  $1/V$  at 300 K for three types of atoms, averaged over ten independent runs. (a) End atoms. (b) Internal atoms. (c) Junction atoms. The volume for (a) is the largest and for (c) the smallest. The frequencies at  $1/V = 0$  in (a) and (b) are 0.028 and 0.074, respectively.



**FIGURE 2.** Mean value of  $1/V$  for bulk atoms divided by that of 250 K versus temperature. Slopes correspond to the local thermal expansion coefficients:  $\kappa = -[1/(1/V)][\Delta(1/V)/\Delta T]$ . The steepest slope for end atoms implies the largest expansion.

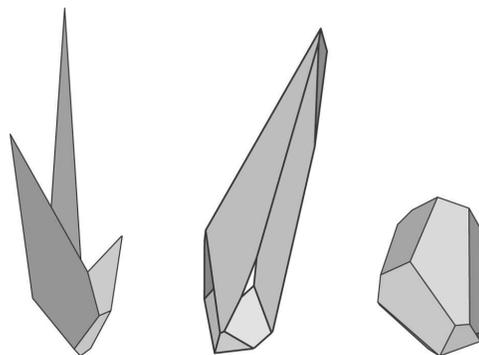


**FIGURE 3.** Probability of surface atoms at 300K versus the number from a junction atom in a side chain:  $i = 0$  (junction),  $i = 6$  (end). The dash line indicates the probability of surface atoms for all atoms, 23.9%. Error bars come from ten independent molecular dynamics starting structures.

to covalent bonding.

The shape of a Voronoi polyhedron containing an internal atom is prolate even in the bulk, and near the surface it becomes more prolate [Fig.4], which can be shown by evaluating shape factors  $g_1 \sim g_2 < g_3$  defined by  $g_n = L_n^2 / (L_1^2 + L_2^2 + L_3^2)$ , where  $L_1^2$ ,  $L_2^2$ , and  $L_3^2$  are eigen values of the gyration tensor calculated by using coordinates of vertices of a polyhedron.

We propose the concept of *bonding faces* defined as the faces that bisect covalent bonds. For typical internal



**FIGURE 4.** Voronoi polyhedra for internal atoms. From left, an open polyhedron ( $1/V=0$ ) and a polyhedron ( $1/V = 0.013 \text{ \AA}^{-3}$ ) at the surface, and a polyhedron ( $1/V = 0.053 \text{ \AA}^{-3}$ ) inside the globule.

atoms, two bonding faces out of 15.3 faces (average) occupy 38.2% of the total surface area of a polyhedron, and the principal direction corresponding to the largest shape factor for the polyhedron is almost parallel to the edge between two bonding faces. Therefore, we conclude that the two bonding faces determine the prolate shape and play significant roles in the Voronoi space division of covalently bonded chains.

In summary, the volume and shape of Voronoi polyhedra strongly depend on the existence of bonds. Soyer et al. [1] pointed out a close relation to random packings of hard spheres and Starr et al. [2] found a universal feature of Voronoi volume distribution functions for dense liquids. The former analyzed an averaged structure (barycenter model) and the latter simulated the bead-spring model, both of which lost chemical character. In contrast to these works, we emphasize the importance of the number of bonds and bonding faces, which represent the characteristic feature of chain molecules.

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