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Rearrangement during Sintering in Two-Dimensional Arrays

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ABSTRACT

Densification of two-dimensional arrays of nearly monosized copper spheres was examined by hot stage optical microscopy. The evolution of the particle arrangement was studied with computer methods, and statistical correlations were sought. Color graphics were found useful for displaying the spatial relationship of the local sintering parameters. It was found that differential densification was the major cause of rearrangement, rather than asymmetric neck formation.

INTRODUCTION

An important aspect of the densification of powder compacts is the interactions between the multitude of particles, especially in the early stages of sintering. These can lead to the development of microstructural imperfections that may dominate the performance of the sintered ceramic component. The interactions involve particle rearrangement and differential densification that strongly influence pore evolution. Information about the interactions cannot be derived from two-particle models or experiments [1]. Various authors have considered the interactions between particles during densification by considering three-particle arrangements or two-dimensional arrays [2–8]. Exner studied three-particle sintering and concluded that asymmetric neck formation was the major cause of rearrangement in powder compacts. He further attempted to show that similar processes dominated rearrangement in two-dimensional arrays [4]. In this study we have re-examined rearrangement in two-dimensional arrays and considered the statistics fully. Local densification rates and interparticle angles were followed. A color coding scheme was developed to describe the spatial relationships of the local densification and rearrangement processes. The observations led to the conclusion that differential shrinkage rather than asymmetric neck formation is the dominant cause for rearrangement.

EXPERIMENTS

Copper spheres with a mean diameter of 41 micrometers were prepared from high purity spheroidized powder. The commercial powder was first sieved, and the fraction of particles with a size between 37 and 45 micrometers was retained. These particles were then dispersed onto a polished vitreous carbon

plate, and melted in an atmosphere of argon + 5% hydrogen. Since the molten copper does not wet the vitreous carbon, surface tension caused the copper to form into nearly perfect spheres.

The two-dimensional sintering compacts were prepared by arranging the copper spheres on a polished, vitreous carbon substrate. The vitreous carbon has the disadvantage that it is not transparent, but it avoids the adhesion of the spheres to the substrate that was found to be a problem when sapphire or quartz were used as substrates. The sample was heated to the sintering temperature, 1225K, in an atmosphere of argon containing 9.5% nitrogen and 0.5% hydrogen in a hot stage optical microscope, under reflected light. A series of micrographs of the same area of the sample recorded the evolution of the array for periods of up to 10 hours. An example of an image of a two dimensional array at the start and after a period of sintering is shown in Fig. 1.

The locations of the sphere centers were determined at 0.5 hour intervals by choosing three points on their perimeter and computing the center. A computer file containing the positions of the sphere centers as a function of time was created in this way, and used to calculate interparticle distances, interparticle angles, and projected local density. The projected local density was defined as the ratio of the average projected sphere area over the Voronoi cell area associated with that sphere. The Voronoi cell for a point in a two-dimensional array is the smallest area enclosed by the perpendicular bisectors of the lines connecting the points. The definitions of the interparticle angles and the Voronoi cell are illustrated in Figs. 2 and 3. The interparticle distances and interparticle angles were only counted for contacting spheres. The local densification rate was defined as the negative of the derivative of the local density versus

sintering time for a particular sphere.

In a number of instances it is useful to display the local quantities in a spatially meaningful manner. For this purpose, a computer graphics technique was developed whereby the local value of the datum of interest was assigned a color that was used in the appropriate Voronoi cell. Such color maps depict graphically how the datum value of a cell relates to that of the neighboring cells. The lowest data values were plotted as a deep blue, while the highest ones were red.

RESULTS AND DISCUSSIONS

Local Density and shrinkage rates - The average local density evolved as expected in a sintering experiment, as shown in fig. 4. While the average density increased monotonically with time, the local densities followed a less obvious trend. If rearrangement is defined as the deviation of the local geometry of the array from that obtained from the macroscopic shape change, then two types of rearrangement are observed. The first type of rearrangement is one in which both the coordination number of the particles and the local density increases. An example of this is shown in Fig. 5a. The second type of rearrangement is a de-densifying one, leading to the formation of large voids in some cases. An example of this type of rearrangement is shown in Fig. 5b. The second type of rearrangement was far more prevalent in the two-dimensional arrays studied here than the first type. The prevalence of the de-densifying rearrangement is the result of the rapid densification of some domains in the array where the packing density is high. The differences in the packing density leads to differential densification with the accompanying development of increased interdomain porosity and a decrease of the overall densification rate.

This is illustrated well in a comparison of the evolution of the average interparticle distances to the average linear shrinkage as a function of sintering time, Fig. 6. This comparison shows that the average nearest neighbor distance shrinks considerably more than the linear shrinkage, a consequence of the pore enlargement produced by the differential densification rates.

The local densities and the corresponding local densification rates are depicted at four successive times in the color maps shown in Fig. 7 and 8. Notice that in figure 7 there are a few areas of very low density that persist into the later stages of sintering and that these are located between areas of higher density. It is evident from these renderings that densification may proceed rather heterogeneously at the particle level for irregularly packed two-dimensional arrays, even though the particle sizes are narrowly distributed. The densification rates are widely distributed early in the process, as is evident from Fig. 8, and become fairly uniform at later times, except for a few areas of expansion that are located between areas of higher density as seen in a comparison of figures 7 and 8. This is a result of the development of larger sintering necks that are capable of transmitting stresses between sintering necks that are shrinking at different rates.

The local densification rate is plotted versus the local density at the beginning of sintering for an area containing about 120 Voronoi cells in fig. 9; no correlation can be found. It is thus concluded that, in general, it is not possible to describe the dependence of the local densification rate in terms of the local density alone. The local densification rate therefore depends on both short range and long range parameters.

Interparticle Angles - A particle in a two-dimensional array of monosized spheres may have up to 6 nearest neighbors. The interparticle angles, as defined in fig. 2, add up to 360 degrees for each particle. The maximum change of a given interparticle angle was defined as the largest value minus the smallest value that the angle had during the sintering. If the smallest value occurred first the maximum change was defined as positive, the maximum change was defined as negative for the largest value occurring first. To display the spatial distribution of the maximum angular change in the Voronoi cell pattern it was necessary to define the maximum angular change for the configuration of angles associated with a particular particle. This quantity was defined as the average of the absolute value of the maximum change of each of the interparticle angles associated with that particle.

Rearrangement involves a change of the interparticle angles in the array, and the angular changes might thus be considered to be some measure of rearrangement. From Exner's experiments on three-particle arrangements [4] a correlation might be expected between the maximum change of an angle and the initial interparticle angle. If the local arrangement and asymmetrical neck formation strongly influenced the change of the interparticle angles, then specific trends should be preserved in a plot of the maximum change of an angle versus the initial interparticle angle itself. Fig. 10 is such a plot, and it is obvious that there is no correlation.

The changes of the interparticle angles are therefore likely to be determined by the stresses generated by the differential densification of the inhomogeneously packed array. A two-dimensional color mapping of the maximum angular changes is shown in fig. 11 and illustrates that the maximum angular

changes are not distributed evenly throughout the array. This clustering of cells of similar angular change is just as expected for a differential densification mechanism.

The average of the absolute value of the rate of angular change might be considered a measure of the degree of rearrangement that is occurring at a given time. Similarly the standard deviation of the absolute value of the local densification rates might be considered a measure of the degree of differential densification. If this measure of rearrangement is plotted versus this measure of differential densification then a fairly strong correlation becomes apparent, as can be seen in Fig. 12. It is thus concluded that most of the rearrangement is driven by the stresses generated due to differential densification, rather than by local packing asymmetries.

CONCLUSIONS

The statistical aspects of local densification in irregularly packed arrays of monosized spheres have been examined. De-densifying rearrangement was found to be far more prevalent than densifying rearrangement in the loosely packed arrays. The spatial relationships of the local densification parameters were displayed using color graphics. Correlations were sought but they could not be found between the local density and densification rate or between the angular changes and local angles. A strong correlation could be found between the standard deviation of the local densification rates and the rates of angular change. It was concluded that differential densification is the main driving force for rearrangement, rather than asymmetric neck formation.

Acknowledgements

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FIGURE CAPTIONS

1. Two-dimensional sintering array showing the different types of behavior that occur during sintering. The areas labeled A and B show the formation of elongated pores. The pore labeled X exhibits rounding without growth. The area labeled D is a highly coordinated area that densifies homogeneously.
2. The definition of the interparticle angles.
3. The definition of Voronoi cell for an array of spheres in two dimensions.
4. The average local density versus sintering time.
5. Micrographs of local rearrangement, the left hand side is prior to sintering and the right hand side is after 7.5 hours. (a) densifying type. (b) de-densifying type.
6. The average interparticle distance and the average linear shrinkage versus sintering time.
7. Spatial arrangement of the local densities at four different sintering times.
8. Spatial arrangement of the local densification or shrinkage rate at four different sintering times.
9. The local densification rate versus the local density at the beginning of sintering.
10. The change in the interparticle angle versus the initial interparticle angle.
11. Spatial arrangement of the maximum angular change.
12. The average of the absolute rate of angular change (rearrangement) versus the standard deviation of the absolute densification rate (differential densification).

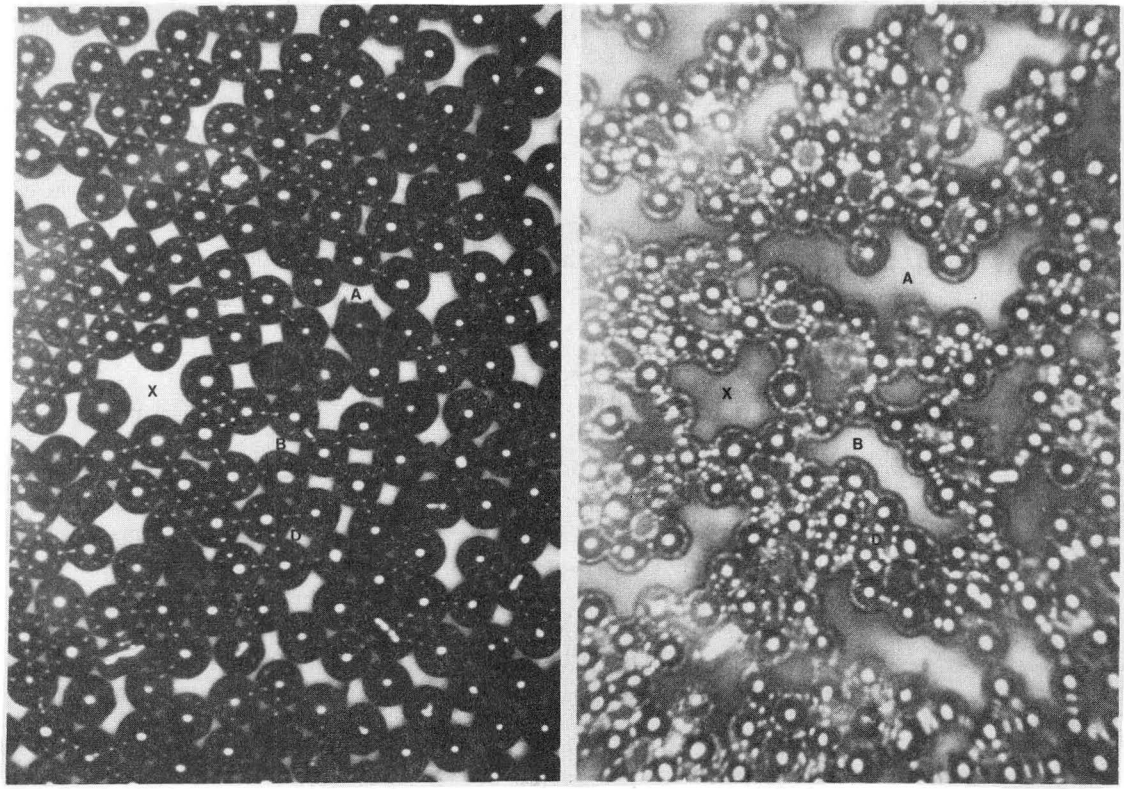

Fig.1

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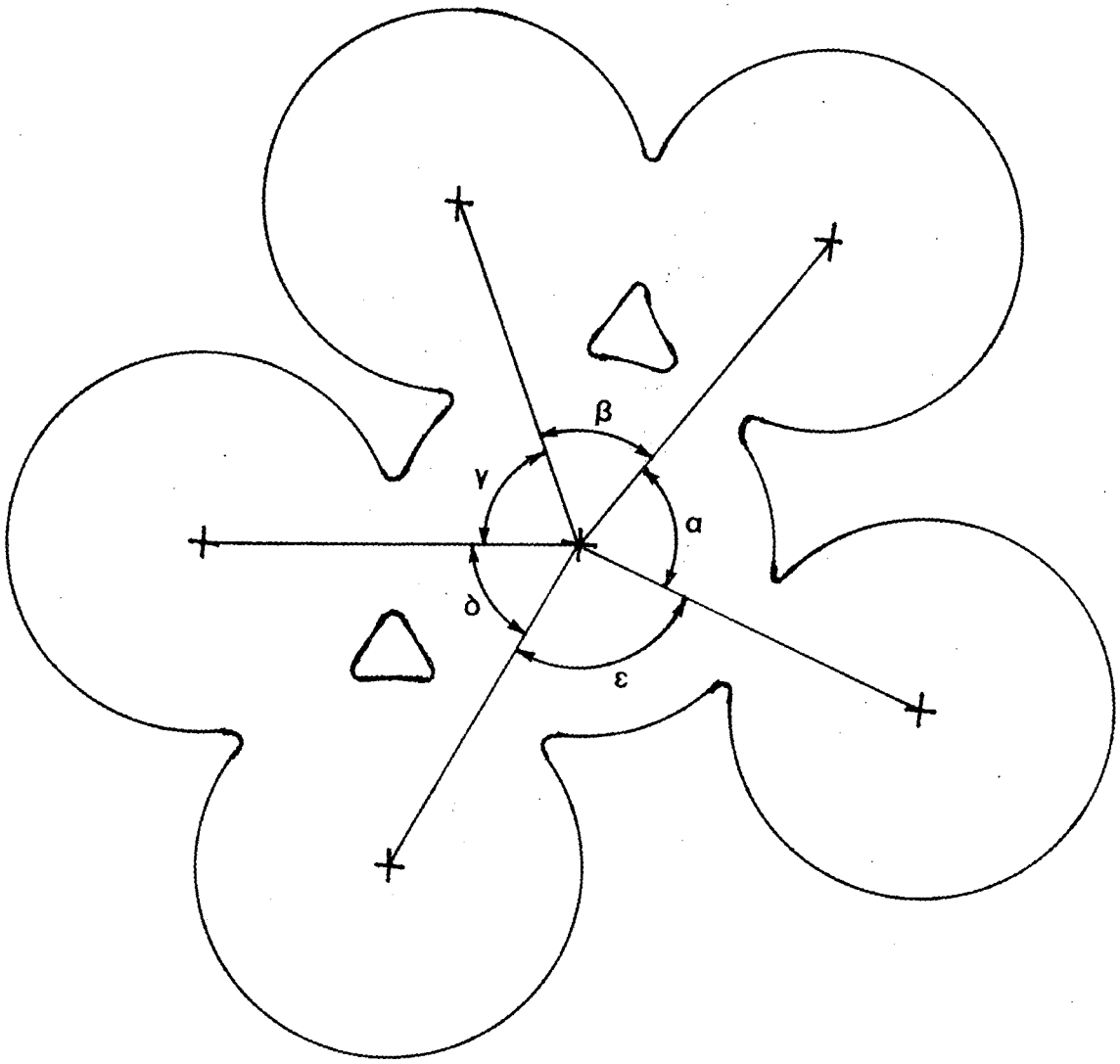

Fig. 2

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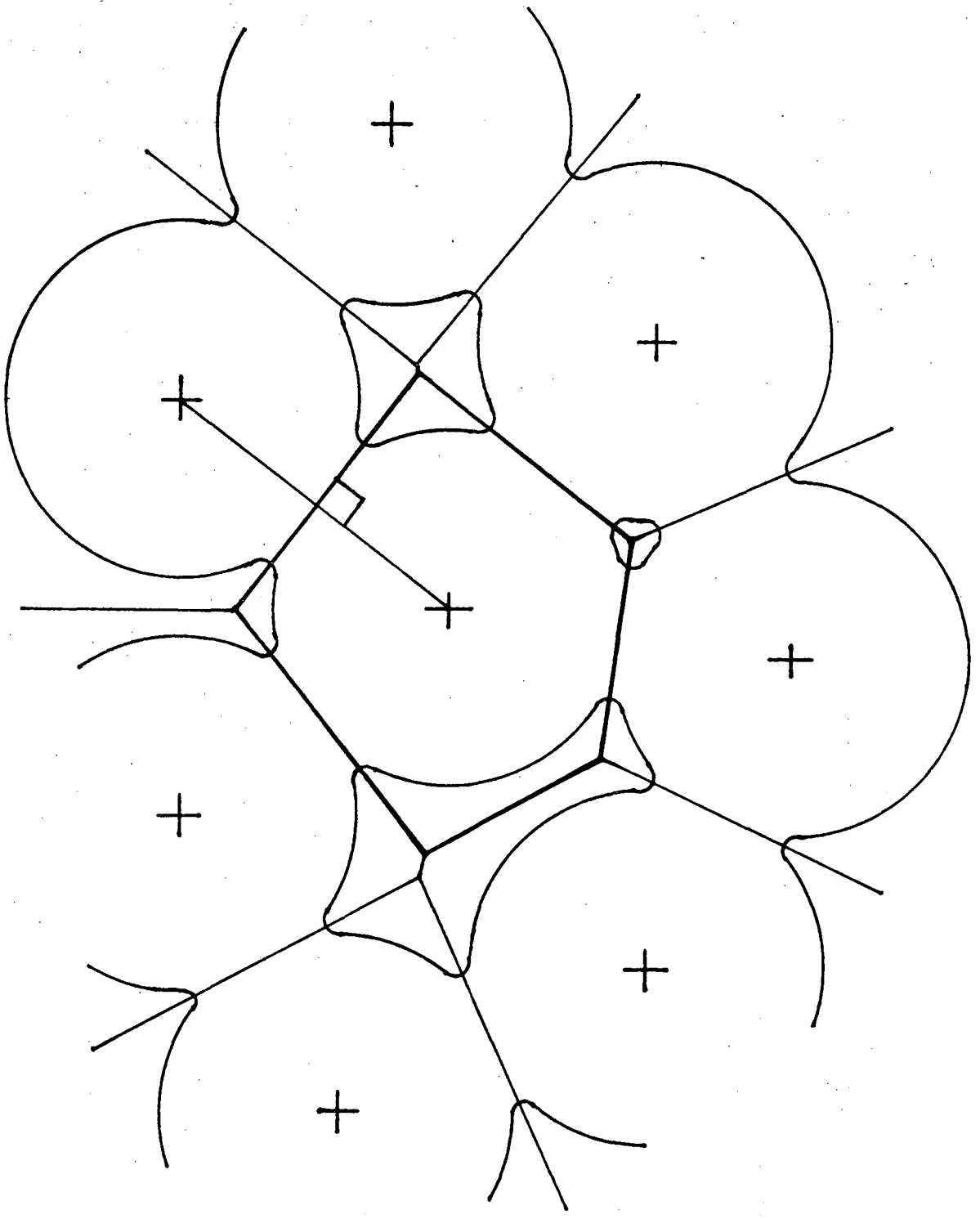

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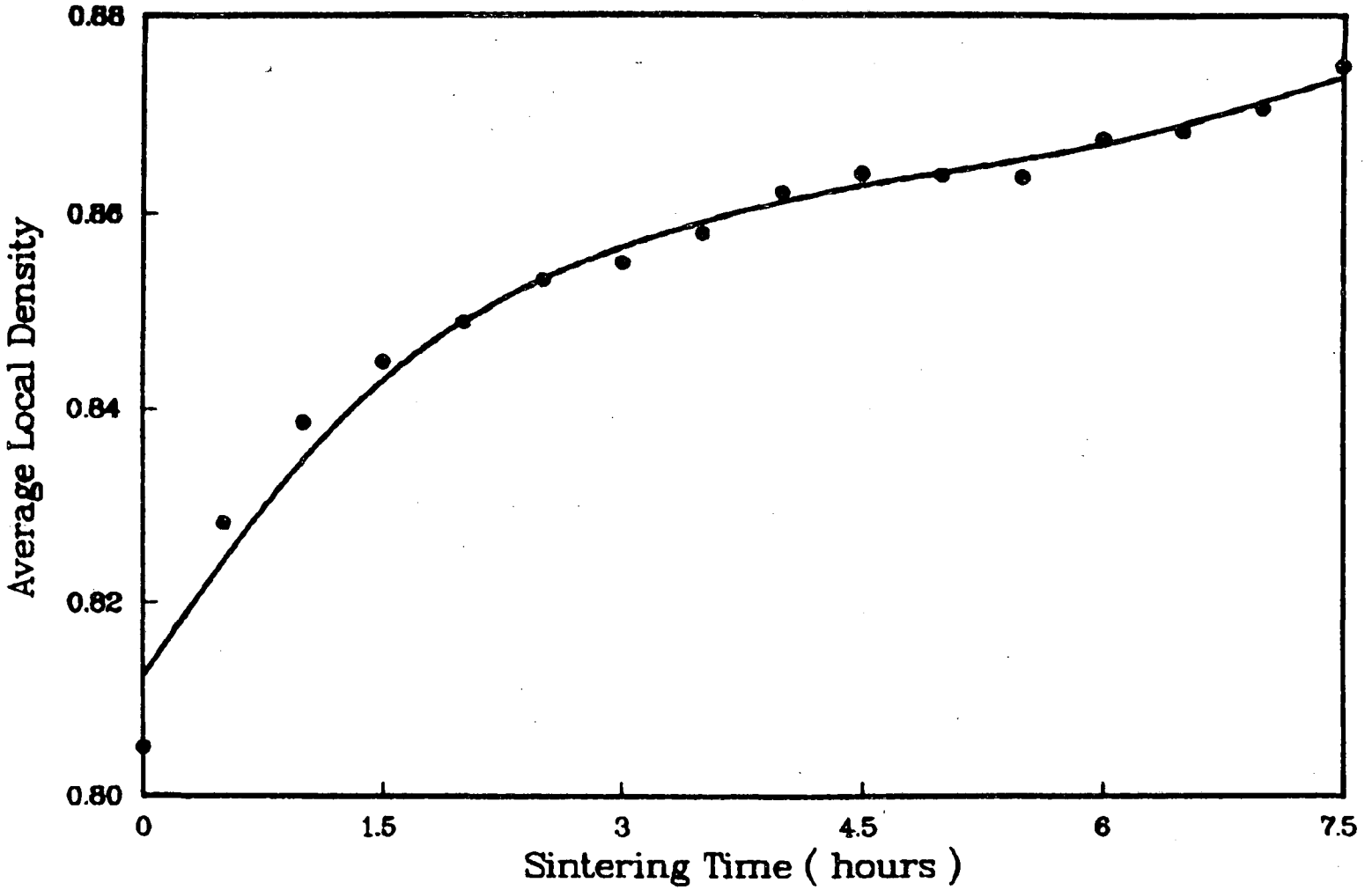

Fig. 4

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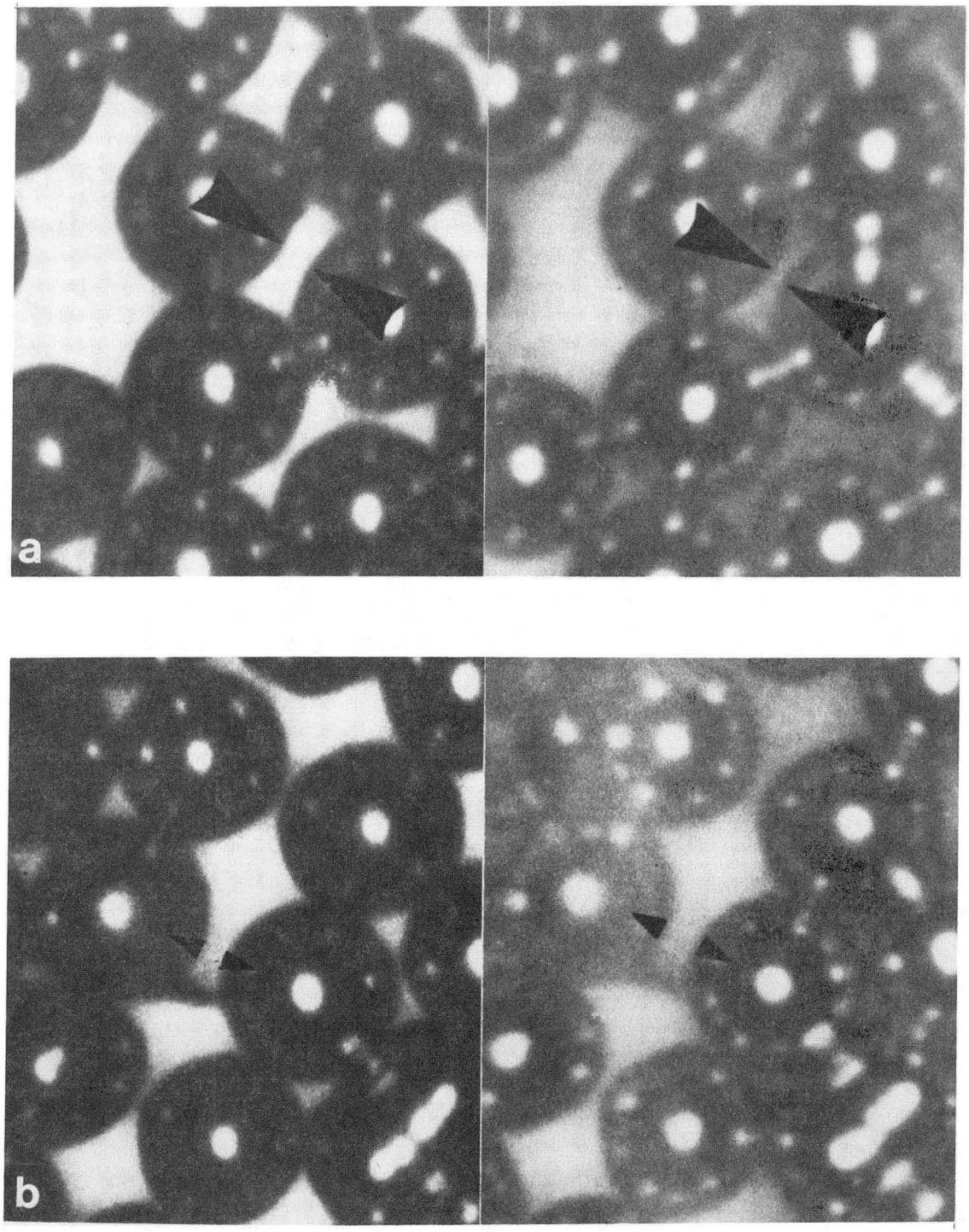

Fig. 5

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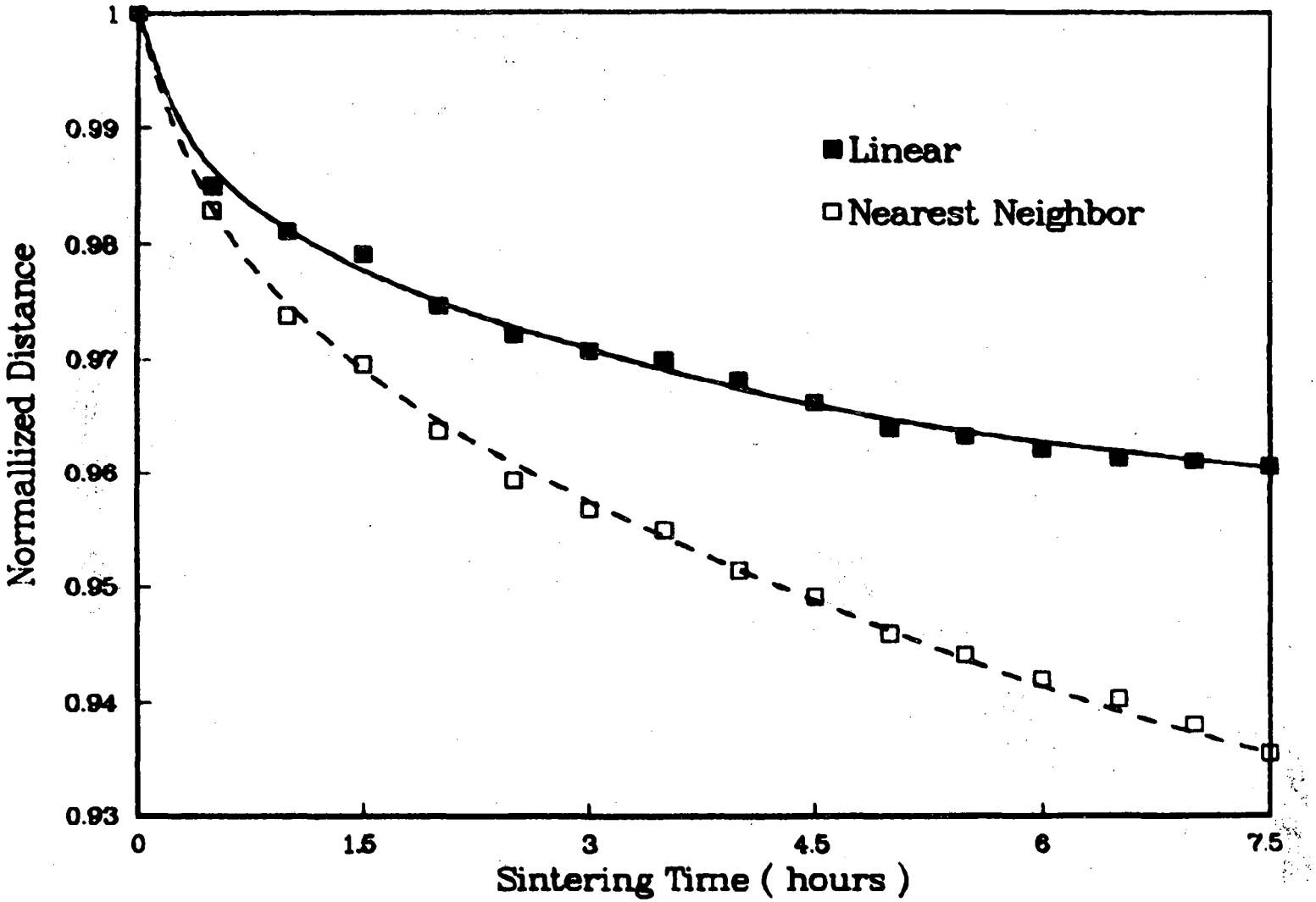

Fig. 6

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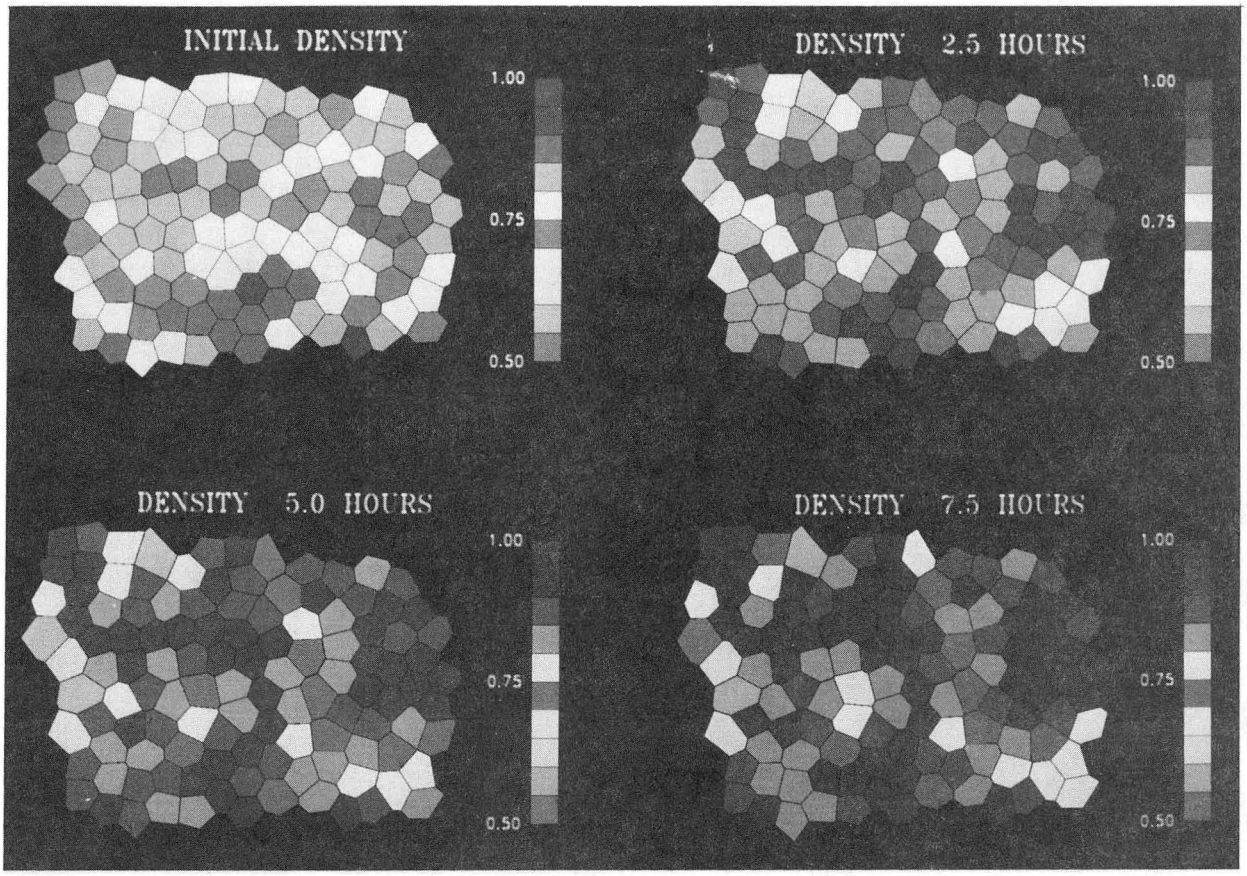

Fig. 7

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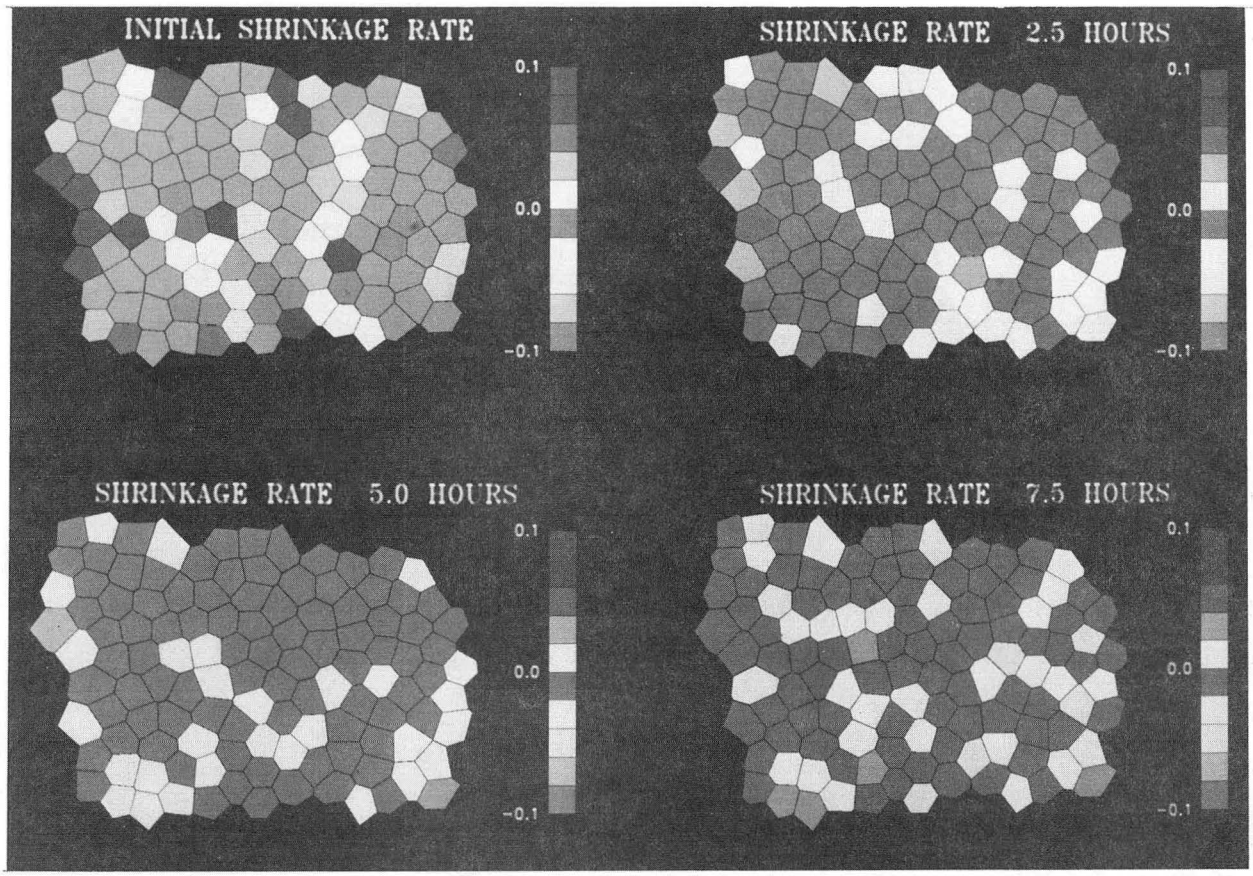

Fig. 8

CBB 851-847

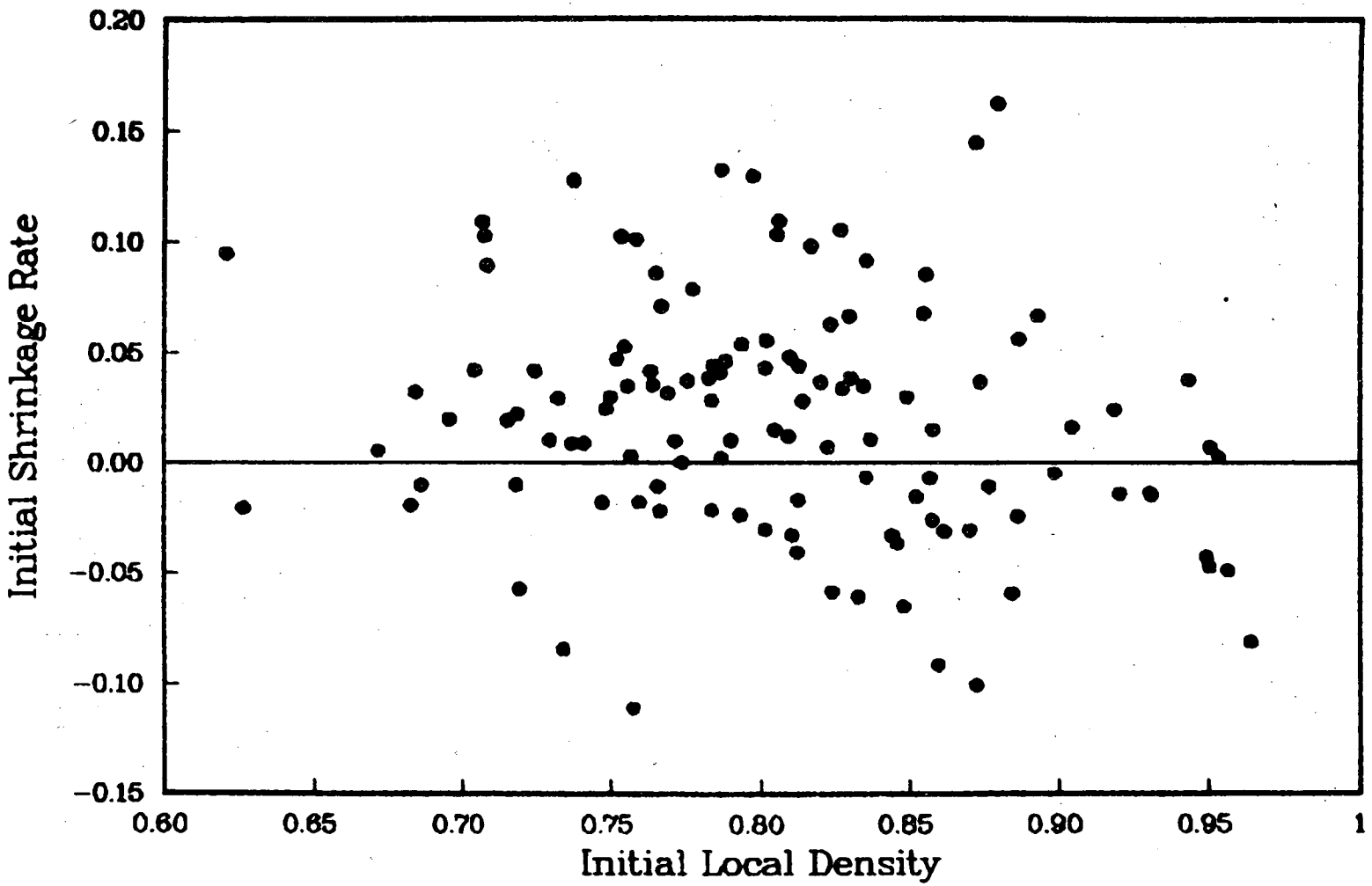

Fig. 9

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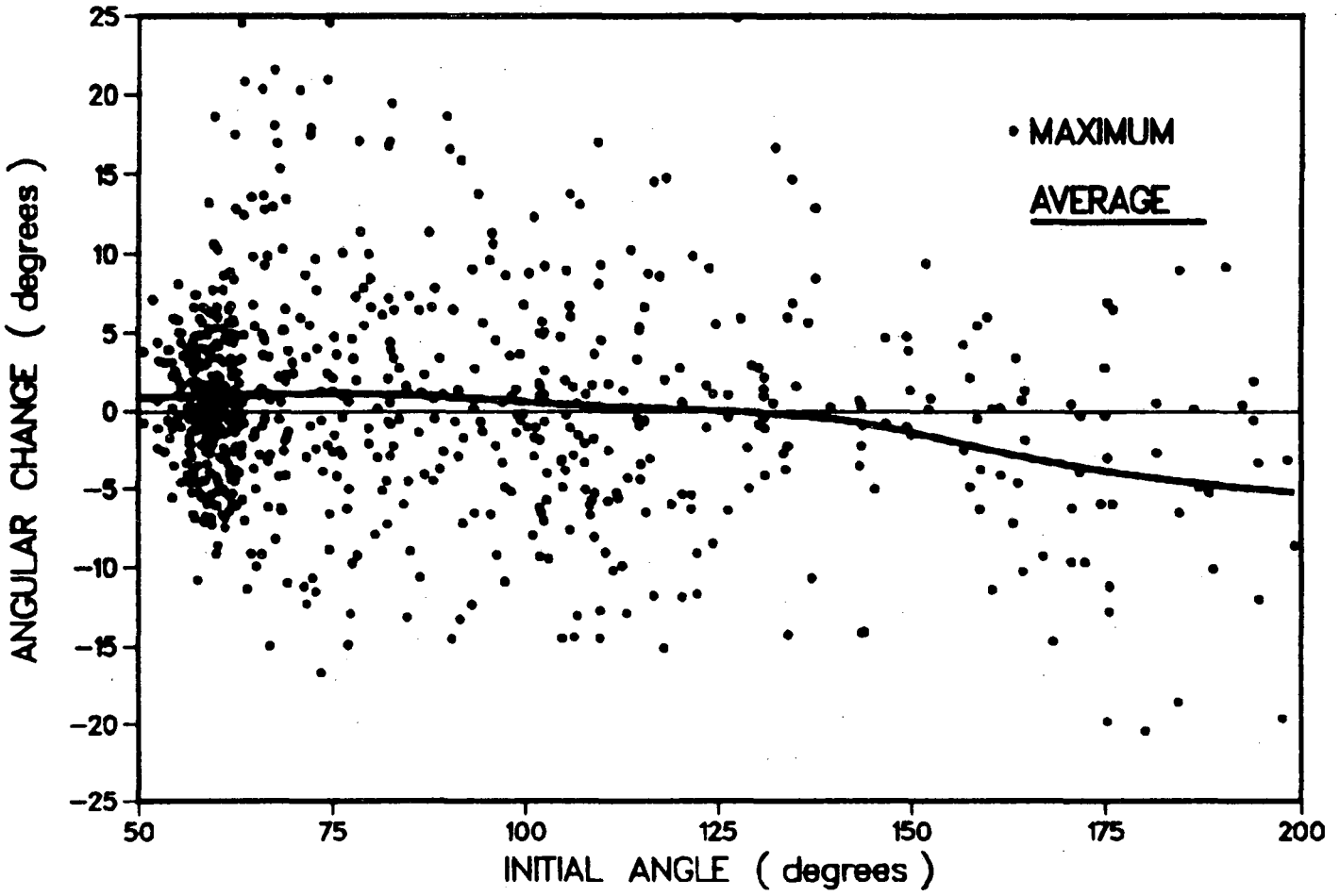

Fig. 10

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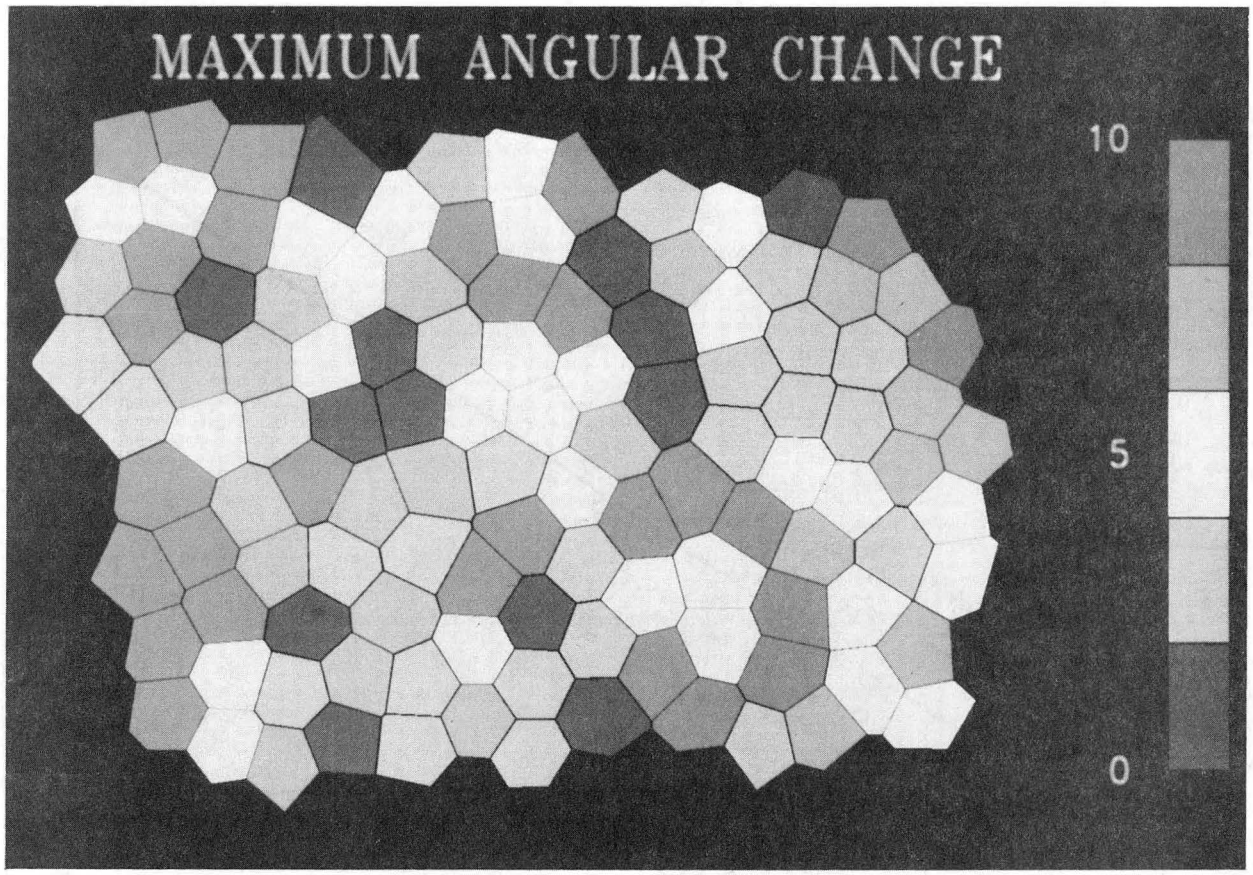

Fig. 11

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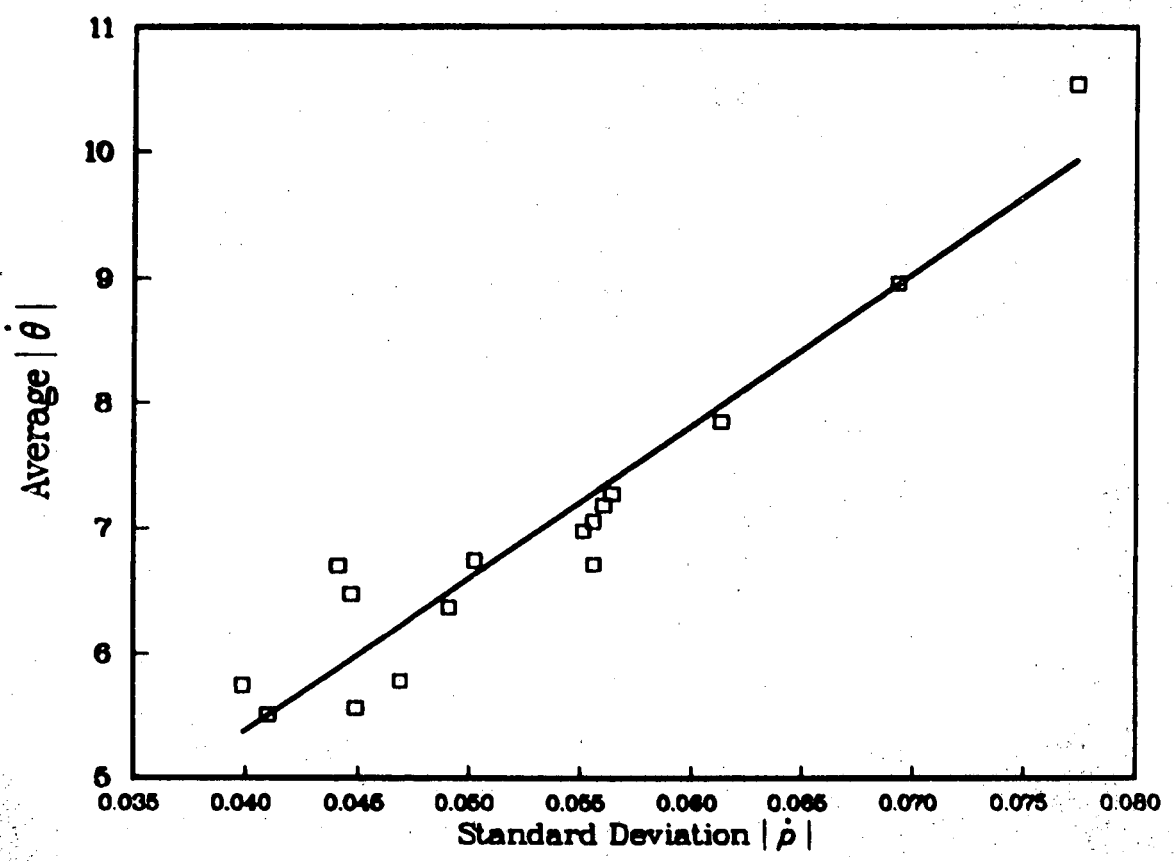

Fig. 12

XBL 8511-4541

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