Letters to the Editor

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Communications

Shape of a Random-Flight Chain*

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The disposition of segments of a flexible long chain molecule about the molecular center of mass must on the long-time average be spherically symmetrical in space, but this will in general not be true of an instantaneous chain conformation. Kuhn[1] long ago pointed out this obvious circumstance, and he considered the loci of various points on the chain contour relative to the end-to-end displacement axis; but his results do not really indicate the instantaneous shape of a randomly coiling macromolecule. Our calculations summarized below indicate a stronger average departure from spherical symmetry than might intuitively have been expected (although a weaker one than that obtained by Kuhn for his special points), and suggest that appreciable corrections may be required to approximate theories based on an invariant spherical cloud of segments as the molecular model.

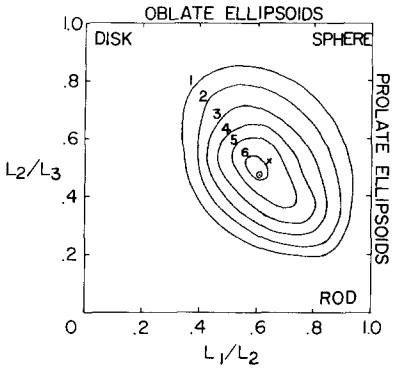

FIG. 1. The shape distribution of the equivalent ellipsoid of inertia for a random cubic-lattice chain of 50 bonds. The probability density is indicated at each contour line. The coordinates of two special points are: circle, $(\langle L_1^2\rangle^{1/2}/\langle L_2^2\rangle^{1/2}; \langle L_2^2\rangle^{1/2}/\langle L_3^2\rangle^{1/2})$; cross, $(\langle L_1/L_2\rangle; \langle L_2/L_3\rangle)$.

As a first measure of asymmetry we considered the quantity $Q=2Z^2-X^2-Y^2$, in which X, Y, and Z are the three orthogonal components along space-fixed Cartesian axes of the radius of gyration of the chain. The first few moments of the distribution of this variable were found with methods given by Fixman[2] and others[3,4]; and the distribution function (which is not symmetrical about the average value of zero) also yields to analytical treatment.[4] For example, the second moment for long chains is given by $\langle Q^2\rangle=$

TABLE I. Several moments of reduced[a] principal axis distribution for a random chain of 50 bonds.

	Monte Carlo				Analytical[c]
	$i=1$	$i=2$	$i=3$	Average[b]	Average
$\langle L_i^2\rangle$	1.097×10^{-2}	2.965×10^{-2}	1.296×10^{-1}	5.673×10^{-2}	5.665×10^{-2}
$\langle L_i^4\rangle$	1.401×10^{-4}	1.083×10^{-3}	2.355×10^{-2}	8.257×10^{-3}	8.351×10^{-3}
$\langle L_i^2L_{i+1}^2\rangle$	3.447×10^{-4}	4.024×10^{-3}	1.432×10^{-3}	1.934×10^{-3}	1.923×10^{-3}
$\langle L_i^6\rangle$	2.096×10^{-6}	4.800×10^{-5}	5.700×10^{-3}	1.917×10^{-3}	1.972×10^{-3}
$\langle L_i^4L_{i+1}^2\rangle$	4.714×10^{-6}	1.547×10^{-4}	2.601×10^{-4}	1.984×10^{-4}	2.025×10^{-4}
$\langle L_i^4L_{i-1}^2\rangle$	1.835×10^{-5}	1.317×10^{-5}	7.396×10^{-4}		
$\langle L_1^2L_2^2L_3^2\rangle$		4.694×10^{-5}		4.694×10^{-5}	4.654×10^{-5}

[a] Reduction is here defined as division of all lengths by $lN^{1/2}$, where l is the length of a bond and N is the number of bonds.

[b] Average over all combinations of indices in same row.

[c] Analytical calculation for freely jointed chains with Gaussian bond length distribution.

$(8/15)\langle S^2\rangle^2$, where $\langle S^2\rangle$ stands for the mean square radius of gyration. It is clear from this number that departures from spherical symmetry are on the average far from negligible. However, the variable Q, being based on space-fixed coordinates, reflects both shape and orientation, so we turned to other measures, for which Monte Carlo methods offered a quicker route to the desired information on shape alone.

Random unrestricted six-choice walks of up to 100 steps on simple cubic lattices were generated on the Dartmouth GE 635 computer. For each walk in the population, the elements of the inertial tensor were evaluated and the principal axes then found. Subsequently, the three principal components $L_1 \leq L_2 \leq L_3$ of the radius of gyration[5] were evaluated along the three principal axes of inertia. These figures, for 2000 walks of 50 steps each and for 1000 walks of 100 steps each, were used to obtain the first several moments as well as to indicate the distribution of shapes.

Some of the Monte Carlo results are given in Table I, along with available analytical values. The generally satisfactory agreement between the analytical and Monte Carlo figures attests to fairly good randomness of the Monte Carlo process. It is obvious at once from the average values $\langle L_1^2\rangle$, $\langle L_2^2\rangle$, and $\langle L_3^2\rangle$ that a flexible chain at any instant is usually quite asymmetric. Similar figures are found for walks of 100 steps.

The actual distribution of shapes is indicated in Fig. 1, which displays contours of constant probability density as a function of the ratios L_1/L_2 and L_2/L_3, and it is seen that the most probable and average shapes do not differ greatly. It must be concluded that the random-flight chain usually looks far more like a cake of soap than like a tennis ball. Detailed results and applications will be presented at a later time.

* Supported by the National Science Foundation and the Michigan Foundation for Advanced Research.

[1] W. Kuhn, Kolloid-Z. **68,** 2 (1934).

[2] M. Fixman, J. Chem. Phys. **36,** 306 (1962).

[3] W. C. Forsman and R. E. Hughes, J. Chem. Phys. **38,** 2118 (1963).

[4] S. R. Coriell and J. L. Jackson, J. Math. Phys. **8,** 1276 (1967).

[5] Here, as before, the term "radius of gyration" is used in the sense commonly employed in chain statistics, rather than that defined in mechanics.

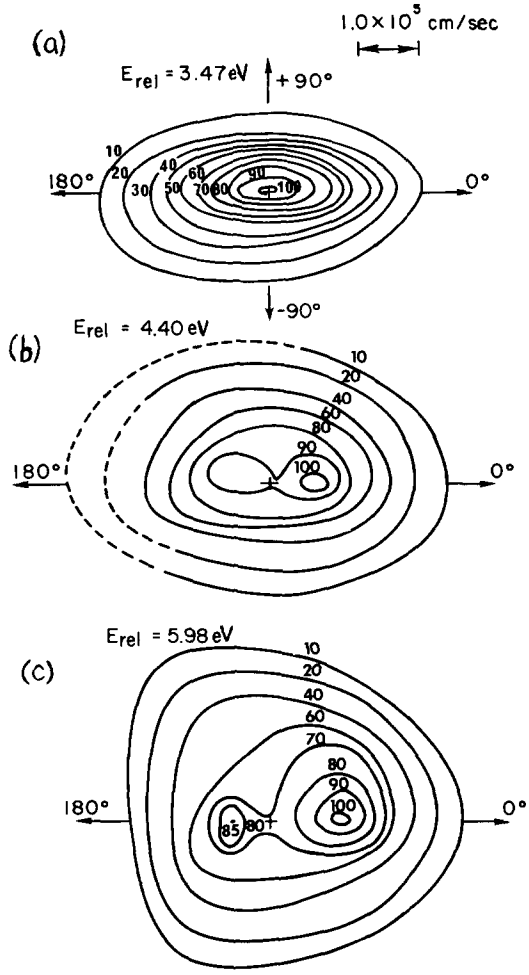

FIG. 1. Contour maps of intensity per unit velocity space volume of CD^+ from the reaction $C^+(D_2, D)CD^+$ for (a) $E_{rel}=3.47$ eV, $V_{C^+}(\text{lab})=1.51\times10^6$ cm/sec, $V_{c.m.}=1.13\times10^6$ cm/sec; (b) $E_{rel}=4.40$ eV, $V_{C^+}(\text{lab})=1.67\times10^6$ cm/sec, $V_{c.m.}=1.26\times10^6$ cm/sec; (c) $E_{rel}=5.98$ eV, $V_{C^+}(\text{lab})=1.95\times10^6$ cm/sec, $V_{c.m.}=1.47\times10^6$ cm/sec.

Complex Formation in the Reaction $C^+(D_2, D)CD^+$

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In recent years, the role of the intermediate complex in chemical reactions has been given increasing attention especially by molecular dynamicists.[1] In some cases, where the persistent complex is especially long lived ($>10^{-6}$ sec), it has been possible to make a direct detection of the intermediate by mass spectroscopy.[2] In other cases, where the lifetime of the complex is much shorter, ion and molecular beam techniques have been shedding considerable light on the phenomena.[3] The qualitative criteria for persistent complex formation can be determined from simple RRK theory.[4] One of the obvious requirements is that the system possess a deep potential well so that the complex can be held together for a significant time.[3] To meet this requirement, the complex should have considerable binding energy relative to the potential energy represented by the projectile and target molecules and it should have a considerable barrier against decomposition. These require-