This is to certify that the

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Contact Nucleation From
Aqueous Dextrose Solutions

presented by

Ponnampalam Elankovan

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Kris A. Berglund
Major professor

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CONTACT NUCLEATION
FROM
AQUEOUS DEXTROSE SOLUTIONS

By

Ponnampalam Elankovan

A THESIS

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Abstract

CONTACT NUCLEATION FROM AQUEOUS DEXTROSE SOLUTIONS

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Ponnampalam Elankovan

This work is presented as two papers. The first, "Technique for Obtaining Raman Spectra of Contact Nuclei *In Situ*" was reviewed and published as a spectroscopic technique in Applied Spectroscopy, volume 40, number 5, 1986. The second, "Contact Nucleation from Aqueous Dextrose Solutions," has been peer-reviewed and accepted for publication in the American Institute of Chemical Engineers Journal.

The first paper demonstrates that the crystallographic phase of contact nuclei can be identified *in situ* with the use of Raman Spectroscopy. These results indicate that the laser Raman miocroprobe technique can be an important tool in the future study of contact nucleation. The second paper is focussed on the contact nucleation process in dextrose crystallization.

Although the precise mechanism is not known, contact nucleation is the primary source of new particles in many important industrial crystallization. Contact nuclei of

both alpha monohydrate and alpha anhydrous dextrose were formed from the contact of an anhydrous parent crystals growing in pure solution indicating that simple breakage does not cause contact nucleation.

Since a small amount of data is available in the literature for this important sugar, and the Raman microprobe technique is a new technique to characterize the growing crystal phase in situ, this work provides the background for subsequent studies. A summary of results, recommendations for future work, and appendix containing the complete raw data obtained during this study are presented after the second paper.

DEDICATION

This work is dedicated to my loving wife Sugendrini Ponnampalam who has been a great source of inspiration and encouragement through my academic career.

ACKNOWLEDGEMENTS

I would like to thank Dr. Kris Berglund, my major advisor, for his guidance and valuable advice during this study.

Acknowledgement is given to the author's co-workers Michel Cerreta, Lie Ding Shiau and Yi Ding Chu for their cooperation and discussion on the field of crystallization.

The assistance of Dr. David Bruce of the department of Physics and Astronomy at Michigan State University is appreciated.

Finally, the financial support from A.E. Staley Manufacturing Company and the laser Raman microprobe provided through the National Science Foundation under grant number CPE - 8409458 and the Michigan Agricultural Experiment Station are greatfully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Technique for Obtaining Raman Spectra of Contact Nuclei *In Situ*

By

P.Elankovan and K.A.Berglund*

Departments of Agricultural Engineering
and Chemical Engineering
Michigan State University
East Lansing, MI 48824

*Auther to whom correspondence should be addressed
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Introduction

Secondary nucleation, the formation of new crystals due to the prior presence of other growing crystals, is the primary source of new particles in most industrial crystallizers (Larson, 1984). Of the various types of secondary nucleation possible, contact nucleation, wherein a disturbance of growing crystal surface results in nuclei,is thought to be the most prevalent (Larson, 1984).

The source of contact nuclei has not been determined; however, two possibilities has been presented in the literature. In the first it is proposed that nuclei come from microattrition of the growing crystal surface. Conversely, in the second the source of the nuclei is thought to be a semiordered layer of solute adjacent to a growing crystal surface. In order to distinguish between the two models it is necessary to produce labeled contact nuclei and to analyze them as to their source. To this end a contact nucleation cell has been developed and used in the dextrose water system.

Apparatus

The cell used in the present study is shown in Figure 1. The upper chamber of the cell has temperature control provided by water circulated in the lower chamber of the cell. Since a temperature gradient is probably present in the cell, a glass cover slip was mounted in the upper chamber to hold the contact nuclei at a precise distance from the water bath chamber. A thermistor allows careful

monitoring of the temperature of the solution in this position and variations are are typically less than 0.1K.

Contact nuclei were analyzed using a laser Raman microprobe in situ. The instrument used was a Spex Model 1406 double monochromator with radiation (1545A and 1W) provided by a Coherent Radiation CR-5 argon ion laser. The sample was illuminated by a Spex 1482 Micramate illuminator using a Ealing Corporation Model 25-0506 15X long working distance objective. Spectra were recorded using a strip chart recorder and the scan speed was 0.05A/seconds.

Experimental

The dextrose-water system was the subject of the study. An interesting feature of this system is that at approximately 308-323K it undergoes a phase transition (Dean, 1974 and Edwards, 1982). That is, above this range alpha monohydrate dextrose is formed. This feature was exploited in the present study.

Contact nucleation experiments were performemd using the same photomicroscopic technique as applied to the citric acid monohydrate system (Berglund and Larson, 1982). Parent crystals of the both alpha anhydrous dextrose and alpha monohydrate dextrose were grown to approximately 1-2mm. The alpha monohydrate parent crystals were not used in contact experiments due to their fragile nature. In each experiment an alpha anhydrous parent crystal was mounted to the moveable rod shown in Figure 1.

After parent crystal was prepared and mounted, a dextrose solution saturated at 318K was added to the preheated cell. The solution was then heated to redissolve any primary nuclei which may have been generated during transfer. Heating also slightly dissolved the parent crystal to insure that no surface irregularities formed by washing and drying remained. The solution was then cooled to 314K; then the parent crystal was growing in a regular manner, it was contacted by gently sliding across the glass cover slip.

Results and Discussion

Two different crystal habits were formed by contact as evidenced by the photomicrographs in Figure 2. For convenience of discussion the well formed nuclei are designated prisms and the elongated nuclei are designated needles. An anhydros crystal (as verified by Raman spectroscopy) was contacted under conditions in which both phases may form.

The laser Raman microprobe was used to identify the two types of crystals <u>in situ</u>. A summary of the Raman spectra are presented in Figures 3 and 4. Figures 3A and 4A show the spectra for reagent grade alpha monohydrate and alpha anhydrous dextrose, respectively. Figures 3B and 4B are spectra of parent crystals of alpha monohydrate and alpha anhydrous, respectively, and closely conform to the reagent grade spectra in Figures 3A and 4B. (It should be

remembered that the alpha monohydrate parent crystal was not used in any contact experiment and is only presented here for the sake of completeness.) The spectra shown in Figures 3D and 4D are of the supersaturated solution in the cell far from any contact nuclei. Figures 3C and 4C are the in situ spectra of the needle and prism contact nuclei, respectively.

Clearly large differences are evident in the Raman spectrum of each type of nuclei. The most proniunced differences occur in the Raman shifts at about 918cm^{-1} and 1078cm^{-1} which are assigned to the C_1-H strech and the C-O-H deformation, respectively (Vasko et al, 1972). Upon comparison of the contact nuclei spectra with the reagent grade dextrose and parent crystal spectra, it is clear that the prism contact nuclei are alpha anhydrous dextrose. On the other hand, the identification of the needle crystals is slightly less definitive. The predominant phase present in alpha monohydrate dextrose, but the additional band at 942cm^{-1} suggests another phase may also be present (Dean, 1974). At any rate, the two habits present corresponds to different crystalline phases.

The present results support the notion that the semiordered solution adjacent to a growing crystal is the source of contact nuclei. Since an anhydrous parent crystal was used in the contact and two different phases were formed, microattrition of the parent crystal does not explain the formation of the monohydrate phase.

Summary

It has been demonstrated that contact nuclei can be identified *in situ* using Raman spectroscopy. The present results suggest that the laser raman microprobe can be an important tool in the future of contact nucleation.

Acknowledgments

This work was supported in part by the A. E. Staley Manufacturing Company. The laser Raman microprobe was provided jointly by the National Science Foundation under grant number CPE-8409458 and the Michigan Agricultural Experiment Station. The assistance of Dr. David Bruce of the department of Physics and Astronomy at Michigan State University is appreciated.

Figure 1. Schematic diagram of nucleation cell (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; and (8) water inlet and outlet;

Figure 2. Typical examples of photomicrographs of contact nuclei of dextrose formed from pure solution at 314K and a supercooling of 4K. The elapsed time between photographs is 72 min. Note the two different crystals forms present.

Figure 3. Raman shift of alpha monohydrate dextrose. (A) pure reagent grade, (B) parent (needle) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

Figure 4. Raman shift of alpha anhydrous dextrose. (A) pure reagent grade, (B) parent (prism) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

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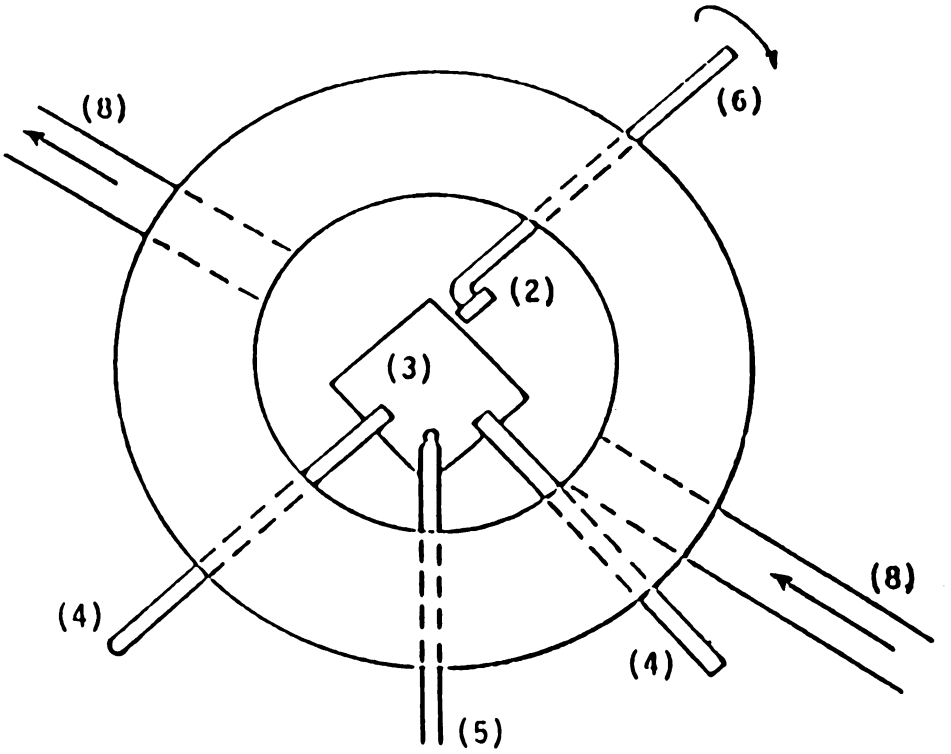
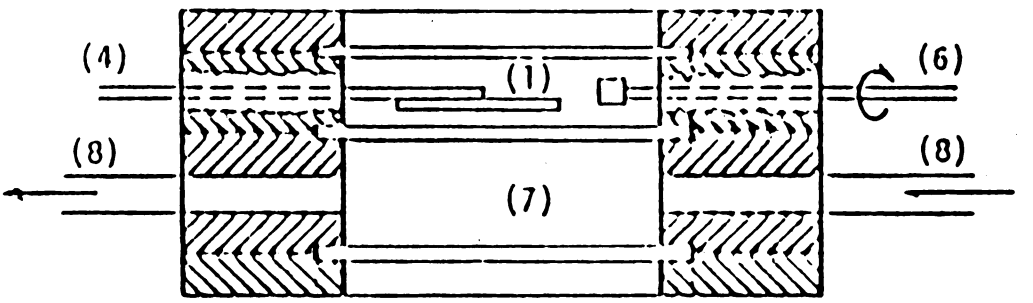
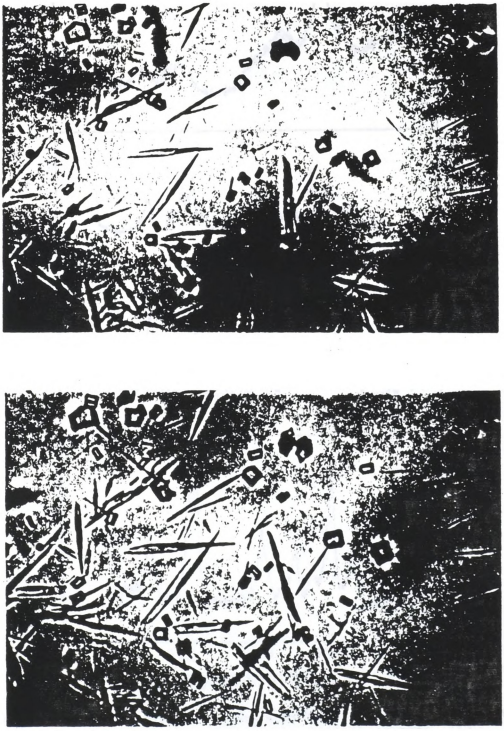


TOP VIEW



SIDE VIEW

Figure 1. Schematic diagram of nucleation cell with the features: (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; and (8) water inlet and outlet;



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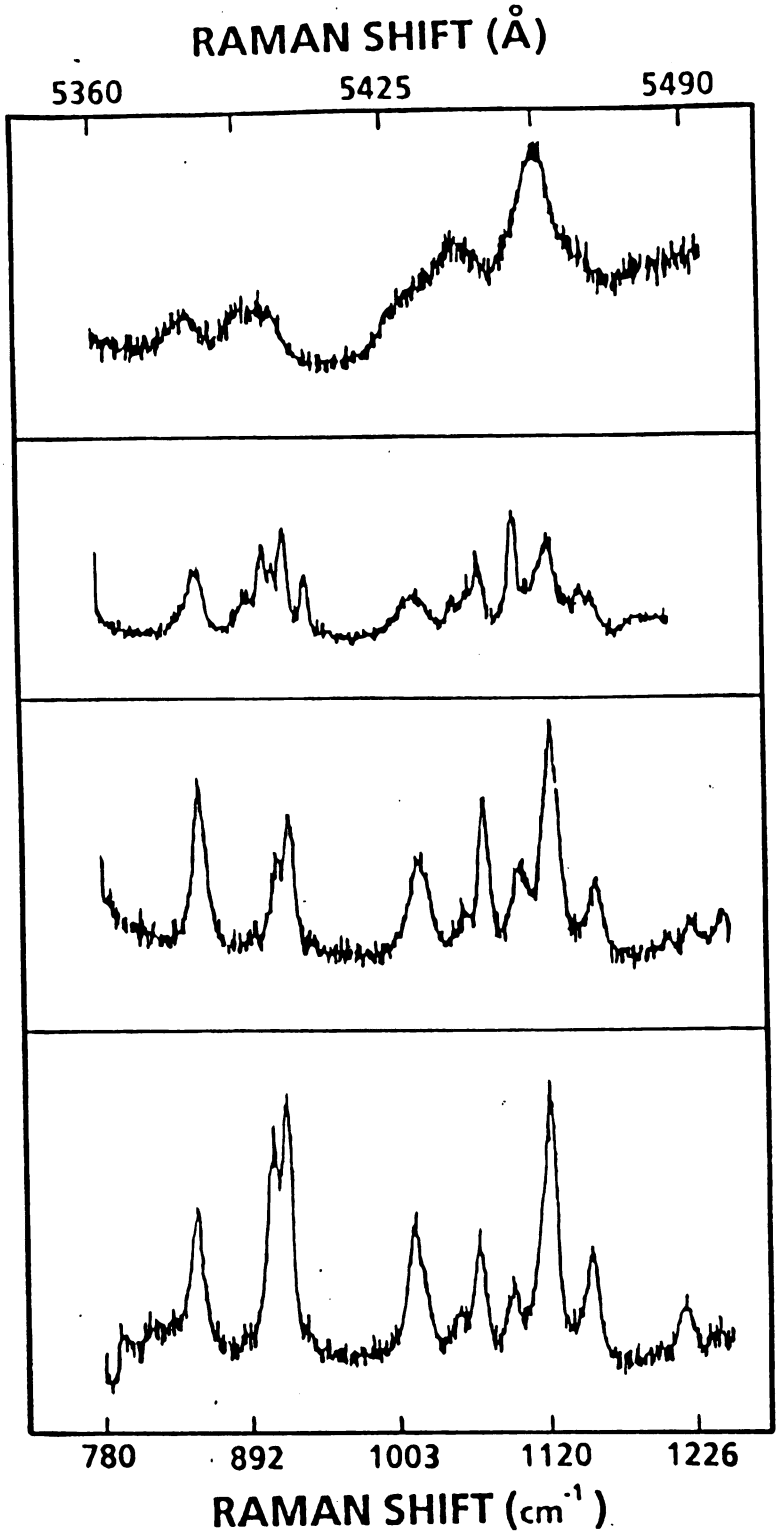

Figure 3. Raman shift of alpha anhydrous dextrose. (A) pure reagent grade, (B) parent (prism) crystal, (C) contact nuclei in situ at experimental conditions favorable to form to different phases, and (D) solution phase spectrum.

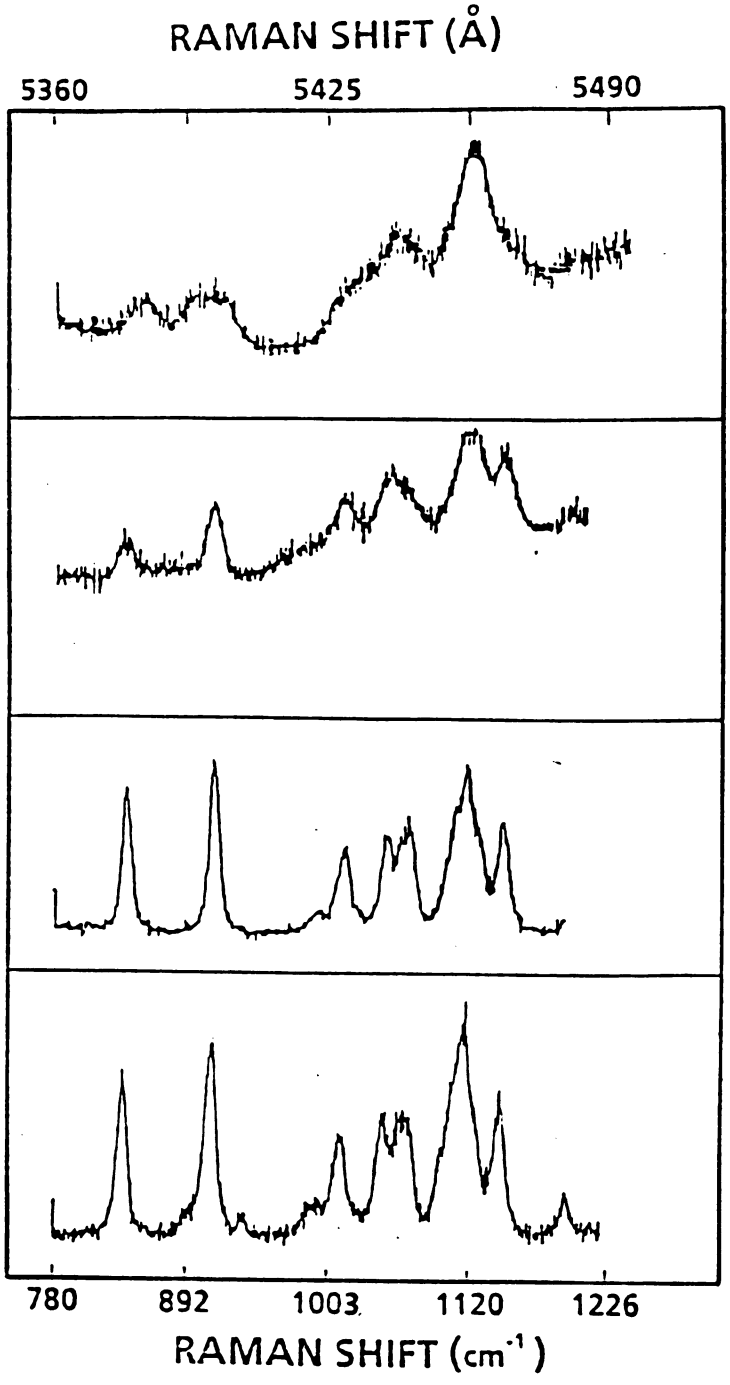

Figure 4. Raman shift of alpha monohydrate dextrose. (A) pure reagent grade, (B) parent (needle) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

Contact Nucleation From Aqueous Dextrose Solutions

by

P.Elankovan
and
K.A.Berglund

Departments of Agricultural and Chemical Engineering
Michigan State University, East Lansing, MI 48824

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Abstract

Contact nucleation studies were performed with the dextrose-water system. Under some conditions two crystallographic phases were formed, which were identified *in situ* using a laser Raman microprobe. In addition, the growth of the contact nuclei was monitored *in situ* using photomicroscopy. The results are discussed in the context of contact nucleation and growth models.

Introduction

Dextrose is the common name for D-glucose, the pure crystalline solid recovered from almost completely hydrolyzed starch. Dextrose (corn sugar, starch sugar, blood sugar, grape sugar) is by far the most abundant sugar in nature and occurs either in the free state (monosaccharide form) or chemically linked with other sugar moieties. It can exist in three different crystalline forms: alpha monohydrate, alpha anhydrous, and beta anhydrous.

Contact nucleation is the primary source of new particles in many important industrial crystallizations. The exact source of these nuclei is not precisely known. This study focused on such behavior in the important industrial process of dextrose crystallization. It was found by laser Raman microprobe that contact nuclei of both alpha monohydrate and alpha anhydrous dextrose result from the contact of an anhydrous parent crystal growing in pure solution. Under similar conditions using an industrial

syrup, only one phase formed. These studies suggest that simple breakage from the parent crystal does not explain the source of contact nuclei.

The contact nuclei of both the anhydrous and monohydrate forms of dextrose exhibit growth rate dispersion, wherein, under the same microscopic conditions crystals grow at different rates.

Review of literature

Several researchers have attempted to prepare pure dextrose from starch conversion liquor either in syrup form or as a solid mass of crystals containing the mother liquor. The solubility curves of ice, alpha monohydrate, alpha anhydrous, and beta anhydrous dextrose were determined for the temperature range from -32 to 62°C by Young (1957). The shapes of these three crystals were reported by Becke (Newkirk,1924) and the optical-crystallographic properties were determined by Dean (1974). The transitional temperature range between alpha monohydrate and alpha anhydrous in various concentrated solutions is 38 to 50°C (Dean, 1974, Edwards and Hillsdale, 1982).

Behr (1881) crystallized individual crystals of anhydrous dextrose by seeding concentrated corn starch with a small amount of very pure anhydrous dextrose crystals. The seeded mother liquor was allowed to stand without agitation in heated rooms and care was taken to exclude any traces of dextrose hydrate crystals. This process was quite

similar to that described by Soxhlet (1886).

In the early 1920's a successful commercial-scale method for production of pure dextrose monohydrate dextrose was invented by Newkirk (1936). Dextrose monohydrate crystals were produced by batch crystallization, by addition of pure dextrose monohydrate seed crystals to a starch solution at a suitable temperature. A mixture of crystals and mother liquor was formed and the crystals were separated by centrifugation. At high supersaturation, nucleation of monohydrate dextrose was increased and the formation of many small crystals increased the surface area per unit weight of crystals. These small crystals required a large amount of wash water to remove the mother liquor and decreased the yields because of dissolution of crystals during centrifugation (Edwards and Hillsdale, 1982).

The crystallization of anhydrous glucose required Successive crystalline crops (Dean and Gottfried, 1950). Newkirk (1936) also invented methods for manufacturing alpha anhydrous and beta anhydrous dextrose in a crystalline form of high purity. However, Dean and Gottfried found that the concentration of impurities in the mother liquor was too great for successful operation. On the other hand, crystallization of dextrose in the monohydrate form proceeded satisfactorily despite the presence of impurities. Another advantage of the monohydrate was stronger temperature dependence of solubility as contrasted with that for the anhydrous form (Newkirk, 1936).

Crystallization

Nucleation is the single most important phenomenon that controls the crystal size distribution. In most cases heavy suspensions do not support "high" supersaturation; therefore, homogeneous nucleation is probably insignificant. Nucleation that occurs at low supersaturations and requires the presence of growing crystals is called secondary nucleation. This has been observed to occur in carbohydrate systems and is usually referred to as "false grain"(Dean and Gottfried, 1950). In investigating the variables affecting the growth of dextrose crystals, Newkirk (1925) observed that great care was needed in cooling the mass in order to grow crystals properly without excessive formation of secondary nuclei.

Botsaris and Denk (1976) presented a comprehensive review of secondary nucleation and de Jong (1978) reviewed the progress in understanding the phenomenon of secondary nucleation. Secondary nucleation itself has been confirmed by several investigators including, Timm and Larson (1968), Bennett et al (1973), and Youngquist and Randolph (1972) when they noted the dependency of nucleation on the suspension density. The work of Randolph and Sikdar (1974) and Bauer et al(1974) also indicated that crystals were being born into a measurable (= 1-10 $m*10^{-6}$) size range.

Contact nucleation is the most important type of secondary nucleation in many industrial crystallizations.

In the work of Garside (1978), Garside (1979), and Rusli et al. (1980), the contact nucleation process was observed both with photomicroscopy and a Coulter counter. They used a contacting device in a batch crystallizer and found that a large number of microscopically visible nuclei were immediately formed with a distribution of sizes as well as some anomalous growth behavior. Gwynn et al.(1980) reported contact nucleation studies with the sucrose-water system using the Coulter counter technique. These studies confirmed that contact nucleation is the primary source of new particles and contact nuclei of sucrose have a measurable initial size distribution, not zero size as assumed in the MSMPR crystallizer model. In addition, by observing the size distribution at subsequent times they inferred size dependent growth.

Using the photomicroscopic techinque, Berglund and Larson (1982) and Shanks and Berglund (1985) studied contact nucleation in the citric acid monohydrate-water and sucrose-water systems, respectively. These studies confirmed size-independent growth rate, growth rate dispersion, and initial nuclei size distribution. A linear regression analysis of time versus size showed a constant growth rate for each crystal. Based on this premise, Ramanarayanan et al. (1982) proposed the Constant Crystal Growth (CCG) model.

The occurrence of growth rate dispersion or size dependent growth are important in modeling of growth rate dispersion. The objective of this research was to study the

growth rate and the initial size distribution of dextrose crystals to discriminate between these two phenomena. In addition, it was hoped that the study of contact nucleation would allow inferences to be made as to its mechanism.

Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy analogous to infrared (IR) spectroscopy. When visible radiation is incident on a sample, it is absorbed, transmitted, reflected, or scattered. The scattered radiation may be elastically scattered (Rayleigh scattering) at the same frequency of the incident radiation or inelastically scattered (Raman scattering) at some shifted frequency. Raman scattered light can be used to determine chemical structures by the study of molecular vibrations at characteristic frequencies.

Several features make Raman spectroscopy uniquely suited to the study of crystallization. The Raman spectrum of water does not obscure the spectrum of the dissolved species. The integrated intensity of a given Raman band is to a very good approximation linear with molar concentration of the species in solution giving rise to the band. Micro-Raman spectroscopy permits the *in situ* analysis of very small regions by focusing laser light through the objective lens of a microscope.

The laser Raman spectra of D-glucose, D-fructose, sucrose, cellobiose, maltose, and dextran for the 300 to

1500 cm^{-1} region were reported by Vasko et al (1971,1972), Cael et al. (1974), Mathlouthi and Luu(1980), and She et al. (1974), respectively. D-glucose, cellobise, maltose and dextran consist of one or more D-glucose residues. Their vibrational spectra are very similar in this region (Vasko et al, 1971). Tu et al (1978) used the advantages of laser Raman spectroscopy to study the muta-rotation of D-glucose in aqueous solutions. Recent studies using the Raman effect provided information permitting reliable characterization of the anomers of D-glucose. In the analysis of alpha-D-glucose, both as a crystalline solid and in aqueous solution, Vasko et al. (1972) obtained reasonable agreement between the calculated frequencies and those observed in the Raman spectrum.

Experimental Apparatus

Contact Nucletion

In the present study, contact nucleation experiments were performed using the same photomicroscopic technique applied to the citric acid monohydrate system by Berglund and Larson (1982). The photomicroscopic contact nucleation cell is shown in Figure 1. Experiments were conducted by first gluing a parent prism dextrose crystal (1-2 mm) to the moveable rod. Growth of large crystals of dextrose was accomplished by carefully cooling a solution of dextrose to induce nucleation, then transferring a few nuclei to a slightly undercooled solution for growth.

After the parent crystal was obtained and mounted, a dextrose solution saturated at a known temperature was added to the cell. The solution was heated to destroy any nuclei that may have been generated by transferring the solution. Heating also slightly dissolved the parent crystal, insuring that no surface irregularities formed by washing and drying remained. The solution was cooled and the parent crystal allowed to grow. When the growth of the parent crystal was proceeding in a regular manner as evidenced by well defined faces, it was slid approximately 0.5 cm. across the glass plate shown in Figure 1 to generate contact nuclei. Contact nuclei were observed after a few minutes and the nuclei were photographed at time intervals using 100X magnification by a camera-equipped microscope. Dextrose solutions saturated at three different experimental temperatures and a standard industrial syrup saturated at 318K were used in these studies.

Data Analysis

An image analyzer was used to determine the area of each crystal in the photographs. The characteristic size of each crystal was taken as the square root of the area, i.e., the geometric mean size. This is the value referred to as "size" in the subsequent discussion.

Laser Raman Spectroscopy

A laser Raman microprobe was used to identify different crystalline phases during contact nucleation. Dextrose solution was saturated at 318K, filtered through a 0.45 m

membrane, and the contact nucleation experiment was performed at 314K as described above. The solution spectrum and the contact nuclei spectra were taken at a few locations after several hours. The Raman spectra of reagent alpha monohydrate dextrose, reagent alpha anhydrous dextrose, and the parent crystals (needle and prism) were also recorded. The spectrometer used was a Spex model 1406 equipped with a photomultiplier. All samples were illuminated with the 5145 A line of a Coherent Radiation Model CR-5 Ar^+ laser using a SPEX Micramate. The recorded region was from 772 to 1221 cm^{-1} (5360 to 5490 A) at a scan speed of 0.05 A/second.

Results and Discussion

For the purpose of discussion, the well-formed crystals are designated prisms and the elongated crystals designated needles. The parent crystals (prisms) were grown at 323K with 3 degrees undercooling which promoted the formation of the anhydrous form. An anhydrous crystal (as verified by Raman spectroscopy) was contacted in all experiments which were favorable to both alpha-monohydrate and alpha-anhydrous formation. At 314K with 4 degrees undercooling two different polymorphs, needles and prisms, were observed in the pure solution and the photographs taken at two different time are shown in Figure 2. However, these two different kinds of nuclei were not obtained simultaneously in the other contact nucleation experiments, or in comparable conditions with industrial syrup. Apparently the impurities present in the industrial syrup

are important in inhibiting formation of needle crystals.

The laser Raman microprobe technique was used to identify the two different phases in pure solution at 314K and 4 degrees undercooling. The Raman shift obtained at two different locations in situ are given in Figures 3 and 4, respectively. The important differences in these figures are the Raman shifts and splits at about 918 and 1078 cm^{-1}. The band assignments for these two wavenumbers are C_1-H stretch and C-O-H deformation (Vasko et al, 1972). The additional water molecule present in alpha monohydrate forms a bond (probably a hydrogen bond) with the C-O. This bond causes splitting and shifting of the bands at these wave numbers. Upon comparison of these spectra with the others recorded for alpha monohydrate and alpha anhydrous crystals, it was concluded that there were two different growing phases present. One phase was primarily alpha monohydrate dextrose (needles) and the other was entirely alpha anhydrous dextrose (prisms). It appears that some other phase may also have been present in the needle, as suggested by Dean (1974) and evidenced by the additional band at 942 cm^{-1}. Since an anhydrous parent crystal was used in the contact and two different phases were formed, simple breakage cannot explain formation of the monohydrate phase. These results support the possibility that a semiordered layer is removed from the surface of a growing crystal in contact nucleation (Berglund and Larson (1982)). However, another possibility in the epitaxial growth of the

monohydrate phase on an anhydrous nucleus. This should not be discounted since the Raman spectra indicate that the needles are not pure monohydrate. Clearly, the mechanism is still in question.

Figures 5 and 6 show examples of size versus time plots for individual alpha monohydrate and alpha anhydrous crystals at different temperatures. The most important feature is their linearity, which indicates that each crystal grew at a constant but different rate. Each line has a correlation coefficient of at least 0.98. The intercepts of these plots also suggest that an initial size distribution may have been present. Unfortunately, it was not possible to study the genesis of the initial size distribution phenomenon due to the time resolution of this experiment. The growth rate was plotted against the apparent initial size and is presented in Figures 7, 8 and 9. The large amount of scatter in these data demonstrates little correlation between initial size and growth rate.

These results verify that the proper method to analyze the growth rate dispersion of this system is the "Constant Crystal Growth" (CCG) model. Berglund and Larson (1984) showed in their analysis of citric acid monohydrate with the CCG model that the curvature in the semilogarithmic population density versus size plot can be attributed to growth rate dispersion; the initial size distribution had a smaller effect. Figure 10 shows an increase in supersaturation causes an increase in mean growth rate of

anhydrous dextrose. It was not the purpose of this work to establish the correlation between growth rate and supersaturation. Figure 11 shows the trend between mean growth rate and variance of growth rate distribution. Faster growing crystals exhibit a larger variance of growth rate distribution. Further, these two figures indicate that growth rate dispersion may be correlated to supersaturation. To better understand or to further correleate this phenomenon, more experiments are needed.

Conclusions

1. Needle crystals are primarily alpha monohydrate and prism crystals are alpha anhydrous dextrose.
2. It is possible to form alpha monohydrate crystals by contacting alpha anhydrous parent crystals.
3. The laser Raman microprobe is a useful technique for *in situ* identification of the phases of alpha monohydrate and alpha anhydrous glucose.
4. Dextrose contact nuclei (anhydrous and monohydrate) appear to grow at a size independent rate.
5. Initial size and growth rate distributions are observed for contact nuclei of both anhydrous and monohydrate phases of dextrose.
6. The "Constant Crystal Growth" model should be used to model growth rate dispersion of contact nuclei in the dextrose water system.

Acknowledgements

This work was supported in part by the A.E. Staley Manufacturing Company. The laser Raman microprobe was provided through the National Science Foundation under grant number CPE - 8409458 and the Michigan Agricultural Experiment Station. The assistance of Dr. David Bruce of the Department of Physics and Astronomy at Michigan State University is appreciated.

Figure 1. Schematic diagram of nucleation cell (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; and (8) water inlet and outlet;

Figure 2. Typical examples of photomicrographs of contact nuclei of dextrose formed from pure solution at 314K and a supercooling of 4K. The elapsed time between photographs is 72 min. Note the two different crystals forms present.

Figure 3. Raman shift of alpha monohydrate dextrose. (A) pure reagent grade, (B) parent (needle) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

Figure 4. Raman shift of alpha anhydrous dextrose. (A) pure reagent grade, (B) parent (prism) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

Figure 5. Size versus time for alpha monohydrate dextrose contact nuclei in the dextrose-water system formed and grown at 3 degrees supercooling at 314K. Each line is for an individual crystal.

Figure 6. Size versus time for alpha anhydrous dextrose contact nuclei formed and grown at 2 degrees supercooling at 323K. Each line is for an individual crystal.

Figure 7. Growth rate versus initial size for anhydrous dextrose contact nuclei formed and grown at 314K.

Figure 8. Growth rate versus initial size for anhydrous dextrose contact nuclei formed and grown at 319K.

Figure 9. Growth rate versus initial size for anhydrous dextrose dextrose contact nuclei formed and grown at 323K.

Figure 10. Mean growth rate versus relative supersaturation for anhydrous dextrose contact nuclei formed and grown at various temperatures.

Figure 11. Variance of the growth rate distribution versus mean growth rate for dextrose contact nuclei formed and grown at various temperatures and supercoolings.

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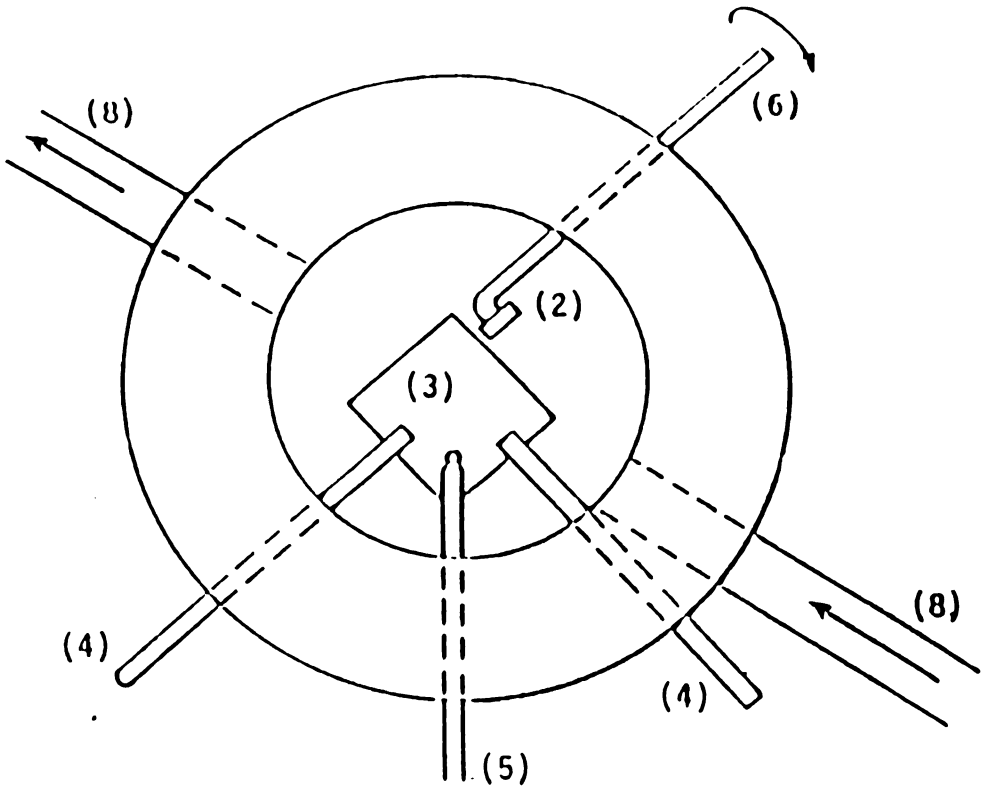
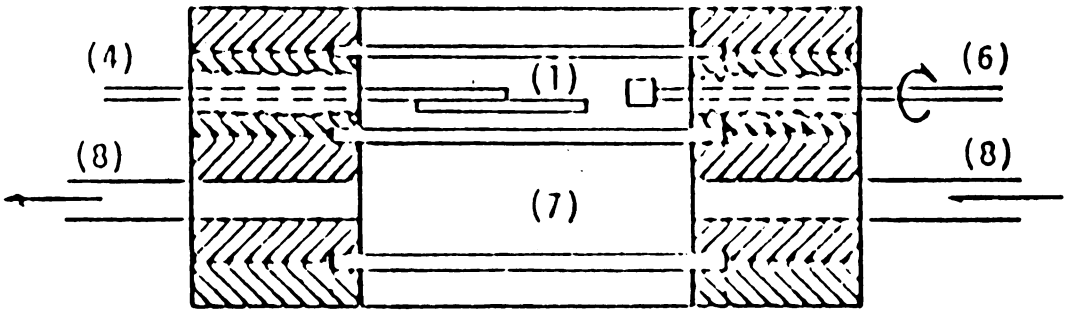


TOP VIEW



SIDE VIEW

Figure 1. Schematic diagram of nucleation cell with the features: (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; and (8) water inlet and outlet;

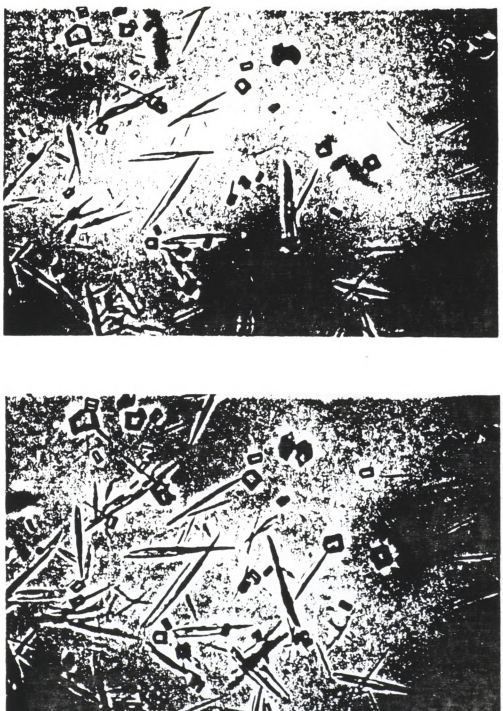


Figure 2. Typical examples of photomicrographs of contact nuclei of dextrose formed from pure solution at 314K and supercooling of 4K. The elapsed time between photographs is 72 min. Note the two different crystal forms present.

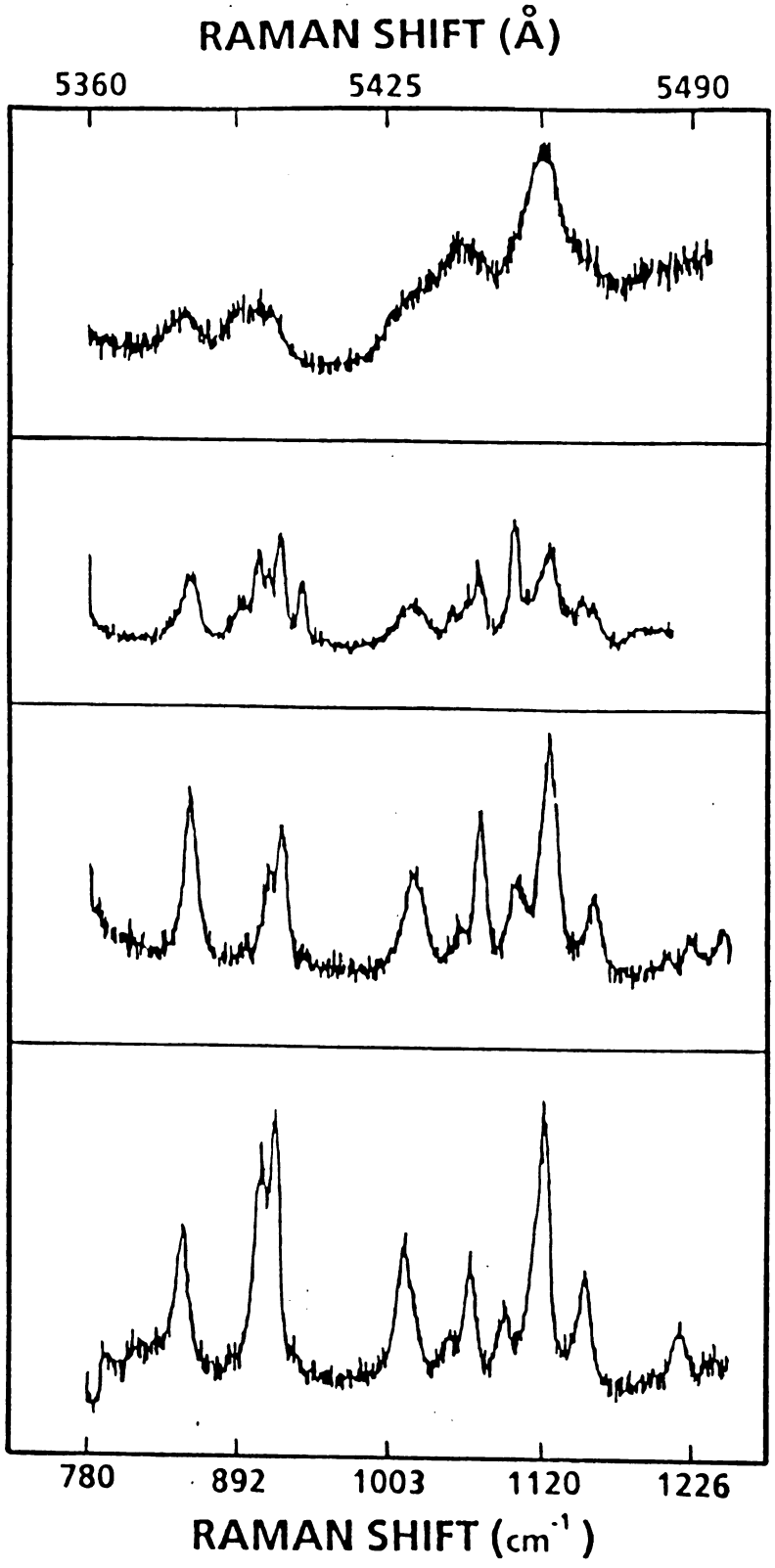


Figure 3. Raman shift of alpha anhydrous dextrose. (A) pure reagent grade, (B) parent (prism) crystal, (C) contact nuclei in situ at experimental conditions favorable to form to different phases, and (D) solution phase spectrum.

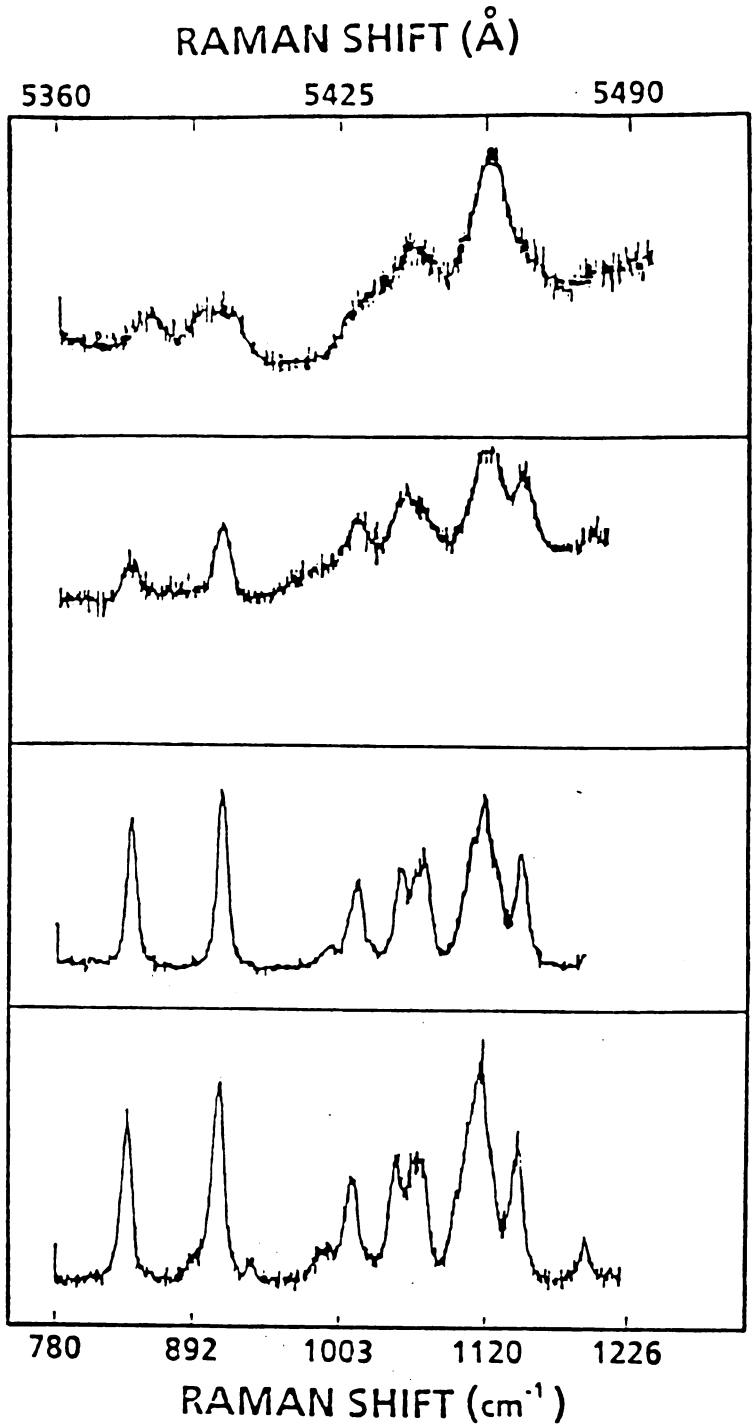


Figure 4. Raman shift of alpha monohydrate dextrose. (A) pure reagent grade, (B) parent (needle) crystal, (C) contact nuclei in situ at experimental conditions favorable to form two different phases, and (D) solution phase spectrum.

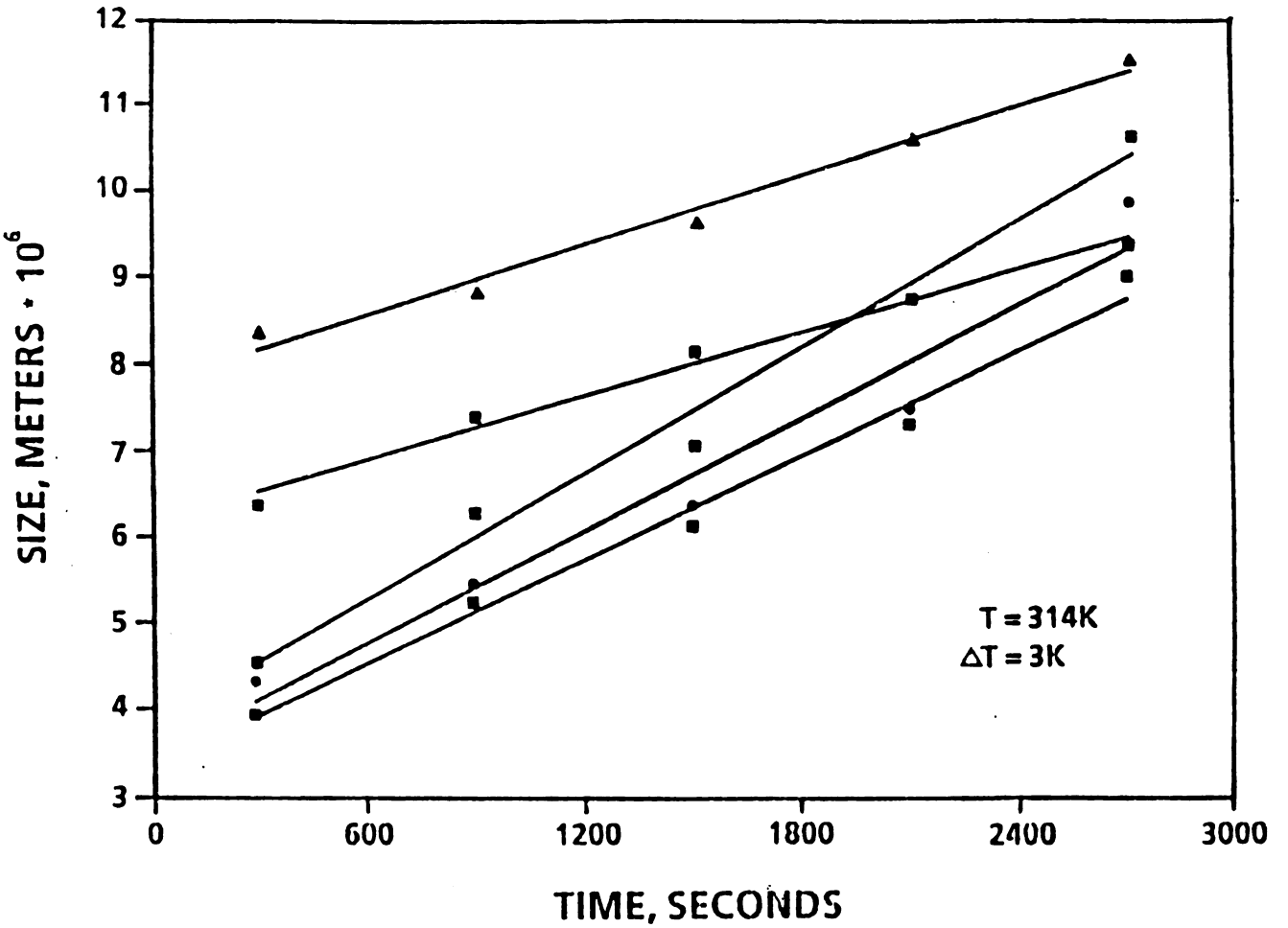


Figure 5. Size versus time for alpha monohydrate dextrose contact nuclei in the dextrose-water system formed and grown at 3 degrees supercooling at 314K. Each line for an individual crystal.

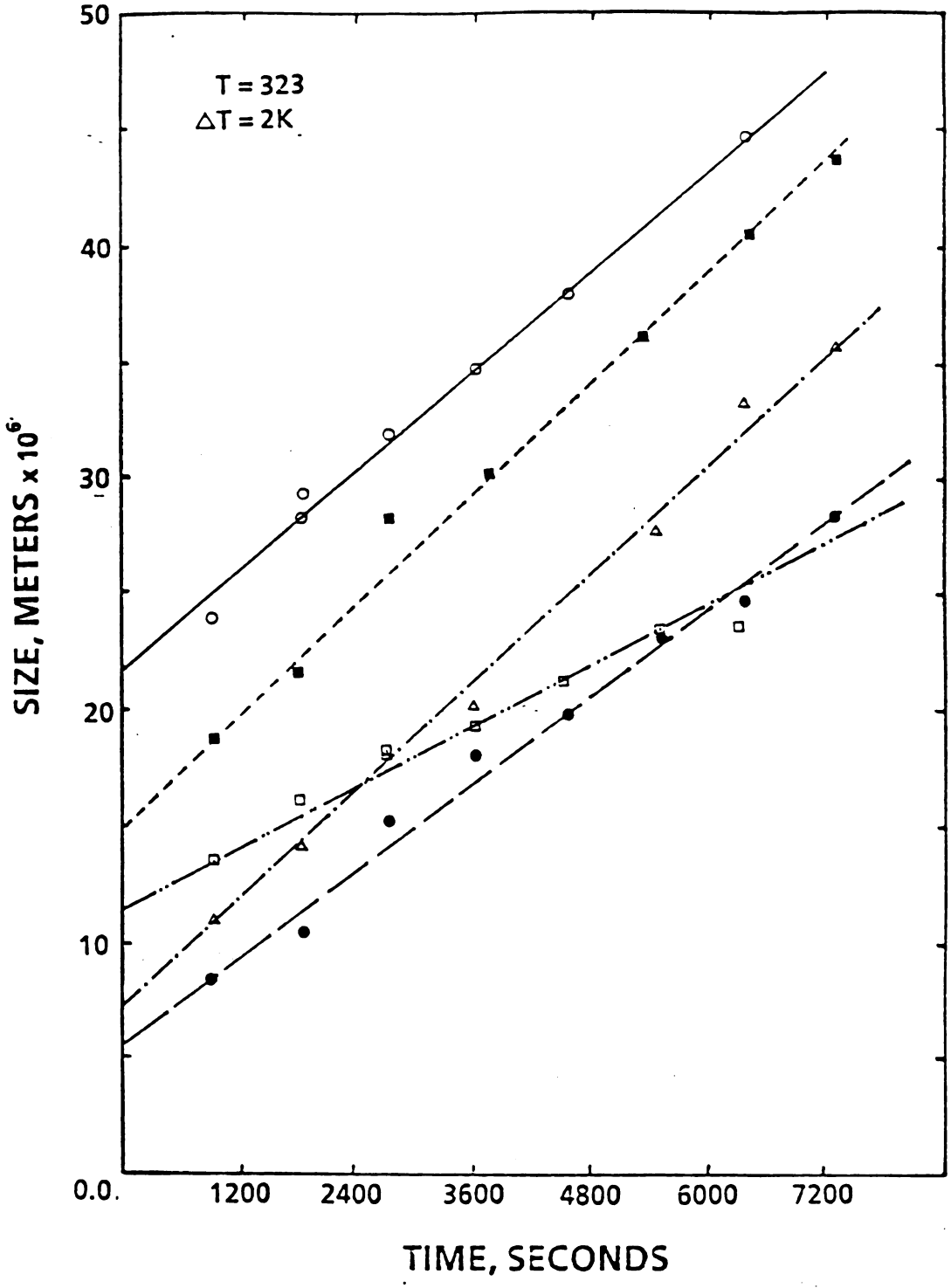


Figure 6. Size versus time for alpha monohydrate dextrose contact nuclei in the dextrose formed and grown at 3 degrees supercooling at 323K. Each line for an individual crystal.

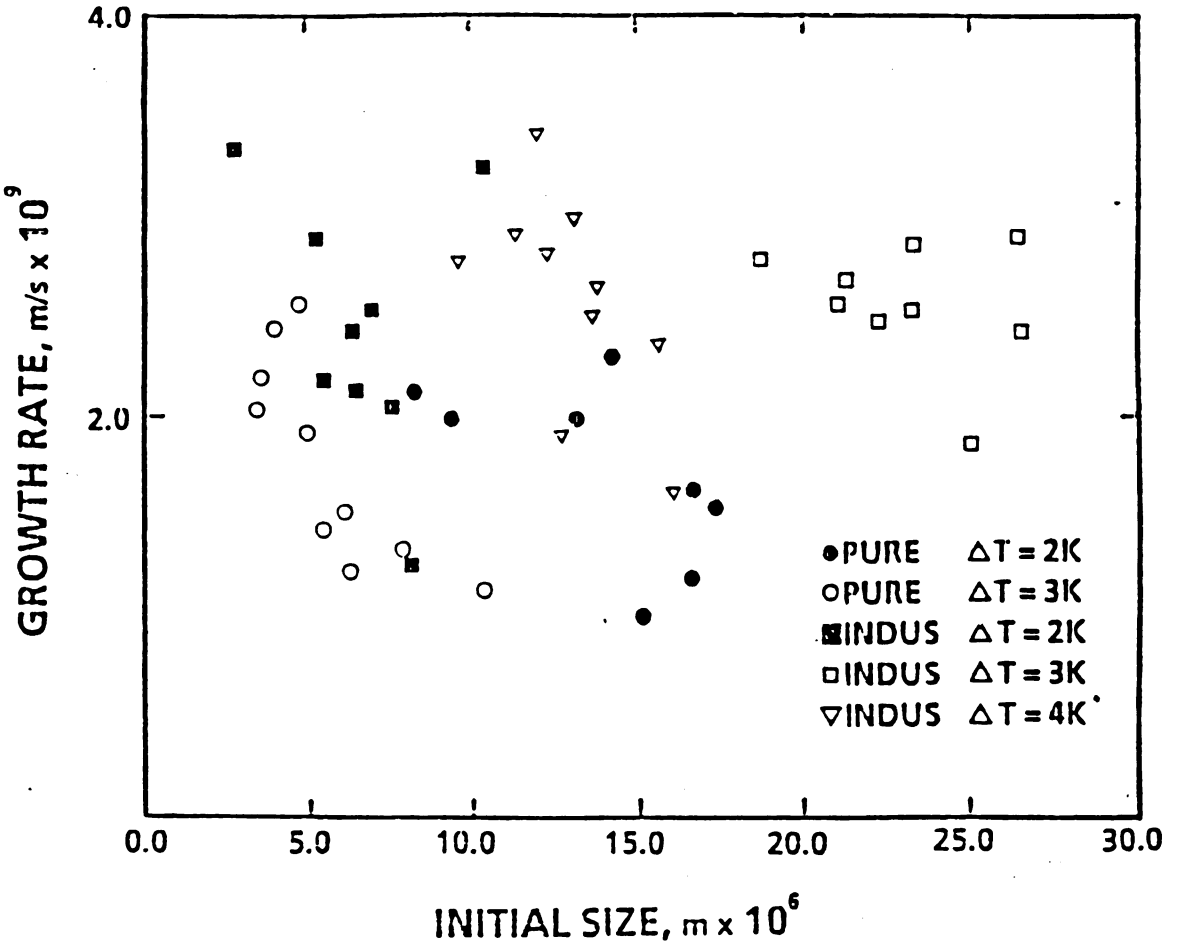


Figure 7. Growth rate versus initial size for anhydrous dextrose contact nuclei formed and grown at 314K.

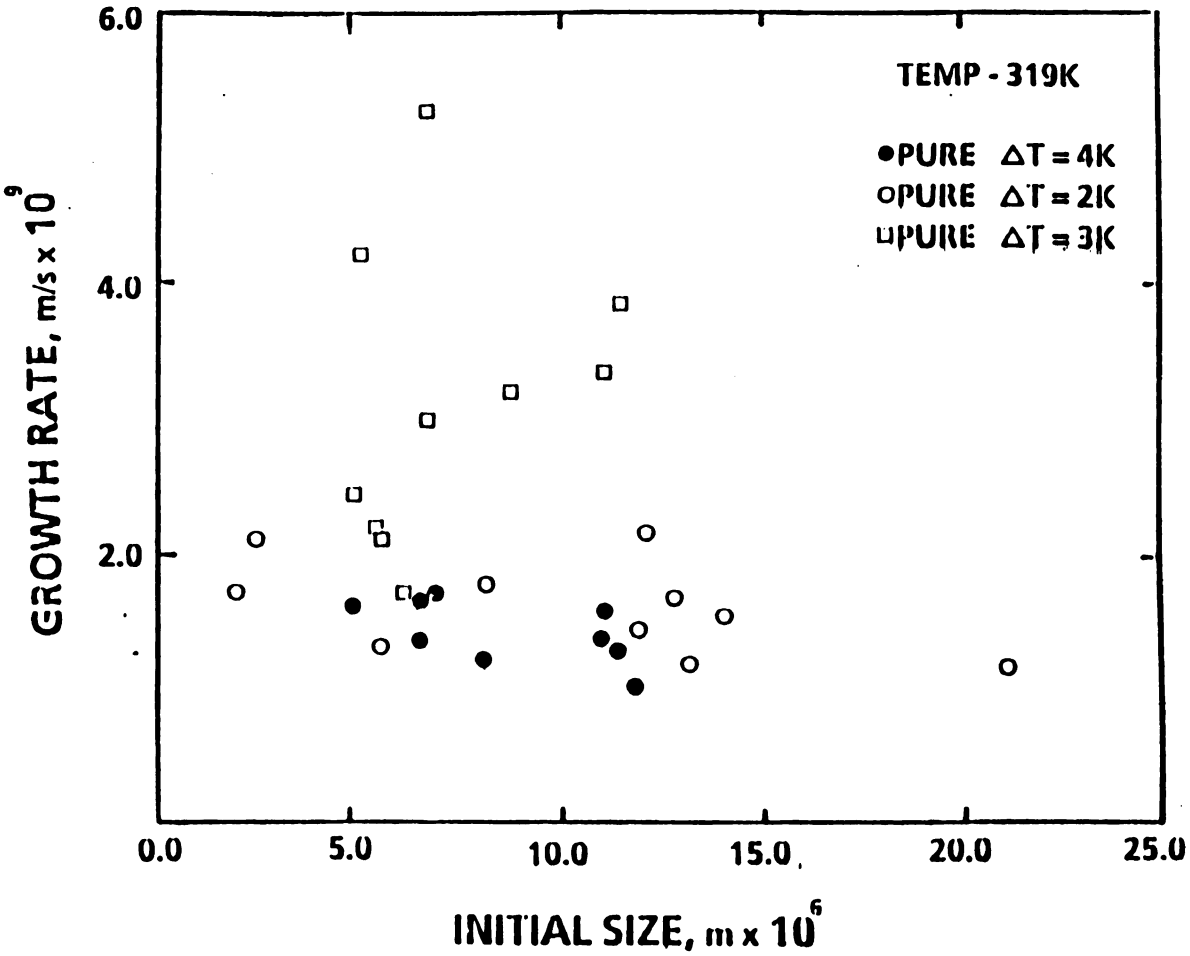


Figure 8. Growth rate versus initial size for anhydrous dextrose contact nuclei formed and grown at 319K.

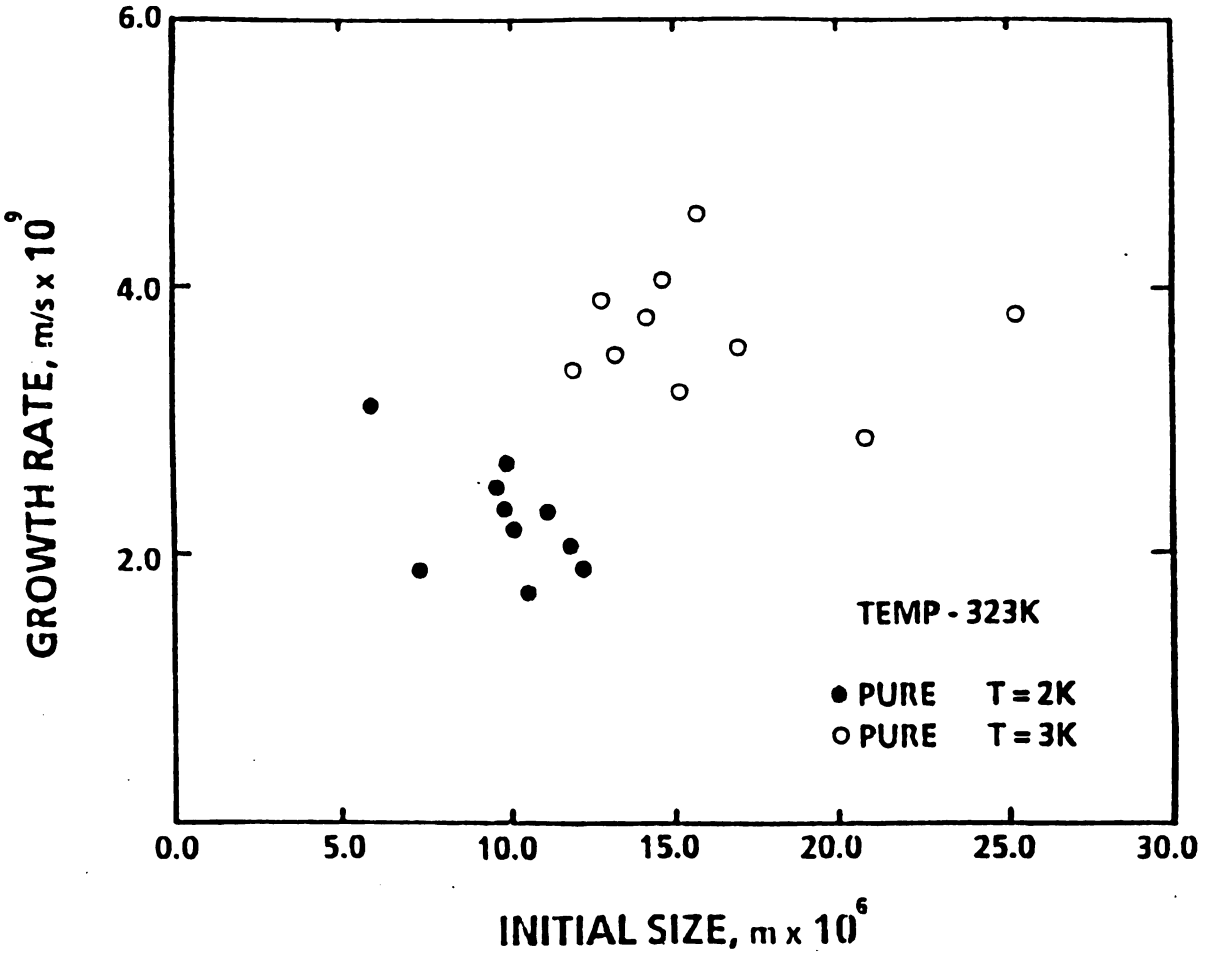


Figure 9. Growth rate versus initial size for anhydrous dextrose contact nuclei formed and grown at 323K.

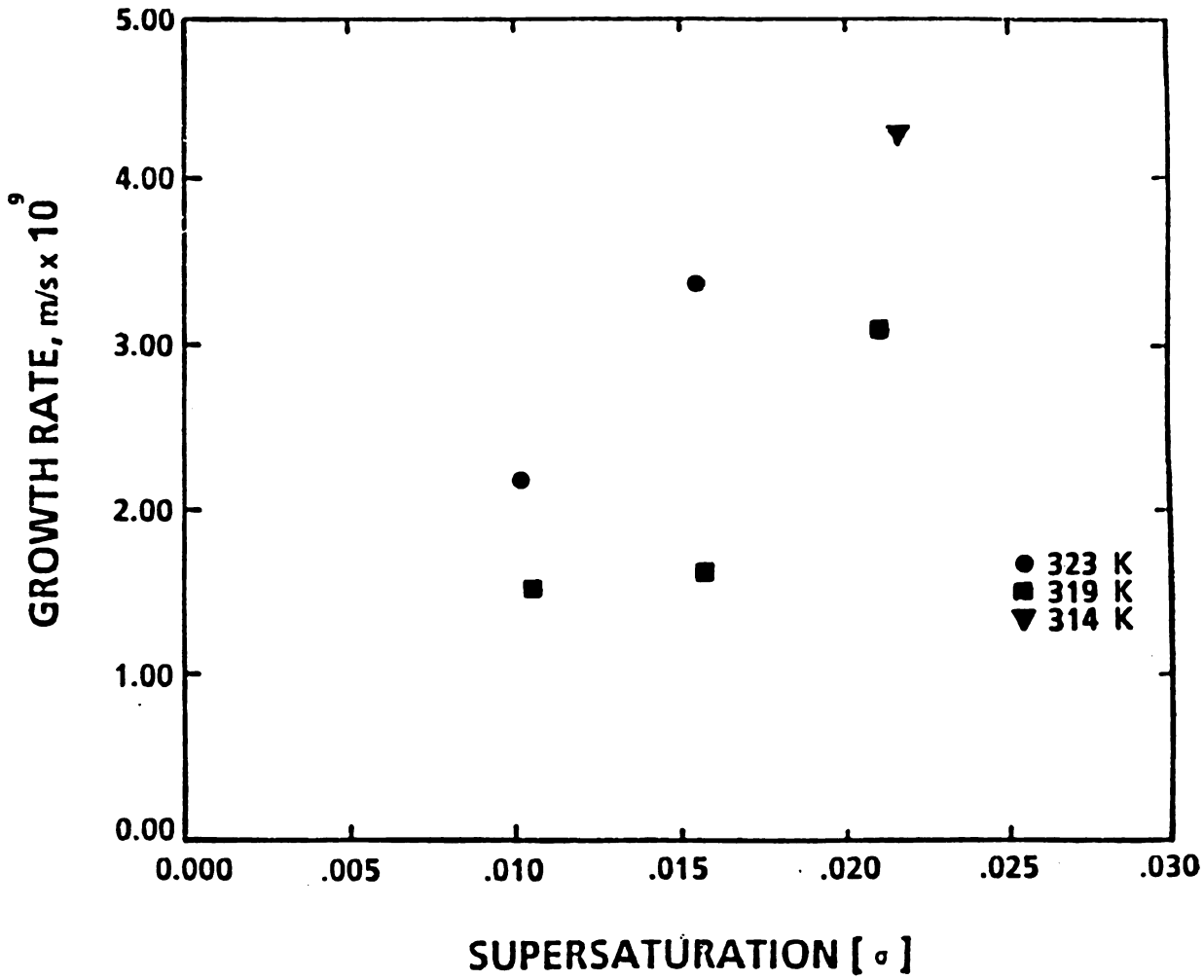


Figure 10. Mean growth rate versus relative supersaturation for anhydrous dextrose contact nuclei formed and grown at various temperatures.

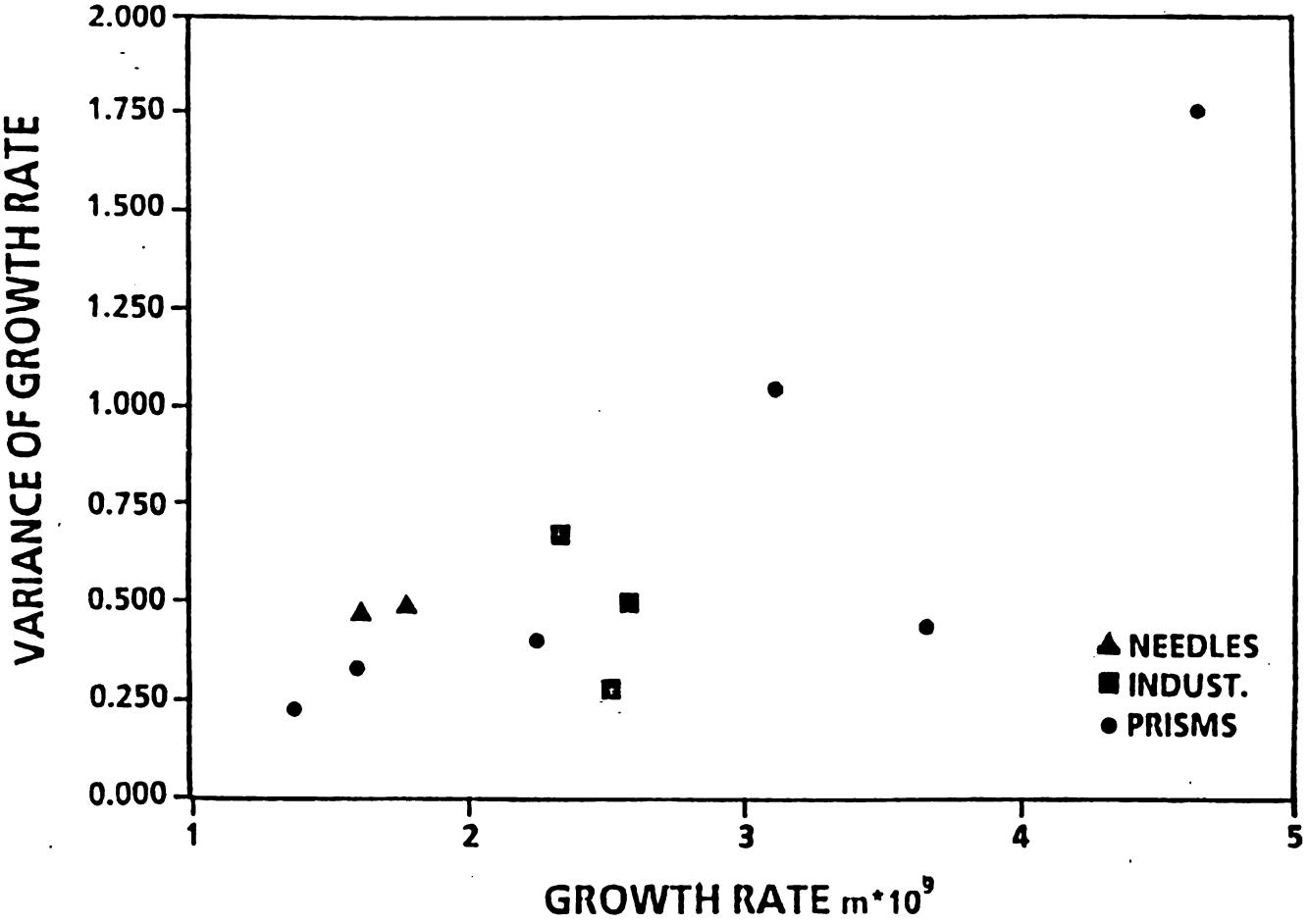


Figure 11. Variance of growth rate distribution versus mean growth rate for dextrose contact nuclei formed and grown at various temperatures and supercoolings.

0.000
0.250
0.500
0.750
1.000
1.250
1.500
1.750
2.000
AVAIANCE OF GROWTH RATE

CONCLUSIONS

1. Needle crystals are primarily alpha monohydrate and the prism crystals are alpha anhydrous dextrose.
2. It is possible to form alpha monohydrate crystals by contacting alpha anhydrous parent crystals.
3. The laser Raman microprobe technique is a useful technique for *in situ* identification of the phases of alpha monohydrate and alpha anhydrous dextrose
4. Dextrose contact nuclei appear to grow at a size independent rate.
5. Both initial size and growth rate distributions are observed for contact nuclei of dextrose in different forms.
6. The "Constant Crystal Growth" model should be used to model growth rate dispersion in the dextrose water system.
7. The variance of the growth rate distribution correlates directly to mean growth rate.
8. Contact nuclei may be formed from disruption of some "intermediate phase" rather than some sort of breakage.

SUGGESTIONS FOR FUTURE WORK

1. A photomicrographic cell should be designed to study crystal growth over longer periods of time without depletion of supersaturation.
2. A thorough study of the relationship between supersaturation and growth rate should be undertaken.
3. More contact nucleation experiments should be done to correlate variance of growth rate versus growth rate.
4. A through study of contact nucleation of dextrose with different impurities should be performed to confirm that impurities inhibit formation of needle type of dextrose crystals.
5. Use of immage analysis equipment should be automated to determine the nuclei size and growth rate of nuclei from photographs or slides.
6. The laser Raman microprobe technique should be used to quantify the polymorphs present in contact nucleation of dextrose. In particular the, possibility of mixed phase crystal formation should be studied.
7. The laser Raman microprobe technique should be used to study the formation of different polymers in other sugar systems.
8. Contact studies of dextrose monohydrate should be undertaken to see if any anhydrous dextrose can be formed.

9. More detailed studies of the surface of the growing crystal needed to detect the presence of exponential growth.
10. More studies needed to find relative growth rate of anhydrous versus monohydrate dextrose crystals.

APPENDICES

APPENDIX A. RAW DATA CRYSTAL SIZE VERSUS TIME

Appendix A: Raw data size($m*10^6$) and time

Run #1 Pure Solution - Prisms T = 314K Supersat. = 4K

Cryst. No	1800 S.	2580 S.	3120 S.	4200 S.	5220 S.
1	17.1	17.8	24.6	27.0	27.4
2	27.2	18.5	22.2	24.8	25.8
3	28.4	36.1	40.3	46.5	48.8
4	48.9	55.4	---	66.7	70.9
5	16.2	18.8	23.2	26.6	31.6
6	20.6	24.7	32.5	35.4	37.7
7	13.4	16.0	---	24.6	25.8
8	21.2	24.1	27.1	28.1	31.5
9	23.4	34.4	37.4	41.2	45.4
10	31.3	38.8	43.4	48.2	52.1
11	33.6	42.1	47.3	52.2	54.7

Run #1 Pure Solution - Needles T = 314K Supersat. = 4K

Cryst. NO	1800 S.	2580 S.	3120 S.	4200 S.	5220 S.
12	41.3	53.7	56.2	65.0	65.0
13	59.4	63.8	94.9	106	108
14	43.7	52.4	57.9	59.7	61.7
15	63.5	72.6	74.7	88.4	91.8
16	70.0	87.1	88.4	94.0	108
17	51.6	57.0	63.8	80.2	92.2
18	50.7	60.6	66.4	69.2	73.8

Run #2 Industrial Solution Sat. Temp. = 318K, Supersat. = 4K

Cryst.	900	1800	2700	3600	4500	5400 Sec.
19	12.9	19.9	21.6	24.8	26.9	29.6
20	15.8	----	19.7	22.3	25.8	26.6
21	14.9	16.0	20.6	21.6	25.0	27.0
22	14.0	19.9	----	----	27.5	27.8
23	15.9	19.1	21.4	----	26.8	27.5
24	15.5	18.5	21.8	22.9	26.1	27.3
25	16.2	21.2	22.5	24.1	25.5	----
26	13.6	15.8	18.6	19.8	20.6	22.5
27	13.0	14.1	15.7	18.9	22.5	24.8
28	12.3	17.1	19.8	22.6	----	25.7

Run #3 Pure solution Expt. Temp. = 314K, Supersat. = 2K

Cryst.	1200	2400	3600	4800	6000
29	19.2	20.2	22.9	----	26.4
30	18.4	18.8	21.0	21.9	23.8
31	17.7	19.4	20.0	25.5	28.4
32	12.6	13.5	15.8	18.3	22.3
33	18.0	20.9	23.0	----	25.9
34	15.3	18.5	18.8	19.5	20.6
35	14.1	19.0	20.9	22.7	24.2
36	10.4	13.6	15.7	16.4	21.5
37	----	17.9	18.1	19.6	21.4

Run #4 Industrial soln. Sat. Temp. = 318K, Supersat. = 2K

Cryst.	1200	1800	2400	3000	3690	4200	4800
38	10.8	----	11.7	13.8	16.8	17.3	19.4
39	9.33	10.3	11.3	----	----	13.2	----
40	8.71	11.0	----	11.7	12.5	13.5	14.0
41	8.78	10.4	11.6	----	15.3	17.6	19.2
42	14.0	15.2	18.7	20.9	----	----	25.5
43	9.92	10.8	12.6	----	14.7	16.2	----
44	8.75	10.1	11.7	---	14.8	----	16.4
45	7.79	8.58	9.58	11.0	15.6	17.3	----
46	7.08	10.3	11.1	----	12.7	14.8	15.8
47	8.59	11.3	12.0	----	14.9	15.9	18.2

Run #5 Pure Solution Expt. temp. = 314K Supersat. = 3K

Cyrst.	300	900	1500	2100	2700 S
48	10.3	11.3	12.3	12.4	13.0
49	5.82	6.96	7.63	7.33	9.83
50	4.88	7.69	8.49	9.07	11.9
51	4.31	5.45	6.38	7.50	9.86
52	5.79	6.20	7.44	8.26	10.5
53	3.93	5.24	6.13	7.32	9.02
54	6.77	7.22	7.58	8.95	10.5
55	6.36	7.40	8.14	8.76	9.37
56	8.35	8.82	9.63	10.6	11.5
57	4.53	6.28	7.07	8.85	10.6

Run #6 Industrial Soln., Sat. Temp. = 318K, Supersat. = 3K

Cryst.	900	1800	2700	3600	4500	5400	6300
58	45.7	49.3	54.5	56.3	57.6	59.3	---
59	38.3	39.3	42.7	46.2	50.3	52.1	55.3
60	31.4	33.6	35.2	37.3	38.6	43.8	42.5
61	27.9	30.5	35.2	38.1	40.2	----	41.6
62	23.0	25.7	27.9	30.4	32.2	34.4	36.1
63	21.8	24.3	28.2	30.6	34.4	36.2	37.8
64	25.7	28.0	31.2	33.8	36.5	37.9	----
65	25.7	27.5	30.4	32.8	33.6	35.9	39.7
66	26.3	28.0	30.6	32.1	33.6	34.4	----
67	28.7	31.9	32.5	33.9	36.6	42.5	----
68	23.1	26.8	29.6	32.0	34.6	36.2	38.3
69	21.2	22.7	26.1	30.3	----	32.8	35.4
70	21.7	24.7	26.5	29.8	32.2	33.0	36.7
71	24.2	26.6	28.3	32.1	----	35.1	----
72	18.3	19.2	23.6	24.5	29.0	31.9	32.7
73	23.3	25.6	28.5	31.5	33.8	35.7	36.4

Run #7 Pure Solution, Expt. Temp. = 319K, Supersat. = 2K

Cryst.	900	2400	3600	4800	6000 S
74	7.79	11.6	13.7	14.2	16.9
75	9.03	10.7	12.5	14.3	14.7
76	12.1	14.1	16.6	17.6	18.7
77	12.2	14.7	16.2	17.5	18.7
78	9.10	11.4	12.8	14.1	15.1
79	8.06	8.79	11.8	12.9	14.5
80	12.3	14.4	16.0	19.7	20.7
81	6.48	7.99	10.5	12.5	14.1
82	13.4	15.7	17.2	19.5	20.6
83	13.1	14.6	16.0	17.4	21.4
84	7.79	10.5	12.4	15.0	16.1
85	8.30	10.6	13.6	15.4	16.4
86	8.13	10.2	12.2	14.7	15.7

Run #8 Pure Solution, Expt. Temp. = 319K, Supersat. = 3K

Cryst.	900	1800	2700	3600	4500	5400
87	3.94	4.66	6.57	8.13	8.88	11.8
88	15.2	16.7	19.0	19.8	21.1	22.2
89	13.0	16.0	17.3	17.9	18.5	18.7
90	3.66	6.98	7.99	10.2	12.2	13.3
91	22.6	24.5	26.0	26.7	29.5	30.5
92	12.9	14.9	16.1	16.6	17.6	20.1
93	9.44	11.4	13.3	14.6	16.0	17.3
94	14.4	15.0	19.4	20.5	22.0	23.7
95	14.4	15.8	17.5	19.2	19.8	22.1
96	6.77	7.69	9.41	10.5	11.6	12.8

Run #9 Pure Solution, Expt. Temp. = 319K, Supersat. = 4K

Cryst.	100	820	1540	2260	2980 S
97	11.3	13.5	15.7	19.2	20.7
98	5.83	7.87	8.91	9.85	11.1
99	11.7	15.3	17.4	19.6	23.3
100	5.65	6.09	7.62	8.73	9.15
101	5.80	7.15	8.39	9.56	12.1
102	6.84	9.34	11.2	13.0	15.7
103	4.76	7.10	8.87	9.95	12.1
104	5.94	7.05	8.27	10.1	12.2
105	8.72	11.7	13.8	16.2	17.9
106	7.08	12.3	14.3	17.2	23.6
107	5.88	7.89	12.1	13.4	18.3

Run #10 Pure Solution, Expt. Temp. = 323K, Supersat. = 2K

Cryst.	900	1800	2700	3600	4500	5400	6300	7200S
108	23.2	27.9	31.5	34.6	37.8	44.0	44.6	52.2
109	13.9	15.1	17.5	19.3	20.0	22.4	25.1	26.8
110	9.89	10.3	11.3	13.9	16.1	----	19.1	----
111	11.1	14.0	18.3	20.1	----	27.6	33.2	35.5
112	12.0	----	15.6	16.7	17.9	19.3	21.2	23.2
113	10.8	13.4	17.3	19.4	----	22.3	24.0	25.7
114	13.4	16.2	17.7	----	20.9	23.1	27.3	----
115	12.8	13.9	17.8	19.1	21.9	23.6	7.2	----
116	8.4	10.4	15.1	17.8	19.5	22.9	24.5	28.1
117	18.5	21.0	28.2	30.3	34.3	36.5	40.0	42.5
118	12.1	17.1	---	18.4	21.4	---	24.0	25.2
119	----	13.6	17.0	----	20.8	23.9	24.6	----
120	12.0	13.8	15.6	16.9	20.1	----	23.6	----
121	13.4	16.8	21.7	23.4	29.1	31.1	34.3	36.1

Run #11 Pure Solution, Expt. Temp. = 323K, Supersat. = 3K

Cryst.	900	1800	2700	3600	4500	5400	6300	7200S
122	14.9	19.5	20.6	----	25.3	----	30.1	33.8
123	15.2	19.2	24.2	29.1	31.6	34.2	36.1	40.8
124	16.6	19.8	22.3	25.8	29.5	32.2	36.4	38.2
125	23.8	25.4	28.6	32.1	34.7	36.9	37.3	42.6
126	29.5	32.6	35.1	37.9	----	47.3	49.2	52.9
127	16.8	22.7	26.3	29.6	33.2	35.5	39.5	43.4
128	12.3	16.5	20.3	----	22.3	23.5	24.4	----
129	15.5	18.8	22.7	26.8	27.4	----	30.9	33.0
130	16.1	19.3	20.2	24.5	27.2	29.5	31.5	33.4
131	17.3	20.4	24.5	29.8	31.0	33.9	37.7	41.3
132	14.1	19.5	20.9	24.0	27.9	31.4	32.2	----
133	16.2	20.6	24.2	28.3	31.8	33.7	34.7	36.3
134	20.6	23.1	26.8	29.0	34.1	----	39.0	43.1
135	18.9	23.5	27.3	33.9	38.8	----	----	46.8

APPENDIX B. APPARENT INITIAL SIZE AND GROWTH RATE OF CONTACT NUCLEI OF DEXTROSE.

Appendix B. Apparent initial size and growth rate of contact nuclei of dextrose.

Run #	Under cooling K	Crystal	Initial size $m*10^6$	Growth rate $m*10^9/s$	Correlation coefficient
1	4	1	11	3.4	0.92
		2	12	2.7	0.96
		3	20	5.9	0.97
		4	38	6.5	0.99
		5	7.9	4.5	0.99
		6	13	5.1	0.95
		7	6.5	3.9	0.98
		8	17	2.8	0.98
		9	17	5.8	0.94
		10	23	5.9	0.98
		11	26	6.0	0.96
		12	34	6.3	0.94
		13	29	17	0.94
		14	37	4.8	0.90
		15	49	8.5	0.98
		16	56	9.9	0.96
		17	27	12	0.99
		18	43	6.3	0.95
2	4	19	12	3.4	0.97
		20	13	2.5	0.99
		21	12	2.8	0.99
		22	13	3.0	0.97
		23	16	1.6	0.97
		24	14	2.6	0.99
		25	16	2.4	0.95
		26	12	1.9	0.98
		27	9.4	2.8	0.98
		28	11	2.9	0.97
3	2	29	17	1.6	0.99
		30	16	1.2	0.98
		31	14	2.3	0.96
		32	9.3	2.0	0.97
		33	17	1.6	0.98
		34	15	2.0	0.92
		35	13	1.9	0.96
		36	8.0	2.1	0.97
		37	15	1.0	0.95

Appendix B Continued

Run #	Under cooling K	Crystal	Initial size $m*10^6$	Growth rate $m*10^9/s$	Correlation coefficient
4	2	38	6.8	2.6	0.97
		39	8.0	1.3	0.99
		40	7.8	1.3	0.97
		41	5.1	2.9	0.99
		42	10	3.3	0.99
		43	7.3	2.1	0.99
		44	6.3	2.2	0.99
		45	2.7	3.3	0.96
		46	5.4	2.0	0.97
		47	6.1	2.4	0.99
5	3	48	10	1.1	0.97
		49	5.3	1.5	0.94
		50	4.5	2.6	0.96
		51	3.4	2.2	0.98
		52	4.7	1.9	0.96
		53	3.2	2.0	0.99
		54	5.9	1.5	0.96
		55	6.1	1.2	0.99
		56	7.7	1.4	0.99
		57	3.8	2.5	0.99
6	3	58	44	3.0	0.97
		59	34	3.5	0.99
		60	29	2.4	0.98
		61	26	2.8	0.97
		62	21	2.5	0.99
		63	19	3.2	0.99
		64	23	2.8	0.99
		65	23	2.5	0.98
		66	25	1.9	0.99
		67	26	2.4	0.97
		68	21	2.8	0.99
		69	19	2.8	0.99
		70	19	2.8	0.99
		71	22	2.5	0.99
		72	15	3.0	0.99
		73	21	2.7	0.99

Appendix B. Continued

Run #	Under cooling K	Crystal	Initial size $m*10^6$	Growth rate $m*10^9/s$	Correlation coefficient
7	2	74	6.9	1.7	0.98
		75	8.0	1.2	0.99
		76	11	1.3	0.99
		77	11	1.3	0.99
		78	8.3	1.2	0.99
		79	6.5	1.3	0.98
		80	10	1.9	0.99
		81	4.8	1.5	0.99
		82	12	1.5	0.99
		83	11	1.5	0.96
		84	6.4	1.7	0.99
		85	6.7	1.6	0.99
		86	12	1.0	0.99
8	3	87	1.2	1.7	0.98
		88	14	1.5	0.99
		89	13	1.2	0.91
		90	2.5	2.1	0.99
		91	21	1.2	0.99
		92	12	1.4	0.98
		93	8.2	1.7	0.99
		94	12	2.2	0.98
		95	13	1.7	0.99
		96	5.5	1.4	0.99
9	4	97	11	3.3	0.99
		98	6.1	1.7	0.99
		99	11	3.8	0.99
		100	5.4	1.3	0.99
		101	5.4	2.1	0.99
		102	6.6	3.0	0.99
		103	4.8	2.4	0.99
		104	5.4	2.2	0.99
		105	8.8	3.2	0.99
		106	6.8	5.3	0.99
		107	5.0	4.3	0.99

Appendix B. Continued

Run #	Under cooling K	Crystal	Initial size $m*10^6$	Growth rate $m*10^9/s$	Correlation coefficient
10	2	108	19	4.3	0.99
		109	12	2.0	0.99
		110	7.4	1.8	0.98
		111	7.0	4.0	0.99
		112	10	1.7	0.99
		113	9.9	2.3	0.98
		114	11	2.3	0.98
		115	10	2.6	0.99
		116	5.8	3.1	0.99
		117	15	3.9	0.99
		118	12	1.9	0.97
		119	9.7	2.4	0.99
		120	9.9	2.2	0.99
		121	10	3.7	0.99
11	3	122	13	2.8	0.99
		123	12	3.9	0.99
		124	13	3.5	0.99
		125	21	2.9	0.99
		126	25	3.8	0.99
		127	15	4.0	0.99
		128	12	2.1	0.95
		129	15	2.7	0.98
		130	14	2.8	0.99
		131	14	3.7	0.99
		132	12	3.4	0.99
		133	15	3.2	0.98
		134	17	3.6	0.99
		135	16	4.5	0.98

APPENDIX C1. PHYSICAL PROPERTIES OF D-GLUCOSE.

C2. CONDITIONS OF EXPERIMENTAL RUNS WITH NUMBER OF NUCLEI ANALYZED.

C3. MEAN GROWTH RATE, VARIANCE OF GROWTH RATE DISTRIBUTION AND RELATIVE SUPERSATURATION AT DIFFERENT CONDITIONS.

C4. LINEAR REGRESSION OF GROWTH RATE VERSUS APPARENT INITIAL SIZE.

Table 1. Physical Properties of D-glucose.

Property	Alpha monohydrate glucose	Alpha anhydrous glucose	Beta anhydrous glucose
molecular formula	$C_6H_{12}O_6 \cdot H_2O$	$C_6H_{12}O_6$	$C_6H_{12}O_6$
melting pt	356 K	419 K	423 K
solubility (g/100g soln.)	32.2-51.2[a,b]	62,30.2-51.2[a]	72-51.2[a]
$[\alpha]^{20}_{D}$	112.2-52.7[a,b]	112.2-52.7[a]	18.7-52.7[a]
heat of soln. (J/g.)	-105.4	-59.4	-25.9

a- Equilibrium value

b- Anhydrous basis

[Kirk - Othmer, 1985]

Table 2. Conditions of experimental runs and number of nuclei analyzed

Run	Super cooling K	Temperature K	Number of nuclei analyzed
1	4	314	18
2	4_I	314	10
3	2	314	9
4	2_I	316	10
5	3	314	10
6	3_I	315	16
7	2	319	13
8	3	319	10
9	4	319	11
10	2	323	14
11	3	323	14

I - Industrial solution

Table 3. Mean growth rate, Variance of growth rate distribution and Relative supers

Tempt. K	Super cooling K	Mean growth rate $m*10^9/s$	Variance $m*^9/s$	Relative supersat. $*10^2$
Prisms				
314	4	4.8	1.723	2.15
319	2	1.4	0.049	1.07
319	3	1.6	0.106	1.59
319	4	3.1	1.081	2.11
323	2	2.7	0.724	1.04
323	3	3.3	0.394	1.57
Needles				
314	2	1.7	0.168	1.07
314	3	1.8	0.241	1.61
Idustrial solution				
316	2	2.3	0.442	1.60
315	3	2.7	0.132	1.61
314	4	2.6	0.494	2.15

Table 4. Linear regression of growth rate versus apparent initial size

Temp. K	Super cooling K	Slope $m*10^6/s$	Intercept $m*10^6/s$	Correlation coefficient
Prisms				
314	4	0.10	3.00	0.66
319	2	0.03	1.72	0.31
	3	0.02	1.89	0.48
	4	0.18	1.71	0.37
323	2	0.10	1.65	0.39
	3	0.04	2.76	0.21
Needles				
314	2	0.11	3.07	0.56
	3	0.19	2.53	0.18
Industrial solution				
316	2	0.11	3.07	0.32
315	3	0.01	2.53	0.18
314	4	0.15	4.62	0.59

APPENDIX D1. EXAMPLES OF SIZE VERSUS TIME FOR ALPHA ANHYDROUS DEXTROSE CONTACT NUCLEI FORMED AND GROWN AT 2 DEGREES OF SUPERCOOLING AT 319K.

D2. EXAMPLES OF SIZE VERSUS TIME FOR ALPHA ANHYDROUS DEXTROSE CONTACT NUCLEI FORMED AND GROWN AT 3 DEGREES OF SUPERCOOLING AT 319K.

D3. EXAMPLES OF SIZE VERSUS TIME FOR ALPHA ANHYDROUS DEXTROSE CONTACT NUCLEI FORMED AND GROWN AT 4 DEGREES OF SUPERCOOLING AT 319K.

D4. EXAMPLES OF SIZE VERSUS TIME FOR ALPHA ANHYDROUS DEXTROSE CONTACT NUCLEI FORMED AND GROWN AT 3 DEGREES OF SUPERCOOLOING AT 323K.

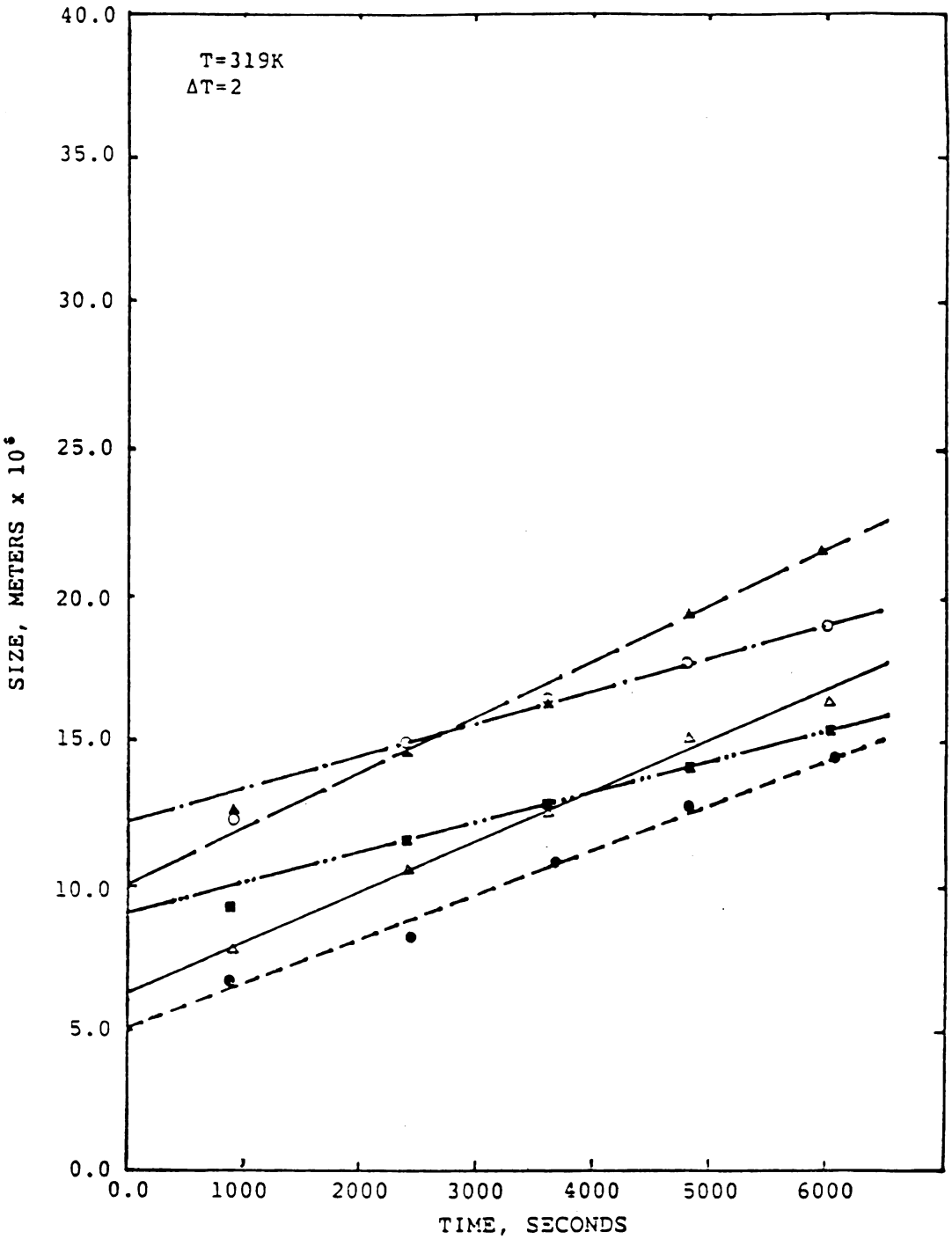


Figure 12. Size versus time for alpha anhydrous dextrose contact nuclei formed and grown at 2 degrees supercooling at 319K. Each line is for an individual crystal.

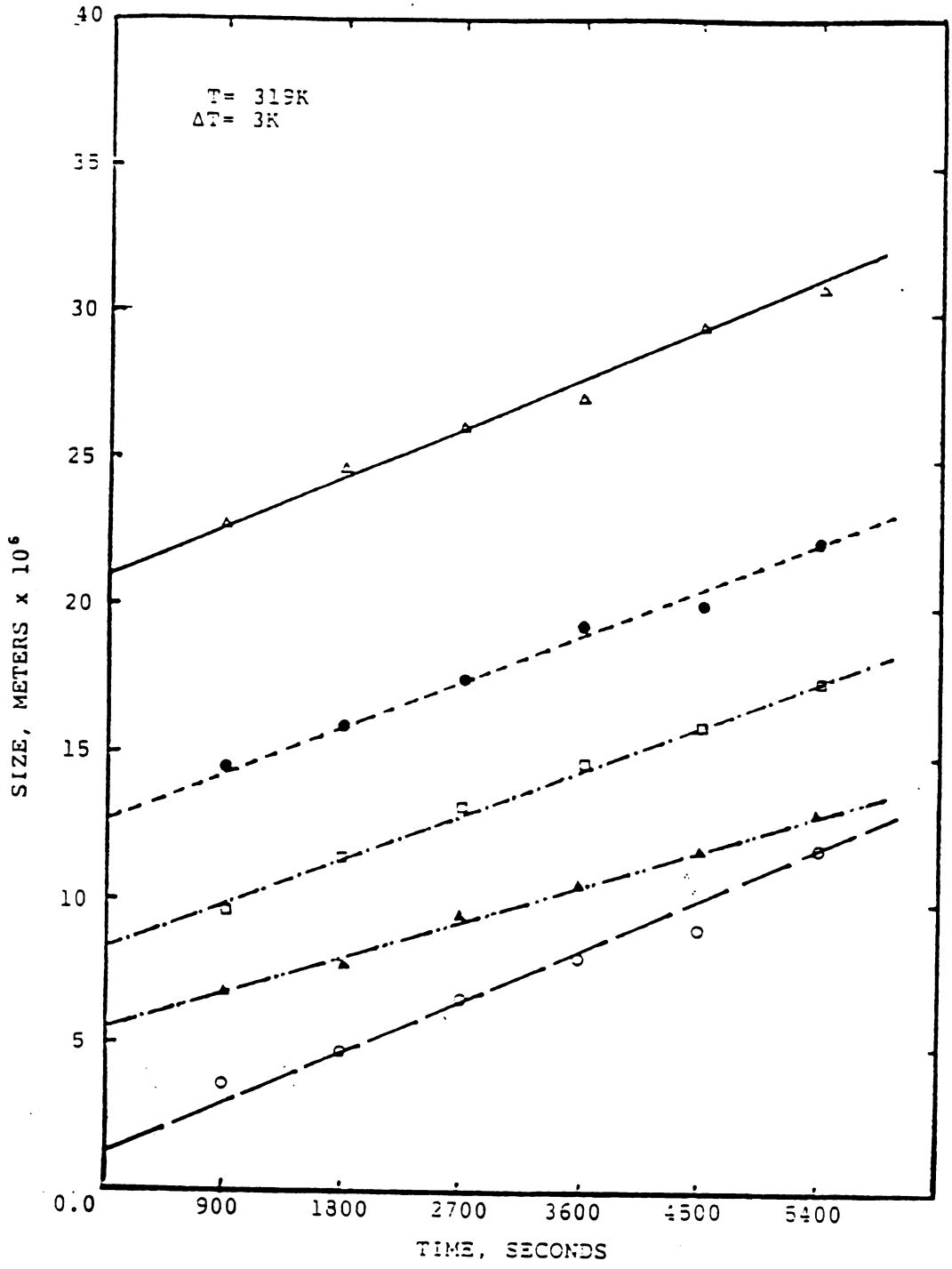


Figure 13. Size versus time for alpha anhydrous dextrose contact nuclei formed and grown at 3 degrees supercooling at 319K. Each line is for an individual crystal.

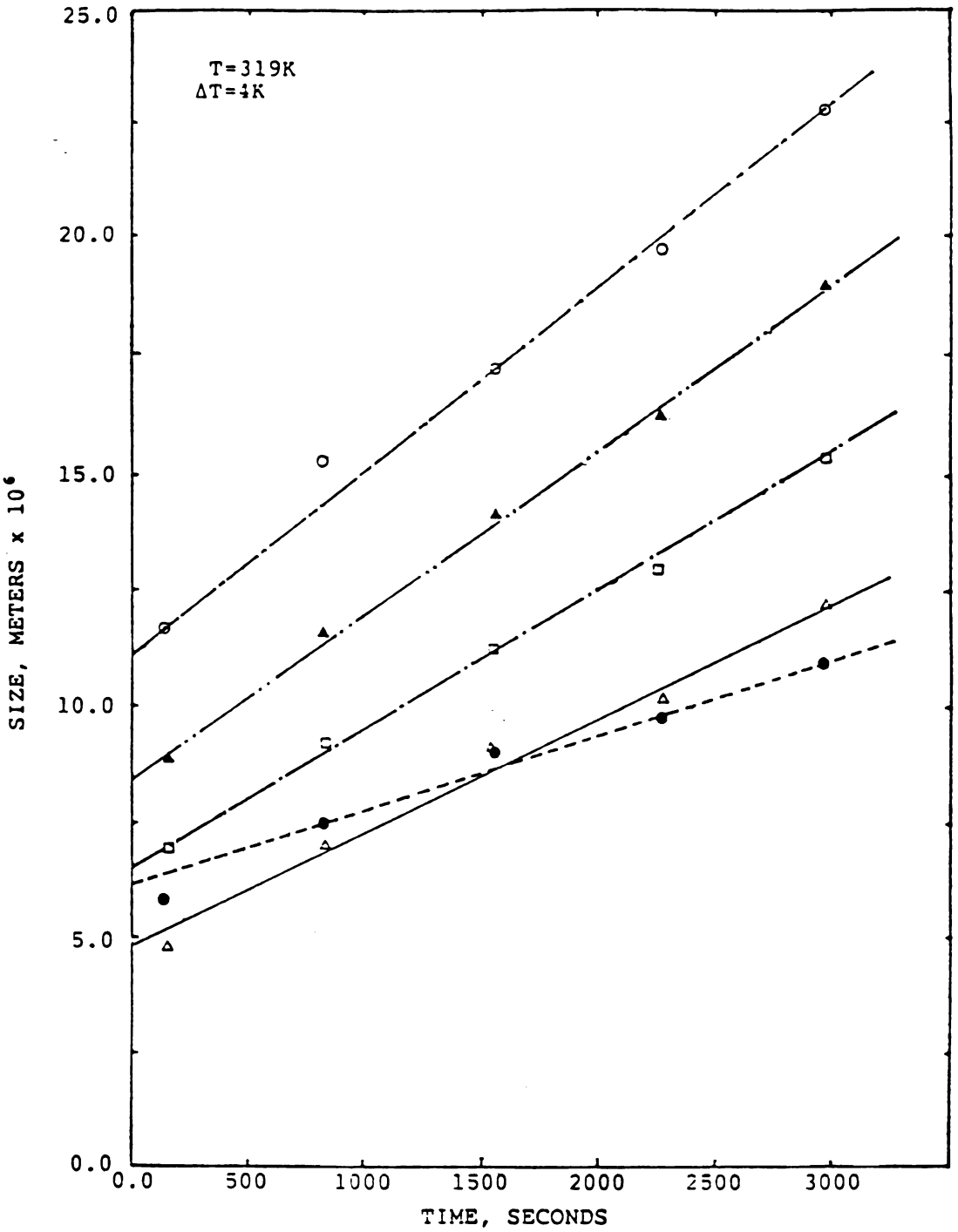


Figure 14. Size versus time for alpha anhydrous dextrose contact nuclei formed and grown at 4 degrees supercooling at 319K. Each line is for an individual crystal.

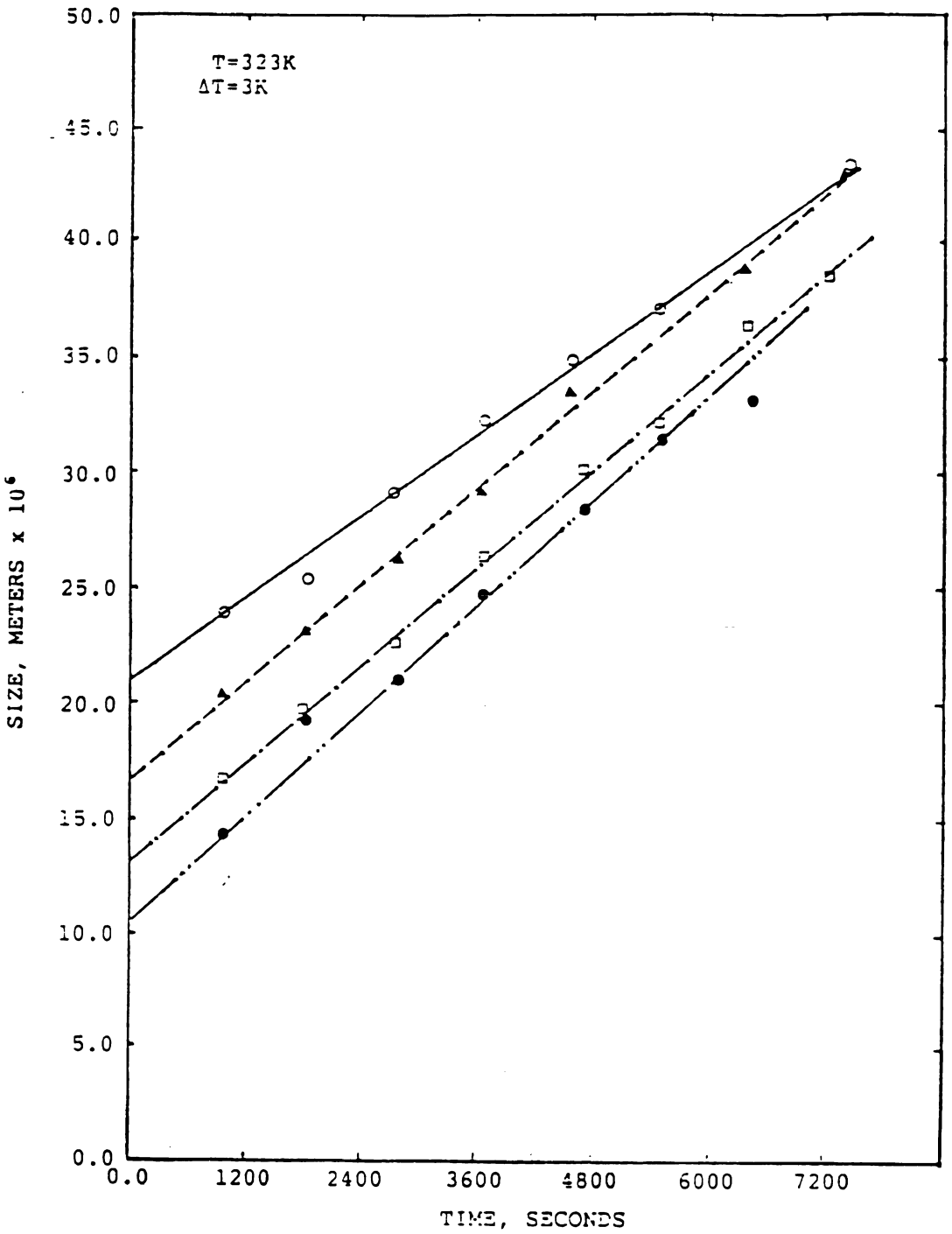


Figure 15. Size versus time for alpha anhydrous dextrose contact nuclei formed and grown at 3 degrees supercooling at 323K. Each line is for an individual crystal.

APPENDIX E. DETAIL DESCRIPTION OF EXPERIMENTAL PROCEDURE.

Appendix E: Materials and Methods

Contact nucleation cell

In the present study, contact nucleation experiments were performed using the same photomicroscopic technique applied to the citric acid monohydrate system by Berglund and Larson (1982). The photomicroscopic contact nucleation cell used in this study is shown in Figure 1 and is similar to the design presented by Berglund (1981). The cell has two different chambers: an upper 5 ml chamber for solution, and a lower 8 ml chamber for water circulation to control temperature. The cell was enclosed with three rounded quartz glass plates which allow the transmitted light to pass through the solution and also to view the nuclei. Two stainless steel rods which held the glass cover slip, a movable rod which held the parent crystal, and a thermistor at the same level of the cover slip were mounted in the upper chamber.

An American Optical model 110 microscope equiped with lenses for 100X magnification was used. The microscope was equiped with a 35 mm Olympus camera in which Kodak EL - 135 color slide film was used. The thermistor for measurement of the solution temperature was connected to an Omega digital temperature indicator, model 410B. The accuracy of the thermistor is $0.27^{o}F$ and of the digital indicater is $0.40^{o}F$. Temperature measurements were precise to $0.01^{o}F$. Water was

circulated to the lower chamber from a Fisher water bath, model 80, which allowed temperature control in the upper chamber of the cell precise to 0.05^{o}F.

Solution preparation

Experiments were conducted at 308, 314, 319 and 322K, and saturated solutions were prepared at different temperatures to provide 0, 2, 3 and 4 degrees of supercoolings. These solutions were saturated by placing a large excess of glucose monohydrate from A.E. Staley manufacturing company in distilled - deionized water while stirring continuously. The solutions were placed in a 35 liter water bath equipped with Haake E2 circulators to control the temperature. The solutions were kept in this manner for at least 72 hours. Approximately 10 ml of this saturated solution was withdrawn from the flask and filtered through a Gelman Acrodise disposable filter No 4184, 0.45 microns, into the preheated nucleation cell for each run.

Parent crystal preparation

A new parent crystal was needed for each experimental run. Typically these parent crystals were 1 to 2 mm in size. A major obstacle that was overcome was the ability to grow such large crystals of dextrose. This was accomplished by carefully cooling a solution of dextrose to induce nucleation, then transforming a few nuclei to a slightly undercooled solution for growth. Parent crystals

were prepared at 308 and 323 K and alpha monohydrate (needle) and alpha anhydrous (prism) parent crystals were obtained, respectively. When they were grown to the desired size, the crystalswere removed from the solution, washed with distilled water and dried. From these crystals only those with good habit, as shown in Figure 2, were chosen for contact nucleation. Since needle type crystals were very thin and fragile, only prism type parent crystals were used for experiments.

Experimental procedure

The experiments were conducted by gluing a parent crystal to the movable rod with epoxy. Always a well grown face of the parent crystal was positioned to be in contact with the cover slip . In each experiment the nucleation cell was preheated $5^{0}C$ above the saturation temperature of solution and the filtered saturated solution was added to the cell. The solution was heated again to destroy any nuclei that may have been generated by transforming the solution. This heating also slightly dissolved the parent crystal to insure that no surface irregularties formed by washing and drying remained. After about five minutes of heating the solution was cooled and the parent crystal was allowed to grow. When the parent crystal's growth was proceeding in a regular manner, it was slid across the glass plate to generate contact nuclei. The length of the slide was approximately 0.5 cm. Contact nuclei were observed after a few minutes and they were

photographed at timed intervals to follow their growth. Each run took about two to three hours. A 50X2 micron scale was also photographed in each run to calibrate the experiment.

Data Analysis

The raw data obtained from the contacting experiments consisted of a series of slides of the same sample of crystals from the general population. The slides were projected on a screen for enlargement without loss of resolution. The outline of each crystal was carefully traced on a piece of paper. This trace was analyzed by an image analyzer to determine the area of each crystal. The characteristic size of each crystal was taken as the square root of the area, or the geometric mean size. This is the value refered to as size or as equivalent size in the subsequent work.

Laser Raman spectroscopy / Raman Microprobe

Raman spectra were recorded with a Spex model 1406 double monochromator with radiation provided by Coherent Radiation model CR-5 Ion laser. The laser beam was directed from the laser by two 45^0 prisms and two mirrors to the microprobe. The light was passed through the microscope objective to illuminate the sample. Inelastically scattered (Raman scattering) light from the sample was again reflected from a 45^0 prism and entered the spectrometer. A Model #R928/115 photomultiplier counted the photons and transmitted the signal to a NIM

adaptor. From this adaptor the signal was sent to a 711B Strip chart recorder to record the spectrum. All samples were illuminated with the 5145 Å line of the Ar^+ laser. Laser power was approximately 1W at the laser.

<u>Raman spectra of glucose</u>

Initially, the Raman spectra of of pure crystalline products alpha monohydrate (a product from A.E.Staley Manufacturing company) and alpha anhydrous (Sigma Chemical company product, No G5000) were recorded from 300 to 1500 cm^{-1} wavenumbers. It was found that the region from 772 to 1221 cm^{-1} (5360 to 5490 Å) was suitable to identify these anomers.

Several specta were recorded in this region to determine optimum operational conditions. Always a Ammonium Paramolybdate spectrum was recorded to align the instrument. Optimal conditions determined were a scan speed of 0.05 Å/sec., a photon count rate $2* 10^6$ counts per second, and a chart speed of 0.1 inch./sec. The following Raman spectra were recorded:

1. The pure crystalline product of alpha monohydrate and alpha anhydrous glucose.
2. The parent crystals (prism and needle).
3. A solution spectrum <u>in situ</u> at 314K at 4 degrees supersaturation.
4. Contact nuclei spectra at the same experimental conditions as in 3 at several locations in the cell after several hours.