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Spatial Nucleation and Crystal Growth

by

John B. Hudson

Materials Division

Rensselaer Polytechnic Institute

Troy, New York 12181

INTRODUCTION

For the period from 1 June 1964, to 30 September 1967, NASA has supported a program in the Materials Engineering Department at Rensselaer aimed at obtaining theoretical and experimental understanding of the processes involved in the formation and growth of solid particles in the spatial environment. This program has involved both experimental measurements of energy transfer, adsorption, and nucleation phenomena in a number of vapor-solid systems and theoretical studies of the relevance of classical theories of nucleation and growth to the process of interstellar grain formation.

This report summarizes the accomplishments of that period and outlines planned continued efforts along the same lines.

THE SCIENTIFIC PROBLEM

It is well known from astronomical observations that large numbers of particles, covering a fairly wide range of particle size and presumably composition and morphology, exist in various regions of interplanetary and interstellar space. The origin of these particles and their subsequent life history are, however, not at all well understood. Consequently, it is a question of considerable importance, to astrophysicists in general and cosmologists in particular, to develop an understanding of the processes involved in the birth, life, and eventual death of these particles.

When the present study was begun, it was implicitly assumed that these particles, at least in most cases, were formed by a homogeneous nucleation mechanism in interstellar space. Calculations based on the classical theory of nucleation, however, indicate that it is unlikely that the required nucleation rate would be achieved under the conditions extant in this environment. More recently[1] it has been proposed that the particle nucleation process takes place in the vicinity of cool, carbon-rich stars. Calculations by Donn *et al.*[2] indicate this to be a much more likely mechanism. Consequently, it is of interest to make measurements of homogeneous nucleation kinetics under conditions appropriate to these stellar atmospheres, in order to test the validity of these calculations.

Assuming for the moment that the nucleation of these particles can be described by the above explanation, questions still remain concerning the subsequent growth processes as a particle moves about in an atmosphere of condensible atomic or molecular species, and about the various processes of attrition, such as ion, electron or photon bombardment and surface chemical reaction which may eventually reduce the particle size or even result in complete destruction of the particle. Very little is known about the growth of solid particles in a dilute, multicomponent vapor such as is involved here. Even less is known about the losses in mass to be expected under the influence of the bombardment process described above, especially when these processes take place in the extreme vacuum environment involved here.

Thus, it is seen that many problems of fundamental importance to an understanding of the production and properties of solid particles in space either cannot be characterized, or at best can be characterized only incompletely in the light of present knowledge. The sections that follow contain a summary of work performed under the current grant, which is aimed at increasing our knowledge of the above-mentioned processes, and indicate the type of additional studies along these same lines which must be performed before anything approaching complete understanding will be possible.

PROGRESS TO DATE-THEORY

In the course of the grant period the principle investigator has collaborated with NASA personnell in developing a theory of the origin of interstellar grains by nucleation of graphite particles in the atmospheres of carbon-rich stars.

The resulting theory is embodied in a paper which has been submitted for publication in the Astrophysical Journal. [redacted]

PROGRESS TO DATE-EXPERIMENTAL

Five experimental programs were pursued in the course of the grant period. Of these one has been followed to the limit of its capabilities and is no longer currently active. Three others have been developed to the point where valuable results are being obtained at present. The fifth is still in its formative stages. Work on these last four is continuing.

A The Study of Heterogeneous Nucleation by Visual Observation

The program which has been completed involved the measurement of the critical supersaturation for nucleation of selenium on pyrex glass under various experimental conditions. The experiments were performed in two small glass ultrahigh vacuum systems in which measurements of the critical supersaturation for nucleation of vapor on a solid substrate could be measured by either static vapor or molecular beam techniques. In both cases the onset of nucleation was characterized by the visual observation of the condensed phase on the surface of interest. This permitted measurements which could delineate effects of vapor temperature and substrate cleanliness on the nucleation process. These systems were used for an extensive study of the nucleation behavior of selenium on pyrex glass. Results have been reported verbally on two occasions (see section on <u>Verbal Presentations</u>) and have been published in the Journal of Chemical Physics. [redacted]

B <u>Mass Spectrometric Molecular Beam Studies</u>

In the early stages of the grant period, development was begun on a system for the measurement of gas-surface interactions by molecular beam-mass spectrometric techniques. This system used a small mass spectrometer to monitor the flux of material evaporated or desorbed from a metal surface in ultrahigh vacuum. By suitable manipulation, measurements could be made of the coefficient of thermal accommodation of vapor beam molecules at the surface, the mean stay-time for adsorption, and the kinetics of the nucleation of the bulk phase of the vapor species on the substrate. Results obtained for cadmium vapor impinging on a tungsten surface have been published in the Journal of Vacuum Science and Technology and the book <u>Gas-Surface Interactions.</u> [redacted]

This work is currently continuing under sponsorship of another agency.

C Electron-Bombardment-Induced Desorption Studies

Another project sponsored in part by the present grant involved the development of a system for the study of electron-bombardment-induced desorption of gases from solid surfaces. In this system a small mass spectrometer is used to monitor the ion current resulting from the desorption of gas molecules (as ions) from a surface in ultrahigh vacuum under the influence of low energy electron bombardment. These measurements provide data on the adlayer coverage as a function of substrate temperature and exposure to various atmospheres, as well as information on the binding energy in the adsorbed state and the cross-section for the desorption reaction. This system is just now beginning to yield positive results for the desorption of various residual gases from a tungsten surface. This work is currently continuing under sponsorship from another group.

D Gas-Surface Interaction Studies by Static Vapor-Mass Spectrometric Techniques

One of the conclusions from the results obtained from the measurements described in part A of this section was that more careful control and measurement of the environment was going to be required in order to obtain completely unambiguous results on the nucleation of vapors on substrates from a static vapor source. The system discussed here was built in response to that need. It consists of a glass ultrahigh vacuum chamber, containing the surface to be studied (up to this time a blown Pyrex glass tip), and connected to a second ultrahigh vacuum chamber through a small orifice. The second chamber contains a mass spectrometer, mounted so that the only material from the first chamber that can reach the spectrometer ion source is material which made its last collision before passing the orifice on the surface under study. That is, the mass spectrometer "sees" only material desorbing or evaporating from the substrate. With this system one can do experiments similar to those described under B above, but without the complication of angle-of-incidence effects that are present when a molecular beam technique is used. This system is presently being used to measure the thermal accommodation and nucleation behavior of mercury on glass, as a function of the cleanliness of the glass surface.

E <u>Homogeneous Nucleation in a Supersonic Molecular Beam</u>

It was recognized at the outset of the present grant period that the nucleation process involved in the formation of interstellar grains must be a homogeneous nucleation process of some sort. However, at that time, no experimental methods for measuring homogeneous nucleation in systems of interest were available. Consequently the initial studies reported above involved heterogeneous nucleation processes. Recently, the developement of systems in which one could form, continuously, molecular beams of high density and high supersaturation have offered a technique whereby the desired homogeneous nucleation measurements could be made. Such a system is now under construction. At this point, construction has proceeded to the point where the system hardware is nearly complete and initial tests of the beam forming process will be made soon. When this system is completed, it can be used to study particle formation in gas mixtures similar to those believed to exist in regions where the formation of interstellar grains may be taking place, in the hope of providing direct evidence in support of the theoretical conclusions discussed earlier in this report and embodied in the paper presented in Appendix A. Work on this system is continuing.

VERBAL PRESENTATIONS

The following verbal technical presentations of work supported under the current grant have been made:

"The Nucleation of Non-Equilibrium Phases From the Vapor", National Vacuum Symposium of the AVS, New York, New York, October 1965

"The Effect of Surfaces in Heterogeneous Nucleation of Condensed Phases From the Vapor", Franklin Institute Research Laboratories. Seminar Series - Philadelphia - May 1966 (invited).

"The Observation of Adsorption and Crystal Nucleation by Mass Spectrometric Techniques", Thirteenth National Vacuum Symposium of the AVS - San Francisco - October 1966 (invited).

"The Adsorption of Cadmium on Tungsten", Symposium on Gas-Surface Interactions, San Diego-December 1966.

"Nucleation and Growth by Mass Spectrometric Techniques" Gordon Conference on Thin Films-Tilton, N.H. - August 1967.

PLANNED FUTURE EFFORT

The experimental and theoretical studies of the past period have served to put the kinetic and thermodynamic processes of interest in the formation of particles in space into much sharper focus then was possible at the beginning of the period. It is thus possible to redefine the objectives of the program, and to suggest further experiments which will lead to realization of these objectives.

The most significant reorientation of effort will be away from studies of heterogeneous nucleation and toward studies of homogeneous nucleation. It was realized at the outset of this work that homogeneous nucleation were of greatest relevance to the spatial nucleation process. However, at that time no experimental method was available by which homogeneous nucleation could be studied in systems of interest. Recently, the technique of sampling the adiabatically expanding flow from a supersonic nozzle discussed above has been developed and shows great promise as a tool for studying homogeneous nucleation. This technique will be pursued further.

While nucleation measurements such as these can provide insight into the birth mechanism of interstellar particles, other techniques are required to investigate the processes mentioned earlier which contribute to their subsequent life history. These processes include the continued growth of the particles either as relatively pure particles or as "mantled" particles, with an overgrowth of some other chemical species occurring on the originally nucleated particle, and the erosive processes associated with exposure to fluxes of ions, energetic neutral atoms, electrons, cosmic ray primaries, and photons. Thus, in order to understand completely the life history of the particles one must make measurements of both the growth and comminution processes under appropriate conditions of exposure.

Two of the experimental systems developed to date, with some modifications, will be used to study those processes. The system developed to study thermal accommodation and nucleation from a static vapor can be modified to study both crystal growth processes and surface chemical reactions with neutral species, possibly even with activated neutrals such as atomic oxygen. The system developed to use electron desorption to study adsorbed layers can be used as is for studying the interaction of electrons with particle surfaces, and with some modification to study the effects of ion and photon bombardment.

Thus, at this point, techniques are either available or in a developmental stage for studying virtually all of the processes involved in the birth, lifetime and death of cosmic particles. Through the information and insights gathered in the current grant period, we are in a position, in the future, to obtain definitive data directly applicable to situations of astrophysical signigicance.

REFERENCES

1. Hoyle, F. and Wickramasinghe, N. C., M.N., 124 417 (1962)

2. Donn, B. Wickramasinghe, N. C. Hudson, J. B., and Stecher, T. P., "On the Formation of Graphite Grains in Cool Stars", submitted to Astrophy. J.