NUCLEATION AND GRAIN GROWTH IN INTERSTELLAR SPACE

By

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1. INTRODUCTION:

There have been a number of suggestions to explain the processes by which interstellar grains may form. The first detailed studies were done by a group of Dutch astronomers in the 1940's (Oort and van de Hulst 1946; ter Haar, 1944; Kramers and ter Haar, 1946; van de Hulst (1946, 1949)). Since that time very little systematic work on this problem has been done until very recently when Hoyle and Wickramasinghe (1962) investigated graphite formation in cool stellar atmospheres. A few papers in the intervening period briefly explored various aspects. van de Hulst's paper in 1949 was the culmination of an intensive attack which had considerable influence on astronomical thought about interstellar grains.

Somewhat ironically, beginning about 1949 a number of significant advances in physics and chemistry having a direct bearing on this problem were made. In 1949, Frank presented a theory which explained how real crystals tend to grow and much work, theoretical and experimental, has been done since then (Hirth and Pound, 1963). Also, starting about 1950, there has

been extensive research in chemical reactions at low tempera-
tures both in solids and on surfaces (Bass and Broide, 1960).
It therefore appeared worthwhile to again investigate the origin
of interstellar grains. This paper reports part of the continu-
ing study. Developments in stellar and galactic evolution in-
dicate that a continuous source of grains is necessary.
Schwartzchild (1958, 1962) estimated the interchange of inter-
stellar material that is needed to explain the rate of star
formation and obtained a turn-over time of 10^9 years. Since
this is short compared with the age of the galaxy, which is of
the order of 10^{10} years, it would mean that the interstellar
material has been pretty well circulated through stars. Priomor-
dial grains that formed at some early stage of the galaxy should
have disappeared. Other destructive processes such as collisions
and passage near hot stars shorten the lifetime further.

This paper deals with the question of nucleation and
subsequent growth in interstellar space. When ter Haar con-
sidered this problem in 1942, the accepted kinetic temperature
for the interstellar gas was $10,000^{\circ}K$. As the "temperature"
corresponding to the internal energy of molecules and grains
would be less $100^{\circ}K$, he was faced with a situation representing
an extreme deviation from thermodynamic equilibrium. It was
necessary, therefore, to resort to a mechanistic treatment of
particle formation with all the complications and uncertainties
of such method.

Today we face a different problem because of the recognition by Spitzer and Savadoff (1950) that extensive low temperature regions, with kinetic temperatures near $100^{O}K$ would occur. It is in these HI regions where all temperatures are below $100^{O}K$ that grain formation would take place. Although thermodynamic equilibrium does not hold exactly, temperature for all degrees of freedom are sufficiently close that thermodynamic results may be expected to yield reasonable answers.

2. NUCLEATION THEORY:

Comprehensive discussions of nucleation theory are given by Frenkel (1955), Turnbull (1956), and Feder, Russell, Lathe and Pound (1966). A more concise treatment including later developments as well as crystal growth has been presented by Hirth and Pound (1963).

The rate of nucleation in a vapor is determinded by the rate at which single molecules add to clusters of critical size to form stable nuclei. The frequency distribution of clusters and the condition of stability is determined by the free energy of formation of a cluster because entropy as well as energy changes must be taken into account. For the frequency distribution one finds:

$$m_i = m \, exp \left[-\Delta G_i / kT \right] \qquad (1)$$

where

m_i = number of clusters of i molecules/cm^3

m = number of molecules per cm^3

ΔG_i = free energy of formation of i'th cluster

and

$$\Delta G_i = 4\pi r^2 \sigma + \frac{4}{3} \pi r^3 \Delta G_v \qquad (2)$$

In equation (2) σ is the surface energy and ΔG_v is the free energy difference per unit volume of liquid between the supersaturated vapor at ambient pressure P and the bulk liquid at its equilibrium vapor pressure. This is given by:

$$\Delta G_v = - \frac{kT}{\Omega} \ln \frac{P}{P_v} \qquad (3)$$

where Ω = molecular volume

P_v = equilibrium vapor pressure of bulk

phase

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One of the weak points of the theory is the assumption that macroscopic thermodynamic properties apply to the small clusters. Equation 1-3 hold for crystals as well as drops when the necessary changes in defining the various quantities have been made.

Initially, ΔG_i increases as molecules add to a cluster with the result that clusters represent unstable fluctuation that form and decay. Equation 3 shows that the second term in equation is negative and the free energy of a cluster has a maximum value obtained by setting

$$\frac{d\,\Delta G_i}{d\,r} = 0$$

This yields the characteristics of the cluster of critical size for which further growth decreases the free energy. Clusters larger than the critical will not tend to spontaneously decay and are the condensation nuclei.

For the critical parameters we obtain:

$$r^* = \frac{2\,\sigma\,r_0}{kT\,\ln\frac{p}{p_v}} \tag{4}$$

$$i = \frac{4\pi r^3}{3\,r_0} \tag{5}$$

and

$$\Delta G^* = \frac{16\pi\sigma^3}{3\left(\frac{kT}{\mathcal{V}}\right)^2 \ln^2 \frac{P}{P_V}} \tag{6}$$

The nucleation rate is the rate at which molecules collide with and stick to clusters of the critical size. This is given by:

$$J = \alpha Z 4\pi \mathcal{V}^{*2} \frac{P}{(2\pi m kT)^{1/2}} m \exp\left[-\Delta G^*/kT\right] \tag{7}$$

J is the number of nuclei formed per cm^2 per sec, α is a sticking coefficient and Z represents a "non-equilibrium factor" arising because critical clusters are reduced from their equilibrium concentration by the growth of stable nucleii into droplets or crystallites.

3. INTERSTELLAR NUCLEATION.

Equations 3 - 7 show the fundamental role of the super-saturation ratio, P/P_V in the nucleation process. Consequently we must determine this ratio in the interstellar medium for all elements of interest. The partial pressure P_i of the ith element is given by:

$$P_i = m_i kT \tag{8}$$

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where m_i is the interstellar concentration of the element.
Table I displays concentrations, partial pressures at 100^OK and
impact frequencies per cm^2 for the more abundant elements and
observed radicals. Relative abundance are from Suess and Urey
(1956). Uncertainties in their compilation are not sufficient
to affect the results of this analysis.

TABLE I

THE INTERSTELLAR GAS

ELEMENT	ATOMIC NO.	M_i CONCENTRATION (atoms/cm^3)	P_i PARTIAL PRESS (torr.)	IMPACT FREQUENCY no/cm^2 sec.
H	1	1	10^{-17}	4×10^4
He	4	0.1	10^{-18}	2×10^3
O	8	5×10^{-4}	5×10^{-21}	5
Ne	10	2×10^{-4}	2×10^{-21}	2
N	7	2×10^{-4}	2×10^{-21}	2
C	6	10^{-4}	10^{-21}	1
Si	14	3×10^{-5}	3×10^{-22}	0.2
Mg	12	2×10^{-5}	2×10^{-22}	0.2
Fe	26	2×10^{-5}	2×10^{-22}	0.1
S	16	10^{-4}	10^{-22}	.07
Ar	18	3×10^{-6}	3×10^{-23}	.03
Al	13	3×10^{-6}	3×10^{-23}	.02
Ca	20	10^{-6}	10^{-23}	.006
Na	11	10^{-6}	10^{-23}	.007
Ni	28	10^{-6}	10^{-23}	.005
CH,CN,		10^{-8}	10^{-25}	10^{-4}
OH		10^{-7}	10^{-24}	10^{-3}

The elements to which this calculation applies and whose vapor
pressure we are interested in are carbon and silicon and the
metals which condense directly and do not require no recombin-
ation reactions first. These are all of low volatility and
vapor pressures cannot be measured at low temperatures.

Vapor pressures can be calculated theoretically using ca-
pacities for the solid and molecular energy levels for the
vapor. The procedure is discussed for example by Zemansky
(1957), Slater (1939), Gurney (1949). The resulting equation
for the vapor pressure is:

$$\ln P_V = -\frac{L_0}{RT} + \frac{5}{2}\ln T - \int_0^T \frac{dT}{RT^2}\int_0^T (C_{P_s} - C_i)dt + i \qquad (9)$$

Where L_0 = heat of vaporization at $0°K$

C_{p_s} = specific heat of the solid

C_i = internal specific heat of gas

i = chemical constant = $\ln g_0 \frac{(2\pi m)^{3/2}k^{5/3}}{h^3}$

m = molecular mass

g_0 = statistical weight of molecule

Vapor pressures, listed as equilibrium constants for solid-vapor

transition, are given in the JANAF Tables (1961 - 1965) at 100° intervals starting at 100^OK. The 100^OK data is appropriate for an HI region. Vapor pressures P and super-saturation ratio, $\rho = \dfrac{P}{P_V}$ in the interstellar medium appear in Table II.

TABLE II

INTERSTELLAR PRESSURE AND SUPERSATURATION

(100^OK)

Element	log P (d/cm^2)	Ln ρ
Al	-157	315
C	-358	780
K	- 35	32
Na	- 45	57
Sv	-130	250
Si	-217	450

In order to find the critical cluster size and number of atoms from equations 4 and 5 the molecular volume Ω and surface energy σ for the elements under consideration are required. The molecular volume Ω is given by:

$$\Omega = \frac{M}{N s}$$

(10)

where   M = atomic weight

          N = Avagadro's number (6×10^{23})

          S = density of bulk material (g/cm^3)

Surface energies are difficult to measure with high accuracy although results sufficient for our purpose are available for some materials (Adamson, 1963; Gilman, 1960; Geguzin and Ovcharemko, 1962). Data for carbon is discussed by Ubbelohde and Lewis (1960) and by Sears (1959). Table III presents the crystal properties for carrying out nucleation calculations.

TABLE III

CRYSTAL PROPERTIES

Element		Density		
Carbon	12	2.2	10^{-23}	130 - 1000
Iron	56	7.9	1.2×10^{-23}	> 1800
Silicon	28	2.4	2.0×10^{-23}	1240
Sodium	23	1.0	4×10^{-23}	150
Zinc	65	7.1	1.5×10^{-23}	105

The application of equations 4 and 5 yield r = 1.7×10^{-8} for sodium and 4×10^{-9} for carbon with σ = 1000 erg/cm^2. In each case n^* comes out less than unity. A straightforward interpretation would mean that a single atom acts as a nucleus for continued growth. However, the proper equivalent of such

macroscopic properties of matter as surface energy, for clusters of a few molecules is one of the stumbling blocks to the development of a rigorous nucleation theory. Although the evaluation of the critical cluster or nucleus is uncertain here, it seems reasonable to conclude that in interstellar space a nucleus will consist of a very small number of atoms. Physically, this comes about because of the low interstellar temperature which leads to a very low vapor pressure for the elements. The low temperature also causes all molecular aggregates to have high stability and independently of an interpretation as a nucleation process we expect any diatomic molecules to be stable against spontaneous decay. As Kramers and ter Haar showed, the steady state molecular concentration is determined by photodissociation. The photodissociation probability of the molecules will be approximately independent of size or even increase for larger molecules as longer wavelengths tend to be effective (Calvert and Pitts, 1966). This behavior is quite different from the decay of clusters in nucleation where the decay probability decreases with size until a critical size is reached corresponding to the stable nucleus.

Some preliminary estimates of the formation rate of interstellar grains based on the preceding analysis can be made. At this stage we might seem to be in the same position as that from which ter Haar (1942) began his analysis. However, several features show this is not actually the case. By restricting

ourselves to crystal growth without recombination among different elements we deal only with the heavier elements already indicated. Secondly, our aggregates are stable molecules undergoing photodissociation not the spontaneously disintergrating clusters. In ter Haar's paper, crystalline properties of the clusters play important roles. In addition to the uncertainties already noted about using these macroscopic properties for small clusters, it does not appear that his growth mechanism is consistent in assuming that it would lead to crystalline grains. This point will be considered later.

4. INTERSTELLAR MOLECULAR PROCESSES

We now examine the kinetics of formation of pure grains using carbon as a significant illustration. Here again chemical reactions involving other species are neglected. If recombination reactions incorporate other atoms the process is the alternative mechanism of ter Haar which will be briefly considered at the end of this section. Should the reactions remove carbon, somewhat akin to the molecular formation process proposed by Stecher and Williams (1966), the growth rate becomes even slower than found here and interstellar formation of crystalline grains still less likely.

Bates and Spitzer obtained a rate coefficient for the reaction:

$$C^+ + H \longrightarrow CH^+ + h_\nu \qquad (11)$$

given by

$$\frac{d\, m_{CH^+}}{dt} = 10^{-15}\, m_{C^+}\, m_H$$
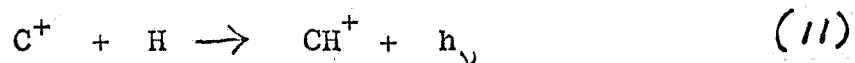
The inclusion of other formation and decay processes yields
a steady state value of 10^{-10} to 10^{-11} molecules/cm^3. For
CN^+, Kramers and ter Haar estimate a total production in 10^9
years of 5×10^{-6}/cm^3 but Bates and Spitzer find those rates
are too high and would have given about 5×10^{-7}/cm^3. These
numbers neglect photodissociation and the actual density by
this process must be less. If photodissociation for CN^+ is
comparable to that for CH^+ a steady state density of about
10^{-14}/cm^3 is obtained. In the absence of more direct evidence
it is assumed that C_2 would behave similarly.

A third atom still has a low probability of adding to a
diatomic molecule as stabilization against rapid dissociation
remains low (Trotman - Dickenson, 1955). Consequently for the
reaction

$$C_2 \;+\; C \;\rightarrow\; C_3 \;+\; h_\nu \qquad (13)$$
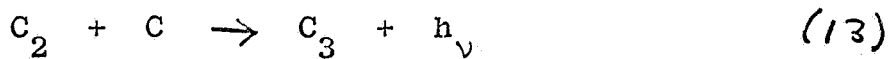
$$\frac{d\, m_{C_3}}{dt} = 10^{-16}\, m_C\, m_{C_2} \qquad (14)$$

When four molecules are involved the frequency with which the
newly formed bond attains the recombination energy and can
break becomes comparable to the reciprocal radiative lifetime.
The probability of capture of a fourth carbon is somewhat less

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than for normal reaction probabilities and will be about normal for additional carbon atoms.

For j = 3 we take

$$\frac{d\,m_{c_4}}{dt} = 10^{-13}\,m_{c_3}\,m_c \qquad \qquad 14$$

and for all succeeding reactions

$$\frac{d\,m_{c_{j+1}}}{dt} = 10^{-12}\,m_{c_j}\,m_c \quad,\quad j \geq 4 \qquad (15)$$

The rate coefficients in equations 13 and 14 are given by the products $0.01\,\sigma\,\mathcal{N}$ and $0.1\,\sigma\,\mathcal{N}$ respectively, where σ is the collision cross section (10^{-15} cm^2) and $\mathcal{N}$ is the average relative velocity (10^4 km/sec).

The formation rate of a specie containing j atoms is given by:

$$\frac{dm_j}{dt} = \sigma_{j-1}\,m_{j-1}\,m_1 - \beta\,m_j - \gamma_j\,m_j + \beta_{j+1}\,m_{j+1} \qquad (16)$$

The $\sigma's$ are the formation rate coefficients and the β's are the photodissociation rates whose values have been discussed above. An approximate solution may be obtained for the steady state by solving each equation sequence starting with the first if the last term in each is dropped. It will turn out that the $m_j's$ decrease rapidly enough to make this legitimate.

This procedure leads to the following solution for the $m_j's$,

$$M_1 = 10^{-3}, \quad M_2 = 10^{-12}, \quad M_3 = 10^{-26}, \quad M_4 = 10^{-24}, \quad M_5 = 10^{-28}$$

For successively larger molecules the frequency is multiplied by 10^{-4} for each additional carbon atom added until the adopted coefficients values change. This will probably occur in the photodissociation process and affect β_j which determines the rate of destruction. Although the building process may well be more efficient than we obtain here, two neglected factors make it less efficient. The dissociation will not always consist of the removal of a single atom. The broken bond in some fraction of the cases will yield larger fragments than single atoms. More significant is the fact that all elements to which our mechanism applies will be largely ionized leading to a positively charged carbon polymer and a reduction in the resultant capture rate of additional carbon ions. It follows therefore that the uncertainties in the calculations are hardly likely to yield the required grain density for conducting grains which for an extinction of 1 mag/kpc is about $10^{-11}/cm^3$.

ter Haas implied in his 1942 paper that the building process may consist of a sequence of the form:

$$C \rightarrow CH \rightarrow CH_2 \rightarrow CH_2O \rightarrow CH_3O \rightarrow CH_3NO$$
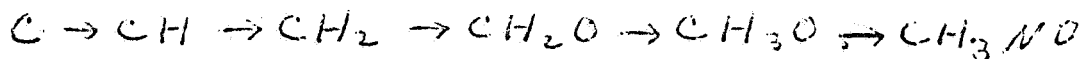
and so on. This is the growth mechanism suggested by Platt (1956), Platt and Donn (1956) and developed further by Donn (1967) which leads to the so-called Platt particle. As this paper is not considering the general chemical reaction aspects

of interstellar grains these problems are left for a forth-coming discussion.

5. STELLAR SOURCES

Because of the problem of forming grains in interstellar space other sources require consideration. A significent contribution was made by Hoyle and Wickramasinghe (1962) and discussed here by Wickramasinghe, namely, graphite formation in cool carbon stars. In commenting on his paper, I pointed out that the graphite formation problem must consider the complete chemical equilibrium in a stellar atmosphere taking all constituents into account. Hydrogen is clearly the most important. Fortunately, the chemical equilibrium of the CH system including graphite stability was investigated by Duff and Bauer (1962). They included seventy hydrocarbons and determined the temperature at which graphite becomes stable as a function of C/H ratio for several pressures. These results are shown in Figure 1, modified from the original diagram for better extrapolation. Solid lines are drawn through the computed points and the dashed lines are extrapolated to a C/H ratio of 10^{-3}, adapted by Hoyle and Wickramasinghe. For a pressure of 10^{-3} atmospheres, the considerable extrapolation yields a sublimation temperature of graphite of about $2100^{\circ}K$. Prof. Bauer expressed the opinion that the pressure extrapolation should be valid. Some time after this symposium, further work (Clarke

and Fox, 1967) extended the calculations to C/H = 0.008 and experimentally studied graphite equilibrium in a hydrocarbon atmosphere. Their theoretical and experimental results are in agreement with the earlier work and our extrapolation. There is a suggestion that sublimation temperatures would be greater by somewhat less than 50°.

At a temperature of $2100^{\circ}K$ conditions are less favorable for graphite formation and the mechanism becomes rather doubtful. (See, however, the comment following Wickramasinghe's paper concerning a recent detailed analysis of this problem by Donn, Wickramasinghe, Hudson and Stecher).

An important feature of the molecular equilibrium in carbon stars of type N is the array of hydrocarbon molecules and radicals present in the atmosphere. If the observed mass ejection for M stars exists for carbon stars also then a significant quantity of these species is carried into interstellar space. It is conceivable that they may serve as nuclei for further growth and that the growth process may compete favorably with photodecomposition of the molecules. As already discussed, a molecule of five or more atoms will add another with a high probability. Whether this scheme would lead to graphitic grains or more nearly ressemble the composition and structure of a Platt particle is not now clear. In examining this problem the possibility of aggregates developing beyond

the normal atmospheric boundry, perhaps in an expanding envelop needs to be considered. This entire process will be considered in greater detail at another time.

It cannot be said that the nucleation problem has been solved. There are many uncertainties in the present discussion and several possibilities have yet to be investigated.

6. CRYSTAL GROWTH

I will conclude with some brief remarks about particle growth on a pre-existing nucleus. On the hexagonal or 'C' face of a graphite lattice carbon atom bonds are highly saturated and the captured surface atom is held by the relatively weak van de Waal's forces. These non-lattice atoms would be capable of diffusing over the surface. Experiments on the formation of carbon whiskers (Meyer, 1959) indicates that this does occur. A study (Donn, 1965) of the kinetics of graphite formation in interstellar space at low temperatures indicates that the captured atoms becomes trapped at the edge of a 'C' face so that a platelet or needle would tend to grow. The growth rate depends upon the surface area of the grain over which atoms are collected. This produces exponential growth until the size becomes larger than the mean diffusion distance after which linear growth occurs.

Growth of a graphite platelet on a 10^{-7} cm nucleus is

shown in Table 2.

<div align="center">

TABLE 2

Growth of Graphite Plalelet

</div>

Time (years)	Radius	(cm)
	$(H) = 1$	$(H) = 10$
10^7	10^{-7}	10^{-6}
10^8	10^{-6}	(10^4)
10^9	(10^4)	-----

With a density of one hydrogen atom/cm^3 practically no change occurs in 10^7 years. In 10^8 years the grain reach a radius of 10^{-6} cm and the rate increases very rapidly for greater time intervals because of the expenential behavior. The figure of 10^{-4} in parenthesis in column 2 is obtained using the expenential growth expression and obviously is meaningless except to show how rapidly the size increases once growth begins. Column 3 shows the size attained for the intervals indicated in denser regions where $M(H) = 10/cm^3$.

We see that the change in size is much greater than the density increase for grains of 10^{-6} cm. This theory can provide for grain size distribution which changes discontinuously from small to large grains in different regions of the galaxy. These results neglect effects of adsorbed atoms or attack by atomic

hydrogen and oxygen which may remove carbon atoms.

Finally, I would like to emphasize a point related to the question of coating grains e.g. graphite cores with ice mantles. To have an efficient substrate for condensing a different molecule, the two species should have similar crystal properties, in particular with regard to crystal structure and lattice spacing. Silver iodide has a hexagonal structure similar to ice I (normal ice) and is an effective nucleating agent for ice. A solution of silver iodide was cooled under sufficient pressure such that ice III was the stable phase (Evans, 1965). However ice I was again obtained. Silver iodide and ice III have dissimilar structure and spacing and silver iodide will not nucleate ice III even in the P-T domain where ice III is the stable phase. In a second type of experiment (Yang, Simnad and Pound, 1954) the sticking coefficient dropped from unity to about 0.65 as the lattice spacing mismatch increased from 0 to 15% for cubic crystals.

These phenomena indicate the necessity of detailed analysis of particle formation. It is not as simple as saying material condenses. An extensive body of theoretical and experimental data exists which must be incorporated into a theory of interstellar grain formation. Much more experimental work is needed particularly for conditions appropriate to astrophysics.

In concluding I want to emphasize, firstly, that what I presented here is a way to proceed and some tentative conclusions. Secondly, a study of interstellar grain formation can now be carried out which is on a sounder basis than was possible in the period 1940 - 1950. It is necessary however to do this in successive stages. This paper discussed the nucleation process in some detail and more briefly, the crystal growth process. Some attention was also given to the role of chemical reactions. Further analysis of the origin and structure of interstellar grains continuing a program outlined in 1953 (Donn, 1953) will be carried out in succeeding papers.

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FIGURE CAPTIONS

Fig. 1   Sublimation temperature of graphite as function
of C/H ratio of atmosphere. Points are taken
from graph of Duff and Bauer (1962). Dashed lines
are extrapolations.