BOEING

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ADDENDUM TO

FURTHER ANALYSIS OF FIELD EFFECTS ON LIQUIDS AND SOLIDIFICATION

FINAL REPORT
CONTRACT NAS8-28664 (MOD I)
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STUDY OF THE LIQUID-SOLID TRANSITION
FOR
MATERIALS PROCESSING IN SPACE

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PREPARED BY
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D256-10024

(ADDENDUM)

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SECTION 1

SUMMARY

OBJECTIVES AND APPROACH

There were two objectives to be pursued during this extension of the Study of the Liquid-Solid Transition for Materials Processing in Space:

(A) to determine the relationship of f_0 (the fraction of lattice sites on the liquid-solid interface to which molecules can be attached) to Gibbs free energy of solidification (also called "driving force for solidification"), to other thermodynamic variables, and hence to changes in external fields, and

(B) to investigate the possibility that calculating derivatives of Gibbs free energy of solidification and diffusion coefficient (or equivalently, molecule mobility) with respect to pressure would provide a better method of determining external field effects on Gibbs free energy and diffusion coefficient than the Free Volume Model method previously employed.

Objectives (A) and (B) were taken as the work statements for tasks (A) and (B) of the contract extension. The approach to task (A) was to utilize newly-acquired information from the Free Volume Model which related f_0 to Gibbs free energy of solidification, specific volume, surface free energy and molecule diameter. In task (B), classical thermodynamics was used to calculate the derivatives $\frac{d\Delta G}{dP}$ and $\frac{dD}{dP}$ and to compare these with equivalent expressions derived from the Free Volume Model. Results of task (A) were used to modify previous calculations of solidification rate changes (see Appendix B). Task (B) required no modification to previous work.

RESULTS AND CONCLUSIONS

The results and conclusions of task (A) are contained in the paper placed in Appendix B. Basically, it was found that including the effects of external fields on f_o in the calculation of solidification rate, U_c, did result in a change in the ratio U_c'/U_c. The change was insignificantly small in the case of microgravity (corresponding to the infinitesimal original value of the field-induced change in U_c), and was on the order of 1% in the magnetic field case. Thus the calculation of field effects on f_o does not change the general conclusions of the previous work contained in the Final Report dated July 9, 1974. But having considered these effects does increase the accuracy and credibility of this work.

In comparing the derivatives $\frac{dD}{dP}$ and $\frac{d\Delta G}{dP}$ to equivalent expressions from the Free Volume Model calculations, order-of-magnitude agreement was found for changes of diffusion coefficient (or molecule mobility) with pressure, but there was no agreement between the two methods for the change of Gibbs free energy of solidification with pressure. Neither of these results affect the validity of the Free Volume Model calculations of solidification rate change with external field effects as reported in Appendix B.

Results and conclusions pertaining to the remainder of the work on Contract NAS8-28664 not covered by this Addendum may be found in References 1 and 2. Symbols and data used in this addendum are also taken from References 1 and 2.

SECTION 2
ANALYTICAL RESULTS

2.1   TASK A - FIELD DEPENDENCE OF f_o

The analyses, calculations and results pertaining to this task are
contained in the revised paper in Appendix B. This paper also con-
tains the calculations of field effects on solidification rate which have
been modified to include the field effects on f_o.

2.2   TASK B - PRESSURE DEPENDENCE OF D AND ΔG

The purpose of this task was to see if there is any similarity between
the calculation of external field-induced changes in diffusion coefficient,
D, and Gibbs free energy of solidification, ΔG, from the Free Volume
Model (see Appendix B), and the calculation of the change in D or ΔG
caused by any arbitrarily produced change in pressure, i.e., $\frac{dD}{dP}$ or
$\frac{d\Delta G}{dP}$.

Changes in diffusion coefficient, or, equivalently, molecule mobility
($v = D/kT$) with pressure may be derived from the expression[3]

$$D = AT^{1/2} e^{-bv_o/v_f} \tag{1}$$

where A and b are constants with b being of the order of unity.
Differentiation with respect to pressure yields

$$\frac{dD}{dP} = \frac{1}{2} D \left[\frac{1}{T} \frac{dT}{dP} + 2 \frac{bv_o}{v_f^2} \frac{dv_f}{dP} \right] \tag{2}$$

According to the Clausius-Clapeyron equation[4], $\frac{dT}{dP}$ is given approximately
by

$$\frac{dT}{dP} \approx T \frac{\Delta V}{\Delta H} = T \frac{\Delta V}{T_m S_c} \tag{3}$$

where ΔV is change in volume between the liquid and solid phases and
is not a field-induced volume change, ΔH is the heat of fusion, T_m
the melting temperature and S_c the entropy of solidification. Since

2.2   (Continued)

by definition[5]

$$v_f = v - v_0 \qquad ,$$

$$\frac{dv_f}{dP} = \frac{dv}{dP} = -\beta v \qquad (4)$$

where β is the isothermal compressibility coefficient and v the specific volume. Thus equation (2) becomes

$$\frac{1}{D}\frac{dD}{dP} = \frac{\Delta V}{2T_m S_c} - \frac{v_0 v}{v_f^2}\beta \qquad (5)$$

since $b \approx 1$.

From the definition of Gibbs free energy, G, the change in G on freezing, i.e., the difference between G of the liquid and G of the solid is

$$\Delta G = \Delta H - TS_c = T_m S_c - TS_c \qquad . \qquad (6)$$

The change in ΔG with pressure will be

$$\frac{d\Delta G}{dP} = \frac{d\Delta H}{dP} - S_c \frac{dT}{dP} \qquad . \qquad (7)$$

To evaluate $\frac{d\Delta H}{dP}$, note that since $H = E + PV$,

$$\frac{d\Delta H}{dP} = \frac{d}{dP}[\Delta E + \Delta(PV)] = C_v \frac{dT}{dP} + \Delta v$$

and from equation (3)

$$\frac{dT}{dP} = T\frac{\Delta V}{T_m S_c}$$

thus

$$\frac{d\Delta G}{dP} = \Delta V[1 + \frac{(C_v - S_c)T}{T_m S_c}] \qquad . \qquad (8)$$

2.2 (Continued)

Now, it was suggested by a reviewer for the paper in Appendix B that
a way to estimate the field effects on the driving force for solidifi-
cation was to say

$$\frac{d\Delta G}{dP} \quad \alpha \quad \frac{dT_m}{dP} \quad \approx \quad \frac{\Delta V}{S_c} \tag{9}$$

Since $\frac{\Delta V}{S_c}$ is on the order of $10^{-10} \frac{cm^3 {}^\circ K}{erg}$, this yields a small value for
$\frac{dT_m}{dP}$, but not necessarily for $\frac{d\Delta G}{dP}$. Values calculated from equation (8)
are found to be much larger.

Comparison of equations (5) and (8) to previous calculations from the
Free Volume Model may be made utilizing the following equivalence
statements

$$\frac{1}{D} \frac{dD}{dP} \quad <=> \quad \frac{1}{\Delta P} \left(\frac{D'}{D} - 1\right) \tag{10}$$

$$\frac{d\Delta G}{dP} \quad <=> \quad \frac{1}{\Delta P} \left(\Delta G' - \Delta G\right) \tag{11}$$

where the right-hand sides are the finite difference expressions corres-
ponding to the differentials on the left. The terms on the right are
calculated from[1]

Microgravity Case:

$$\Delta P = - \rho z \Delta g \tag{12}$$

$$\Delta G' - \Delta G = - \beta v [\rho z \Delta g]^2 \tag{13}$$

Magnetic Field Case:

$$\Delta P \approx - \frac{1}{2} \mu_0 H^2 \tag{14}$$

$$\Delta G' - \Delta G = - v(x_\ell - x_s) H^2 \tag{15}$$

2.2 (Continued)

Using the above equations and the data given in Table I, the expressions on both sides of (10) and (11) were calculated yielding the results shown in Tables II and III. Agreement between the two calculation methods is good (to an order of magnitude) for the change of diffusion coefficient with external pressure (Table II). There is no agreement between methods for the change of Gibbs free energy of solidification with pressure. Had one assumed that

$$\frac{d\Delta G}{dP} \approx \frac{dT_m}{dP}$$

then agreement would have been good, particularly with the microgravity case calculated from the Free Volume Model. Although the right-hand portion of equation (6) tempts one to make this assumption, the analysis leading to equation (8) points out its fallacy. Thus there seems to be no similarity between the calculation of external field effects on ΔG from the Free Volume Model and from $\frac{d\Delta G}{dP}$. Since the term of interest in the calculation of field effects on solidification rate is

$$(1 - e^{\Delta G'/kT'})/(1 - e^{\Delta G/kT})$$

and not $\frac{d\Delta G}{dP}$, the comparison indicated by expression (11) is, perhaps, meaningless. At any rate, there is no reason to doubt the accuracy of the Free Volume Model calcualtions, because the reviewer himself expected a small value for the change in ΔG with external pressure, and therefore approved the work in Appendix B.

2.3 REFERENCES

1.   R. I. Miller and W. S. Chen, <u>Further Analysis of Field Effects on Liquids and Solidification</u>, Final Report on Contract NAS8-28664, Boeing Document D256-10024, July 9, 1974.

2.3 (Continued)

2.   R. I. Miller, Analysis of Field Effects on Dense Liquid
      Materials, NASA CR-124294, May 9, 1973.

3.   D. Turnbull and M. H. Cohen, in Modern Aspects of the
      Vitreous State, edited by J. D. Mackenzie, Butterworths,
      Washington, 1960.

4.   R. Wood, Chemical Thermodynamics, Appleton-Century-Crofts,
      New York, 1970.

5.   D. Turnbull and M. H. Cohen, J. Chem. Phys., 34, 120, 1961.

6.   A. N. Krestovnikov, S. B. Evgen'ev and V. M. Glazov, Doklady
      Phys. Chem., 174, 634, 1967.

TABLE I

MATERIAL PROPERTY DATA[†]

MATERIAL	ΔV* $cm^3/mole$	v $cm^3/mole$	ρ cm/cm^3	β $cm^2/dyne$	$x_\ell - x_s$ cm^{-3}	C_v $erg/mole\ °K$	S_c $erg/mole\ °K$	T_m $°K$	T $°K$	v_o/v_f^2 $mole/cm^3$
InSb	2.28183	18.2	6.43	3.15×10^{-11}	7.94×10^{-8}	3.347×10^8	6.211×10^8	803	793	.197
Ge	0.62624	13.0	5.57	1.19×10^{-11}	1.223×10^{-7}	3.138×10^8	2.443×10^8	1210	1200	.177
Hg	0.50605	14.6	13.7	3.9×10^{-12}	-3.38×10^{-7}	2.837×10^8	9.8×10^7	234	224	.228
Na	0.64145	24.6	0.93	1.916×10^{-11}	9.63×10^{-8}	3.15×10^8	7.01×10^7	371	361	.325

*REFERENCE 6

†SEE REFERENCE 1

TABLE II

DIFFUSION COEFFICIENT CALCULATION COMPARISON

MATERIAL	MICROGRAVITY CASE			MAGNETIC FIELD CASE			$1/D \, dD/dP$
	ΔP	D'/D	$1/\Delta P(D'/D-1)$	ΔP	D'/D	$1/\Delta P(D'/D-1)$	
	$dyne/cm^2$	—	$cm^2/dyne$	$dyne/cm^2$	—	$cm^2/dyne$	$cm^2/dyne$
InSb	-6301	1.0000005	-7.9×10^{-11}	-3.98×10^{-8}	1.02237	-5.60×10^{-11}	-1.06×10^{-11}
Ge	-5448.6	1.0000003	-5.5×10^{-11}	"	1.00624	-1.57×10^{-11}	-2.63×10^{-11}
Hg	-13426	1.0000007	-5.2×10^{-11}	"	0.99805	$+0.49 \times 10^{-11}$	-0.95×10^{-11}
Na	-911.4	1.0000001	-11×10^{-11}	"	1.02139	-5.37×10^{-11}	-4.08×10^{-11}

TABLE III

SOLIDIFICATION DRIVING FORCE (GIBBS FREE ENERGY)
CALCULATION COMPARISONS

MATERIAL	MICROGRAVITY CASE			MAGNETIC FIELD CASE			$d\Delta G/dP$
	ΔP	$\Delta G' - \Delta G$	$1/\Delta P(\Delta G' - \Delta G)$	ΔP	$\Delta G' - \Delta G$	$1/\Delta P(\Delta G' - \Delta G)$	
	$dyne/cm^2$	$erg/mole$	$cm^3/mole$			$cm^3/mole$	$cm^3/mole$
InSb	-6301	-.0228	36×10^{-7}	-3.98×10^{8}	-14450	3.6×10^{-5}	1.24
Ge	-5458.6	-.0046	8.4×10^{-7}	"	-15900	39.9×10^{-5}	0.80
Hg	-13426	-.0103	7.6×10^{-7}	"	+49300	-12.4×10^{-5}	1.46
Na	-911.4	-.0039	4.3×10^{-7}	"	-23700	6.0×10^{-5}	2.82

APPENDIX A

REVISED SUMMARY OF PUBLICATIONS AND PRESENTATIONS PRODUCED
UNDER CONTRACT NAS8-28664

PUBLICATIONS

1.   A Summary of Liquid State Models for Materials Processing
     in Space, Boeing Document D5-17268, August 1972.

2.   Analysis of Field Effects on Dense Liquid Materials, NASA
     CR-124294, May 1973.

3.   "Qualitative Effects of Oscillating Magnetic Fields on
     Crystal Melts", Journal of Crystal Growth, 20, 310,
     November 1973.

4.   "Thermodynamic Properties Derived From the Free Volume
     Model of Liquids", Metallurgical Transactions, 5, 643,
     March 1974.

5.   Further Analysis of Field Effects on Liquids and
     Solidification, Boeing Document D256-10024, July 1974.

6.   "External Field Effects on Solidification: Macroscopic
     and Microscopic Models", Proceedings of the 1974 AIAA/ASME
     Thermophysics and Heat Transfer Conference, July 1974.

7.   "External Field Effects on Diffusion and Solidification
     Derived from the Free Volume Model", Journal of Applied
     Physics, 46, #1, January 1975.

PRESENTATIONS

1.   "The Free Volume Model Equation of State", Annual Meeting
     of SESAPS*, November 1972.

2.   "External Field Effects on Solidification Rate", Annual
     Meeting of SESAPS*, November 1973.

APPENDIX A (Continued)

3. "Some Aspects of Present and Future Research in Space" (Invited Paper), Annual Meeting of SESAPS*, November 1973.

4. "External Field Effects on Solidification: Macroscopic and Microscopic Models" AIAA/ASME Thermophysics and Heat Transfer Conference, July 1974.

5. "External Field Effects on Microsegregation", Annual Meeting of SESAPS*, December 1974.

*Southeast Section of the American Physical Society

APPENDIX B

To Be

EXTERNAL FIELD EFFECTS ON DIFFUSION AND SOLIDIFICATION DERIVED FROM THE FREE VOLUME MODEL*

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DERIVED FROM THE FREE VOLUME MODEL

ABSTRACT

Expressions for diffusion coefficient, D, and solidification rate, U_c, from the Free Volume Model of liquids developed by Turnbull and Cohen have been used to estimate the effects which microgravity and magnetic fields will have on these quantities. The mathematical formalism describing changes in D and U_c is the same for both the microgravity and magnetic field cases, but the difference between the magnitudes of the two effects is quite large. The change in D and U_c is found to be less than 10^{-4}% for the microgravity case and on the order of 0.1 to 1.1% for the magnetic field case for four representative materials. D and U_c are found to increase under the influence of an applied magnetic field, and this is in agreement with experimental observations.

EXTERNAL FIELD EFFECTS ON DIFFUSION AND SOLIDIFICATION

DERIVED FROM THE FREE VOLUME MODEL

INTRODUCTION

Solidification phenomena form one of the most important classes of problems in the Materials Processing in Space discipline of the NASA Space Science and Applications Program. The objective of this discipline is to develop new or superior products for use on Earth by utilizing the unique environment of space in the processing of materials. In many solidification situations, such as growing crystals from the melt, the state of the molten material greatly influences the solidification process. It is therefore necessary to consider the liquid state aspects of the solidification process, primarily convection, the contamination of a liquid by its container, and diffusion of molecules in the liquid and the effects these have on the process. Since convection and contamination problems in Space Processing are being investigated elsewhere [1,2], it was decided to concentrate on diffusion and thermodynamic questions relating to solidification from the melt. A method of treating liquids analytically is to employ one or more of the liquid state models [3] which have been developed during the past 80 years, and the Free Volume Model of Turnbull and Cohen [4 - 7] provides a conceptually and mathematically simple picture of the kinetics of solidification. In addition to approaching the solidification problem from the liquid state point of view, it is instructional to consider what similarities and differences

may exist between solidification processes in microgravity and the same processes carried out on Earth but in the presence of magnetic fields. This approach is suggested by several experimentally observed effects [8 - 12] which magnetic fields produce in solidification processes and which are qualitatively similar to effects anticipated in microgravity solidification. The work reported here is an elementary attempt to deduce from the Free Volume Model what changes, if any, will occur in the diffusion coefficient and solidification rate of a material which solidifies either in microgravity or in the presence of a magnetic field.

FREE VOLUME MODEL EQUATIONS

The rate of growth of a rough interface into an undercooled melt [13] where molecules are added to the interface by diffusion is given by Turnbull [5] as

$$U_c = D \frac{f_o}{R_o} [1 - e^{\Delta G/kT}] \tag{1}$$

where k is Boltzmann's constant, T is absolute temperature, ΔG is the Gibbs free energy of solidification, R_o is the molecular diameter and f_o is the fraction of lattice sites in the liquid-solid interface to which molecules can be attached. Strictly speaking, D is the kinetic constant for solidification. But Turnbull finds that, in molecular liquids, this kinetic constant may be replaced with the liquid self-diffusion coefficient with reasonable accuracy [7]. According to the Free Volume Model, the diffusion coefficient is approximated by [6]

$$D = \frac{\psi}{3} \bar{u} \, v^* e^{- \frac{\gamma v^*}{v_f}} \tag{2}$$

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where ψ is a parameter relating the distance traveled by a molecule between collisions to the average specific volume, v, of the liquid, and γ is an overlap factor lying between $\frac{1}{2}$ and 1. v^* is the critical value of free volume for the onset of diffusion, $\bar{u}$ is the diffusion velocity given by

$$\bar{u} = \sqrt{\frac{3kT}{m}} \qquad (3)$$

i.e., the gas kinetic velocity, and v_f is the free volume defined as

$$v_f = v - v_0 \qquad (4)$$

where v_0 is the molecular volume calculated from the diameter and m is the molecular mass.

Now if equations 3 and 4 are substituted into 2, one obtains

$$D = \phi \, T^{\frac{1}{2}} \, e^{-\frac{\gamma v^*}{v} (1 - v_0/v)^{-1}} \qquad (5)$$

where $\phi = v^* (\frac{\psi^2 k}{3m})^{\frac{1}{2}}$ is a constant for a given material and values of ϕ and of $\frac{\gamma v^*}{v}$ have been tabulated by Cohen and Turnbull [4] for some simple liquids. The ratio of the available interface lattice site fraction to molecular diameter, f_0/R_0, is found by Turnbull and Hillig [14] to be

$$\frac{f_0}{R_0} = \frac{\Delta G}{4\pi\sigma v} \qquad (6)$$

where σ is the surface free energy at the interface, a constant for a given material [15].

FIELD EFFECTS ON U_c, D AND f_0

From equations 1, 5 and 6, it is seen that solidification rate of a given
material depends only on the variables D, f_0, ΔG and T while the diffusion
coefficient itself depends on T and specific volume, v, and f_0 depends on
ΔG and v. If a prime on a quantity indicates the value of that quantity under
changed field conditions, i.e., in a magnetic field or in microgravity, then
from equation 1 the ratio of the new solidification rate to the unperturbed
value will be

$$\frac{U_c'}{U_c} = \frac{D' \, f_0' \, (1 - e^{\Delta G'/kT'})}{D \, f_0 \, (1 - e^{\Delta G/kT})} \tag{7}$$

with

$$\frac{D'}{D} = (1 + \frac{\Delta T}{T})^{\frac{1}{2}} \exp \{\frac{\gamma v^*}{v} [\frac{\Delta v/v}{(1-v_0/v)^2 + \frac{\Delta v}{v}(1 - v_0/v)}]\} \tag{8}$$

and

$$\frac{f_0'}{f_0} = \frac{\Delta G' v}{\Delta G v'} = \frac{\Delta G'/\Delta G}{1 + \Delta v/v} \tag{9}$$

from equations 5 and 6. Here $T' = T + \Delta T$ and $v' = v + \Delta v$, where ΔT and Δv
are changes in T and v due to external field effects. It is worth noting that
using either Fick's law or equation 3, one can show that the ratio of diffusion
coefficients in equation 8 is approximately equal to the ratio of diffusion
velocities, $\bar{u}'/\bar{u}$, of liquid molecules if $\frac{\Delta v}{v} \ll 1$. It will be seen that this
condition is realized in microgravity, and to a lesser extent in magnetic

fields. Thus the change in solidification rate, lattice site fraction and diffusion coefficient due to external field conditions as measured by the ratios of 7, 8 and 9 depend, for a given material, only on the fractional changes $\frac{\Delta V}{V}$, $\frac{\Delta T}{T}$ and on the change in Gibbs potential, $\Delta G'$. These parameters will now be discussed in terms of their ultimate effect on solidification rate for both the microgravity case and for the magnetic field case.

MICROGRAVITY CASE

From the definition of isothermal compressibility [16], the fractional change in a volume of a liquid due to a change in pressure, ΔP is

$$\frac{\Delta V}{V} = -\beta\Delta P \tag{10}$$

where β is the isothermal compressibility of the liquid. If a container of liquid is envisioned as being moved from the Earth's surface into an orbiting laboratory where microgravity conditions prevail, there will be a change in the hydrostatic pressure within the liquid of

$$\Delta P \approx -\rho g z \tag{11}$$

where ρ is the liquid density, g is the acceleration due to gravity and z is the distance of the reference pressure point below the free surface of the liquid on Earth. Equation 11 would be exact if the factor g were corrected for non-gravitational accelerations experienced aboard spacecraft, but since these are on the order of $10^{-3}g$ to $10^{-6}g$, equation 11 is a good approximation. Thus from 10,

$$\frac{\Delta V}{V} = \beta \rho g z \tag{12}$$

From the definition of the thermal expansion coefficient, α [16], one can write

$$\frac{\Delta T}{T} = \frac{\Delta V/V}{\alpha T} \tag{13}$$

so the temperature change corresponding to the pressure-induced volume change may be calculated from 12.

Since the Gibbs free energy of solidification is given [15] by

$$\Delta G = S_c \, \delta T \tag{14}$$

where S_c is the entropy of solidification (a negative number) and δT is the amount of undercooling $(T_m - T)$, external effects must be of the form

$$\Delta G' = \Delta G + \Delta V \Delta P$$

or, from 10

$$\Delta G' = \Delta G - \beta V \, (\Delta P)^2 \tag{15}$$

with ΔP given by equation 11 for the microgravity case. With these equations, the free energy term

$$(1 - e^{\Delta G'/kT'}) \, / \, (1 - e^{\Delta G/kT}) \quad ,$$

the change in available lattice site fraction f_0'/f_0, the diffusion coefficient change D'/D, and the solidification rate change U_c'/U_c may be calculated for any material if the characteristic parameters are available for the liquid

state of the subject material. Table I lists values of the parameters required for calculations in both the microgravity case and in the magnetic field case for four representative materials.

MAGNETIC FIELD CASE

Equation 10 may be used to determine fractional volume changes in a liquid placed in a magnetic field if ΔP is now the magnetic pressure [17]

$$\Delta P = -\frac{1}{2} \mu_0 [H_0^2 - \chi H^2] \tag{16}$$

where μ_0 is the permeability of free space (.1257 dyne/amp^2), χ is the magnetic susceptibility, H_0 is the initial field strength before the liquid was placed in the field and H is the resulting steady-state of the field internal to the liquid. Thus

$$\frac{\Delta V}{V} = \frac{1}{2} \beta\mu_0 [H_0^2 - \chi H^2]. \tag{17}$$

To estimate $\Delta v/v$ without having to specify boundary conditions of a particular system, one may assume that for paramagnetic or diamagnetic liquids, $H \approx H_0$. Since χ is on the order of 10^{-7} for such liquids,

$$\frac{\Delta V}{V} \approx \frac{1}{2} \beta\mu_0 (1-\chi)H^2 \approx \frac{1}{2} \beta\mu_0 H^2 \tag{18}$$

An alternative method for calculating the volume change would be to use the theory of magnetostriction. According to the theory [18], the fractional change in volume due to the magnetostrictive form effect is a function of demagnetizing factor, bulk modulus of elasticity and the square of magnetic field strength.

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The dependence on H^2 is in agreement with equation 18, and $\frac{\Delta V}{V}$ is generally positive, even for values of H beyond those applying to the form effect in solids.. But demagnitizing factors are not available for liquids, so a quantitative comparison between equation 18 and the theory of magnetostriction is impossible, even though both predict a positive Δv in a magnetic field.

In his paper describing magnetic field effects on the dissolution and solidification rates of paramagnetic crystals in solution, Schieber [11] derived the following expression for the change in temperature of a solidifying system due to the application of a magnetic field, H

$$\frac{\Delta T}{T} = (x_\ell - x_s) \frac{H^2}{4Q} \tag{19}$$

where x_ℓ is the magnetic susceptibility per unit volume of the liquid, x_s is the susceptibility of the solid and Q is the latent heat of solidification. Thus the temperature at the interface of a solidifying material in a magnetic field can increase or decrease depending on whether the material is diamagnetic or paramagnetic and on the relative magnitudes of x_ℓ and x_s.

The Gibbs free energy of a material in a magnetic field is given by Wood [19] as

$$G' = G - v\vec{H} \cdot \vec{M} \tag{20}$$

where $\vec{M}$ is the magnetization, $x\vec{H}$. Thus the change in G at the interface with a magnetic field applied will be

$$\Delta G' = \Delta G - v(x_\ell - x_s)H^2 \tag{21}$$

It is easy to show that, as long as $S_c \delta T > 4Qv$ and the difference $x_\ell - x_s$ is positive, the free energy term

$$(1 - e^{\Delta G'/kT'}) / (1 - e^{\Delta G/kT})$$

is less than unity while if $x_\ell - x_s$ is negative, the free energy term is greater than one. The same conditions on $x_\ell - x_s$ determine whether ΔT is positive or negative, thus yielding a somewhat more complicated criterion for determining whether solidification rate increases or decreases than was found by Schieber [11].

DISCUSSION OF CALCULATION RESULTS

From equations 12, 13, 15, 18, 19 and 21 and the parameter values given in Table I, the various terms in equations 7, 8 and 9 can be calculated and used to determine values for f_o'/f_o, D'/D and U_c'/U_c for both the microgravity and magnetic field cases of altered external field conditions. Note that the references for the input data are indicated under the appropriate values in Table I. Estimated values of v_o and $\frac{\gamma v^*}{v}$ were determined from atomic and ionic radii shown on the Sargent-Welch Table of Periodic Properties of the Elements (1968). In such estimations, a 50% composition for InSb is assumed. Values of the variable parameters which were assumed for the examples presented here are given below the table. A magnetic field strength of 10^5 Oersteds was chosen because it is in the range of high field measurements made by Carruthers and Wolfe [12] and by Schieber [11].

Table II presents the values for U_c'/U_c, D'/D, f_0'/f_0 and the free energy term which were computed from equations 7, 8 and 9. For numbers as close to unity as these, the percent change in a quantity X is approximately $100(\frac{X'}{X} - 1)$ where X' is the perturbed value. Expressed this way, the changes in both diffusion coefficient and solidification rate are in the range of $10^{-5}\%$ for the micro-gravity case and 0.1 to 1.1% for the magnetic field case. The diffusion coefficient is seen to increase slightly, except for mercury in a magnetic field, while the solidification rate decreases insignificantly in microgravity but increases slightly in magnetic fields. The decrease in diffusion coefficient for mercury in a magnetic field is due primarily to the low value of the parameter $\gamma v^*/v$ for Hg. If the magnetic field strength were increased sufficiently, however, this would cause D'/D to be greater than one for mercury as well as for the other materials. Mercury is also the only material to exhibit a negative difference in magnetic susceptibility, and thus the free energy term for Hg is greater than one, as expected. Neither of these deviations produce a significant effect on the solidification rate of Hg. The data in Table II also show that the free energy term is insensitive to external field changes, but that the diffusion coefficient is sensitive to changes in magnetic field. This is due to the more direct dependence of the diffusion coefficient on field-induced volume change and to the fact that volume changes are much larger (by factors proportional to H^2) in magnetic fields than microgravity where $\frac{\Delta v}{v}$ is on the order of 10^{-8}.

The percent changes in diffusion coefficient and solidification rate derived here can at best be considered only order-of-magnitude estimates for three reasons. First, in the magnetic field case, approximations were made based on

the relative magnitudes of H and H_o, and in the microgravity case, the change in gravitational (or other) accelerations was an approximation. Second, each calculation contained at least one parameter which was estimated rather than being obtained from experimental data, as well as three parameters which were assumed in order to carry out example calculations. Finally, the Free Volume Model does not consider any possible effects of bulk fluid motion (convection) on solidification rate. The convection problem in multi-component liquids, which is the primary reason for studying solidification processes in microgravity or magnetic fields, is best handled by other theoretical methods [29]. Thus the data of Table II can be interpreted as providing an indication of the direction of change in D and U_c due to external field effects and a rough estimate of its magnitude.

CONCLUSIONS

From the foregoing discussion it appears, within the framework of the Free Volume Model, that reducing the acceleration (gravitational) forces on a solidifying system has only an insignificant effect on the diffusion coefficient (and thus also the diffusion rate) and on the solidification rate. This of course does not mean that microgravity has no effect on the overall solidification process, but only that acceleration forces have very little _direct_ effect on D, $\overline{u}$ and U_c. Indirect effects such as those caused by gravity-driven convection have, as was mentioned, not been considered. On the other hand, magnetic fields have a small but significant effect on the three properties of interest, causing them to increase for all materials considered if the field strength is sufficiently high. That this increase in solidification rate is a measurable effect has been

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confirmed by Schieber [11]. Schieber's experimental observations agree qualitatively with the results derived here.

Qualitatively, the effects of microgravity and magnetic fields on diffusion coefficient and solidification rate are identical, insofar as the mathematical formalism of equations 7, 8 and 9 are the same and the effects are dependent on changes in temperature, volume and free energy. The major difference between the two cases is in the magnitude of the effects, with microgravity causing infinitesimal changes and magnetic fields producing small, but finite changes. In the magnetic field case, the amount of change could be increased since there theoretically exists the capability to increase the field strength and thus the important ratio, $\frac{\Delta T}{T}$, beyond the values in the examples reported here. By showing that microgravity has almost no direct effect on diffusion coefficient and solidification rate, this analysis supports the thesis that the primary benefits of materials processing in space arise from the suppression of convection by the elimination of as many acceleration forces as possible, and from the reduction of contamination by containerless, free suspension processing.

TABLE I PARAMETERS USED FOR CALCULATING FIELD EFFECTS*

MATERIAL	x_ℓ cm⁻³	x_s cm⁻³	Q erg/cm³	β cm²/dyne	α °K⁻¹	S_c erg/mole°K	$\frac{\gamma v^*}{v}$	v_o cm³/mole	v cm³/mole	T °K	ρ_ℓ gm/cm³
InSb Reference	-6.816×10^{-7} [20]	-7.612×10^{-7} [20]	2.69×10^{6} [11&21]	3.15×10^{-11} [28]	.000341 [28]	-6.211×10^{8} [21]	0.3 [E]	10.8 [E]	18.2 [25]	793	6.43 [25]
Ge Reference	-4.902×10^{-7} [20]	-6.125×10^{-7} [20]	2.15×10^{6} [11&21]	1.19×10^{-11} [28]	.0001574 [28]	-2.443×10^{8} [22]	0.3 [E]	6.8 [E]	13.0 [25]	1200	5.57 [25]
Hg Reference	-2.466×10^{-6} [26]	-2.128×10^{-6} [26]	1.52×10^{5} [11&21]	3.9×10^{-12} [23]	.00018 [23]	-9.8×10^{7} [21]	.0935 [4]	8.5 [E]	14.6 [24]	224	13.7 [24]
Na Reference	5.859×10^{-7} [27]	4.896×10^{-6} [26]	1.02×10^{5} [11&21]	1.916×10^{-11} [24]	.00028 [26]	-7.01×10^{7} [21]	.236 [4]	17.3 [E]	24.6 [24]	361	0.93 [24]

* H is assumed to be 10⁵ oersteds (7.96X10⁴ amp/cm)

δT is assumed to be 10°K

z is assumed to be 1 cm

E indicates estimated values

TABLE II   EXTERNAL FIELD EFFECTS ON REPRESENTATIVE MATERIALS

MATERIAL	MICROGRAVITY CASE				MAGNETIC FIELD CASE			
	FREE ENERGY TERM	f'_0/f_0	D'/D	U'_c/U_c	FREE ENERGY TERM	f'_0/f_0	D'/D	U'_c/U_c
InSb	.9999993	.99999980	1.0000005	.99999960	.99993	.9876135	1.02237	1.010
Ge	.9999997	.99999993	1.0000003	.99999989	.99987	.9952899	1.00624	1.001
Hg	.9999987	.99999995	1.0000007	.99999935	1.00539	.9983990	.99805	1.002
Na	.9999998	.99999998	1.0000001	.99999991	.99771	.9924613	1.02139	1.011

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