D5-17254

ANALYSIS OF FIELD EFFECTS ON DENSE LIQUID MATERIALS

FINAL REPORT
CONTRACT NAS8-28664
(1-2-50-23598[IF])

STUDY OF LIQUID-SOLID TRANSITION
FOR
MATERIALS PROCESSING IN SPACE

MAY 9, 1973

PREPARED BY

BOEING
MATERIALS RESEARCH
HUNTSVILLE, ALA.

S. J. HENDERSON - PROGRAM MANAGER
R. I. MILLER - PRINCIPAL INVESTIGATOR

BOEING AEROSPACE COMPANY
(A Division of The Boeing Company)
P. O. BOX 1470
HUNTSVILLE, ALABAMA 35807

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
MARSHALL SPACE FLIGHT CENTER, ALABAMA

ANALYSIS OF FIELD EFFECTS ON DENSE LIQUID MATERIALS

CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS

a_0	Free Volume Model proportionality parameter, v/r^3
a	a_0/N_0
$\vec{B}$	Magnetic induction, $\mu\vec{H}$
B	magnitude of $\vec{B}$
B_z	Transverse component of magnetic induction
b_0	$(2/3)\pi N_0\sigma^3$
C	Arbitrary constant
c	Bulk modulus of elasticity
c_v	Specific heat at constant volume
D	Diffusion coefficient
D'	Diffusion coefficient in a magnetic field or low gravity
d	1/2 separation of electromagnet pole faces
E	Internal energy
$\vec{E}$	Electric field vector
$\vec{E}_t$	Electric field transverse to magnetic field
$\vec{E}'$	Electric field "moving with" a flowing liquid
e	Base of natural logarithms
$\mathcal{E}_e$	Eddy current electromotive force ($\vec{B}$ field-induced)
F	Helmholtz free energy
F_M	Magnitude of magnetic force
$F_0, F_2, F_4 \dots$	Constant coefficients of magnetic field expansion
$f(\vec{r},\vec{u},t)$	Boltzmann distribution function
f_0	Interface lattice site fraction
$\vec{f}_1$	Gravitational force term
$\vec{f}_2$	Static magnetic force term
$\vec{f}_3$	Magnetodynamic force term
$\vec{f}_T$	Total external body force (force/volume) field

LIST OF SYMBOLS
(Continued)

G	Gibb's free energy (potential)
ΔG	Change in G across liquid-solid interface
$\Delta G'$	Free energy change in a magnetic field or low gravity
$\vec{g}$	Acceleration due to gravity
g	Magnitude of $\vec{g}$
$\vec{H}$	Magnetic field strength
H	- Enthalpy (Section 2.1) - Magnitude of $\vec{H}$ (Section 2.2)
H_o	Magnitude of H in air or free space
H_r	Radial component of $\vec{H}$
H_θ	Angular component of $\vec{H}$
h	- Planck's constant (Section 2.1) - Hartmann number (Section 2.2), $\sqrt{\frac{\eta_m}{\eta}}$
I	Nucleation rate
I_o	Zeroth order Bessel function
i	$\sqrt{-1}$
$\vec{J}$	Electric current density
$\vec{J}^*$	Complex conjugate of $\vec{J}$
$\vec{J}_e$	Eddy current density
k	- Boltzmann's constant - Arbitrary constant
k_2	Diffusion coefficient proportionality constant in Stokes-Einstein model
k_3	Diffusion coefficient proportionality constant in Swalin model
L	Length characteristic of liquid system geometry, i.e., cylinder height

LIST OF SYMBOLS
(Continued)

M	- Volume magnetization of a liquid (Section 2.1)
	- Magnetic surface charge (Section 2.2)
m	- Mass of one molecule
	- Magnetic dipole moment of one molecule
N	- Number of molecules in a liquid (Section 2.1)
	- Demagnitization factor (Section 2.3)
N_o	Avogadro's number, 6.025×10^{23} mole^{-1}
N_1	Number of solvent molecules
N_s	Number of solute molecules
n	Molecular number density, $N/V = 1/v$
P	Pressure
P_s	Pressure at liquid-vapor interface
P_z^E	Pressure on earth at a point z below surface of a liquid
P_z^s	Pressure in space at a point z
ΔP	Pressure change
Q	Heat rate (watts)
$Q(N,V,T)$	Configuration partition function
R_o	Molecular diameter
R_m	Magnetic Reynolds number, $Lu\mu\sigma$
r	- Average intermolecular separation (Section 2.1)
	- Radial coordinate (Section 2.2)
r_{ij}	Separation of molecules i and j
r_g	Radius of electromagnet pole face
r_m	Radius of cylindrical liquid container
$\hat{r}$	Radial unit vector
$\vec{r}$	Position vector

LIST OF SYMBOLS
(Continued)

S	Entropy
$d\vec{s}$	Surface element
T	Temperature
ΔT	Temperature change
T'	$T + \Delta T$
t	Time
$\vec{u}$	Liquid flow velocity
u	- Magnitude of $\vec{u}$ - Molecular diffusion velocity
$\vec{u}_t$	Liquid flow velocity transverse to magnetic field
u_c	Crystal growth velocity or solidification rate
V	Total liquid volume
ΔV	Volume change
V_1	Volume of solvent
v	Average specific volume, V/N
v_f	Average molecular free volume, $v-v_o$
v_o	Actual molecular volume, $(\pi/6) R_o^3$
v^*	Critical free volume
W	Compressibility factor, PV/NkT
$\vec{w}$	"$\vec{E} \times \vec{B}$ drift" velocity
x	$-(r_m-r)$ -Generalized coordinate
Z	Liquid partition function
Z^o	Solvent partition function
z	Axial coordinate
z_k	Kinetic partition function

LIST OF SYMBOLS
(Continued)

z_{ks}	Solute kinetic partition function
$\hat{z}$	Axial unit vector
$\vec{\nabla}$	Vector partial differential operator
∇^2	Laplacian operator, $\vec{\nabla} \cdot \vec{\nabla}$
α	Thermal diffusivity
β	Isothermal compressibility
γ	Free Volume Model "overlap" parameter
δ	- Ratio of mean-free-path to "instantaneous" free volume (Free Volume Model) - Skin depth (Electrodynamics)
ε	Lennard-Jones energy parameter
η	Viscosity
η_m	Magnetic viscosity
$\Delta\eta$	Viscosity change, = η_m
θ	Angular coordinate
θ_o	$\mathrm{Tan}^{-1}(r_g/d)$
$\hat{\theta}$	Angular unit vector
λ	Thermal wavelength, $\sqrt{\frac{h^2}{2\pi mkT}}$
λ_s	Solute thermal wavelength
μ	- Magnetic permeability (Electrodynamics) - Chemical potential (Thermodynamics)
μ_o	Permeability of free space
μ_s	Solute chemical potential
μ_1^o	Pure solvent chemical potential
ν	Magnetic diffusivity, $1/\mu\sigma$
ρ	Mass density, mn
$\vec{\Sigma}$	Sum of non-electromagnetic forces in the Navier-Stokes equation
Σ	Summation symbol

LIST OF SYMBOLS
(Continued)

σ	- Lennard-Jones distance parameter (Section 2.1)
	- Electrical conductivity (Section 2.2)
σ_l	Liquid-solid surface tension parameter
τ	Time constant
Φ	Total liquid potential energy
Φ_η	Viscous heat dissipation factor
$\phi(r)$	Intermolecular pair potential
χ_m	Magnetic susceptibility
χ_s	Average potential energy seen by a solute molecule
ψ	Gravitational potential, $\vec{g} = -\vec{\nabla}\psi$
ω	Field or current oscillation frequency

SECTION 1

SUMMARY

Objectives

The contract "Study of the Liquid-Solid Transition for Materials Processing in Space" has two primary objectives:

1. To analyze the behavior of dense liquids near the solidification point while the liquid in question is under the influence of magnetic fields or near-zero gravity conditions, and
2. to do this within the framework of existing liquid state models and classical field theory.

These objectives have been accomplished, and this report presents the results obtained thereby.

Approach

The approach taken to this study began by defining four tasks:

Task 1 - Model Identification and Assessment

Task 2 - Determination of Alternate Approach(es) as Required

Task 3 - Incorporation of Models into Field Theory and Thermodynamic Property Derivation

Task 4 - Analysis of Convection, Diffusion and R-F Field Effects.

The models and approaches identified in Tasks 1 and 2 were combined formally with classical field theory in Task 3. In Task 4, the equations derived were used to qualitatively analyze the effects which external fields have on dense liquids.

Liquid models are concerned primarily with liquid structure (thermodynamic properties) or liquid transport properties. The transport properties considered are generally diffusion coefficients, viscosity (fluidity), nucleation rate and crystal growth rate. Calculation of these quantities from first principles is the purpose of the models. However, these quantities by themselves do not entirely describe liquid transport, particularly convection. Natural convection is described by Boltzmann transport theory and convection in a magnetic field is described by magnetohydrodynamics (MHD) which is a combination of Boltzmann transport theory and classical field theory. Determination of the form of MHD theory that is required to discuss dense liquid behavior in a magnetic field was the function of Task 2. The models do contribute to MHD analysis though, by providing an equation of state for the liquid and by deriving parameters such as viscosity, heat capacity and magnetic permeability which are important constituents of the MHD equations.

Approach (Continued)

Field effects on diffusion were discussed in terms of the Free Volume Model description of diffusion coefficient and crystal growth rate augmented by the defining equation for isothermal compressibility. This equation relates the change in liquid volume to the external field-induced pressure change in the liquid. Gravitational pressure changes between the earth's surface and earth orbit were derived as were magnetic pressure changes in the laboratory.

Results

A thorough search of the literature identified thirty-six independent liquid state models plus at least six models based on the Distribution Function approach to liquid state theory. Most of the thirty-six models treat limited aspects of the liquid state. That is, they attempt to explain a few liquid properties (in some cases, only one) rather than describing the entire liquid state. Those models which do try to explain a large number of liquid properties are still being tested by the scientific community against experiment to ascertain their accuracy and the range of parameters to which they are applicable.

The Free Volume Model (see Section 2.1) was selected as the best of these models on the basis of its simple view of liquid structure combined with successful prediction of liquid transport properties, and its derived capability for explaining thermodynamic properties. The Guggenheim Dilute Solution Model was selected for description of two-component ("doped") liquids while the Curie Law of paramagnetism was chosen to describe the magnetic permeability of liquids.

"Backup" models determined to have possible application to materials processing problems include:

Significant Structure Theory (1 and 2-Component Models)

Onsager Dielectric Theory

Kaiser & Rosenweig Ferrofluid Model

Kuhlmann-Wilsdorf Model

Ookawa Model

Tong Model

Walls and Upthegrove Model

Shereshefsky Model

Two Structure Model

Widom Model

Central Atoms Model

Kirkwood Dielectric Theory

Results (Continued)

These are described in varying detail in the Task 1 report, A Summary of Liquid State Models for Materials Processing in Space (Reference 1). The remaining 20 models were considered not suitable for materials processing problems for one or more of the following reasons:

1. the model is grossly inaccurate when compared with experiment,
2. the model is not yet sufficiently developed,
3. the mathematical description of the model involves extremely large sums or products ($\sim 10^{23}$ terms) or requires other calculations which cannot be performed analytically,
4. the model is designed for special applications which are outside the scope of this study.

Thus, several models are required to describe dense liquid phenomena, but these models compliment each other in creating a basis for materials processing in space research. It should be noted that the need for several models (or approximations) would have been the same had the Distribution Function approach (Reference 1) been chosen, since all approaches to describing the liquid state are imperfect at present.

In Task 3, the five simultaneous equations of magnetohydrodynamics were specialized to the case of a dense liquid in the transverse field of a laboratory magnet. Thermodynamic properties were derived from the partition functions of the Free Volume Model and the Guggenheim Model, and the distribution of eddy currents in a conducting liquid with alternating magnetic field was calculated. Also, time-dependent equations for the velocity and distribution function of diffusing molecules were found, though solutions to these equations were not obtained. Finally the explicit mathematical form of the magnetic field due to a laboratory electromagnet was determined. This explicit representation of magnetic fields in terms of spatial coordinates is required to calculate vector derivatives of the fields (on which the magnetic forces depend).

The magnetic field effects on liquids are really of three types: static and dynamic body forces and eddy current effects. Since the materials of interest in this contract (group III and group V elements and their compounds) are paramagnetic and conducting ($\sigma \sim 10^3$ ohm^{-1} cm^{-1}), the static body forces are completely negligible compared to the dynamic effects. The dynamic body force arises from the convective motion of the liquid with velocity $\vec{u}$ in the presence of a static magnetic field, while the eddy current force is present only when the field changes in time. Both these forces depend on the term $\vec{J} \times \vec{B}$ where $\vec{B}$ is the magnetic induction in the liquid.

In the dynamic case, $\vec{J}=\vec{\nabla} \times \vec{H}$, while in the case of eddy currents, $\vec{J}$ is proportional to the time derivative of $\vec{B}$. In either case, the fields can in principle be arranged so that the magnetic body force opposes

Results (Continued)

the convective flow caused by gravitational body forces. However, the actual laboratory configuration which successfully eliminates or drastically reduces convection may be extremely difficult to achieve because of the field geometry and field strength required. Furthermore, the fact that the region which the magnetic field occupies is limited in extent also limits the usefulness of this technique for materials processing. In earth orbiting laboratories, magnetic field strength, geometry and extent considerations are of course not required to reduce convection.

The analysis of field effects on diffusion (within the framework of the Free Volume Model) yields the interesting result that application of a magnetic field or removal of a gravitational field will increase the rate of crystal growth from an undercooled melt. The conditions under which this occurs, and the different methods used to derive this result are discussed in detail in Section 2.3. Actually, by knowing the effects which magnetic and gravitational fields have on volume, viscosity and temperature, one can use several models to predict that the diffusion coefficient will increase with an increase in magnetic field or a decrease in gravitational field. The Free Volume Model then predicts that growth rate increases with increasing diffusion coefficient and decreasing Gibbs free energy. This increase in growth rate has been observed in the laboratory by Schieber (see Section 2.3).

Although the equations which predict the increased growth rate are similar in both the magnetic and gravitational cases, this provides only a formal, qualitative comparison. To determine which case would predict the most significant increase, and to compare the magnetic case to Schieber's results, quantitative calculations are required. This also involves improved understanding of the way free volume is distributed in liquids and more accurate determination of some of the Free Volume Model parameters.

Conclusions and Recommendations

The major conclusions to be reached from this study are:

1. the Free Volume Model is the most practical model for use in the study of materials processing in space,
2. other models (suggested in Reference 1) are required to deal with a wide variety of dense liquid problems,
3. both magnetic fields and low gravity conditions will produce an increase in diffusion coefficient which will result in a increased growth rate of a crystal,
4. laboratory magnetic fields and low-gravity conditions produce qualitatively similar results (i.e., pressure terms) with respect to inhibition of convection and enhancement of diffusion,

Conclusions and Recommendations (Continued)

5. time-varying magnetic fields induce eddy currents in the liquid which produce body forces and tend to disrupt convection,

6. much quantitative and experimental comparison is needed before the relative merits of ground-based magnetic field techniques and space processing can be ascertained,

7. the space environment provides a perfect "textbook" laboratory for the study of those aspects of the liquid state which are not yet understood, because in space the gravitational perturbation (so often ignored in liquid state theory) is not present.

Thus, it is seen that the behavior of dense liquids in space and their behavior under the influence of magnetic fields are formally quite similar. But this does not indicate which of the two environments is most practical for actual materials processing. Determination of the most practical environment will require a quantitative assessment of field geometries and field strengths required to completely offset gravitational effects. This assessment should be performed for a number of realistic materials processing situations.

Before calculations of this nature can be performed however, a great deal of liquid parameter data must be obtained for each material of interest. Parameters required include: electrical conductivity, magnetic Reynold's number, magnetic permeability, thermal diffusivity, viscosity, average density, characteristic convective flow velocity, Lennard-Jones potential parameters, hard sphere molecular diameters and liquid P-V-T data. Obtaining these parameters for liquid materials of interest will be a major task and should begin as soon as practicable. It is also recommended that calculations be performed utilizing the equations of Section 2.3 to determine quantitatively the relative effects of low gravity and magnetic fields on diffusion and solidification rate in dense liquids. These calculations should also be compared to the results obtained experimentally by Schieber. Finally, it is recommended that a number of space experiments be defined and initiated to measure dense liquid thermodynamic and transport properties under low-gravity conditions. Specifically these properties should include temperature, pressure, volume, internal energy, Gibbs free energy, enthalpy, entropy, diffusion coefficient, viscosity and solidification rate.

THIS PAGE LEFT BLANK INTENTIONALLY

SECTION 2

ANALYTICAL RESULTS

2.1 A REVIEW OF LIQUID STATE MODELS

There are two analytical approaches available for the study of the liquid state: the Distribution Function approach and the Liquid Model approach. The Distribution Function approach is the more rigorous of the two, but often its mathematical formulation involves integral equations or other computations which cannot be solved in closed form. Even when solution is possible, the results do not compare more favorably with experiment than do results obtained from the model approach. The Distribution Function approach is particularly inaccurate in its description of liquids near the liquid-solid transition. On the other hand, liquid models are available which are specifically designed to describe dense liquids near the liquid-solid transition, and which are constructed to be mathematically more practical than the Distribution Function approach. In addition, most models are based on combinations of experimental observations and simple assumptions which make them conceptually easy to understand. For these reasons, the Liquid Model approach is recommended for application to practical materials processing problems in the space environment.

In general, different models describe different liquid properties. For instance, some models describe thermodynamic properties while others describe transport or electric or magnetic properties. A few models such as the Free Volume Model (as developed by Boeing) or the Significant Structures Model, address both thermodynamic and transport properties. A detailed discussion of liquid state theory and liquid models is contained in the Interim Report for Task 1 of this contract (Reference 1). However, a brief review of liquid state concepts, assumptions and models important to the study described by this report is appropriate here.

Basic Assumptions

The most important assumption in the study of liquids is that almost all the properties of a liquid may be calculated from the interactions of pairs of molecules, and that contributions from "3-body" or higher order interactions can be neglected. Equally important is the assumption that these interactions are additive. Specifically, it is assumed that the total potential energy of a system of molecules is given by:

$$\Phi = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \phi_{ij}(r_{ij}) \tag{1}$$

2.1 (Continued)

where ϕ_{ij} (r_{ij}) is the potential energy between molecules i and j, which are separated by a distance r_{ij}. While it is obvious that the force on a molecule in a liquid is due to the effects of all other molecules in the liquid, the pair approximation (equation 1) is necessary to simplify mathematical analysis and has been justified by agreement with experiment in many instances.

Thermodynamic and mechanical properties of liquids are derived from a quantity called the partition function (P.F.) which has the form:

$$Z = z_k Q(N, V, T) \quad . \tag{2}$$

The first factor, z_k, is the kinetic P.F. which is derived from the motions of the individual particles in the liquid. If only translational motion of the particles is considered, the kinetic P.F. is simply:

$$z_k = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} = \lambda^{-3N} \tag{3}$$

where T is absolute temperature, N is the number of particles, k is Boltzmann's constant, h is Planck's constant, m is the mass of one particle and λ is the thermal wavelength.

The second factor in equation 2 is called the configuration partition function and is defined by the expression:

$$Q(N,V,T) = \frac{1}{N!} \int_V e^{-\Phi/kT} \, d^3x \tag{4}$$

which is an integration over the three space coordinates of the N particles in the system where Φ is the total energy of the system. As equation 1 indicates, for real liquids Φ is an extremely complicated function of coordinates. This is why many different models of the liquid state have been developed - to allow one to calculate approximate expressions for Q(N,V,T) from certain simplifying assumptions about the liquid situation of interest, which will then yield predictions about that situation which are reasonably accurate.

An assumption usually made to evaluate equation 4 is that all ϕ_{ij} have the same form. Then equation 1 reduces to:

$$\Phi = \sum_{i=1}^{N} \phi\,(r_i) \tag{5}$$

2.1 (Continued)

where i now labels the distance vector, r_i, between each pair of molecules. In cell models of liquids it is assumed that all molecules are situated in cells defined by their nearest-neighbors. The average radii of all cells are assumed to be equal, that is $r_i = r_j$, so that (Reference 2):

$$\Phi = N\phi(r) \tag{6}$$

This greatly simplifies the integration over coordinates and thus the configuration P.F. itself. Unfortunately, the correct form for $\phi(r)$ is not known, though several approximate forms which are based on careful experimental observation are available. The most widely used of these is the Lennard-Jones potential:

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{7}$$

where ε is an interaction energy constant and σ is a distance parameter equal to the value of the intermolecular separation, r, which makes $\phi(r) = 0$. Thus the assumptions of equations 5, 6 and 7, coupled with the specific assumptions of a given model, allow one to obtain approximations for Q(N,V,T).

Finally, the thermodynamic properties of the liquid are obtained from the partition function by the following set of equations:

FREE ENERGY: $$F = -kT \ln Z \tag{8}$$

INTERNAL ENERGY: $$\frac{E}{kT} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{9}$$

EQUATION OF STATE: $$\frac{P}{kT} = \left(\frac{\partial \ln Z}{\partial V}\right)_T \tag{10}$$

INTERNAL ENTROPY: $$\frac{S}{k} = \ln Z + T\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{11}$$

ISOTHERMAL COMPRESSIBILITY: $$\beta = -\frac{1}{V}\left[kT\left(\frac{\partial^2 \ln Z}{\partial V^2}\right)_T\right]^{-1} \tag{12}$$

2.1 (Continued)

Once these basic functions are known, all other thermodynamic properties may easily be found (References 3 and 4). The next three subsections will discuss the three models most applicable to the Liquid-Solid Transition Study.

The Free Volume Model

The Free Volume Model, which has been developed by Turnbull and Cohen (References 2 and 5-7), is perhaps the most simple model of the liquid state which is at the same time realistic in concept, practical in its mathematical formalism and reasonably accurate in its predictions of liquid properties. Development of this model has been motivated by observed liquid properties which, relative to solid properties, appear to be strongly correlated with the corresponding volume differences. The Free Volume Model makes no specific assumption about molecular shapes, and thus leaves one free to assume spherical shapes, or more realistic shapes when considering polyatomic molecules, depending on the accuracy one wishes to achieve.

The basic assumption of this model is that a liquid molecule is caged most of the time by its nearest neighbors, and that within this cage its free volume is defined by:

$$v_f = v - v_o \tag{13}$$

where v is the specific volume (or volume of the cage), V/N, and v_o is the actual volume of the molecule. v_o is dependent on pressure, though for normal pressures this dependence is negligible. It is also assumed that the potential energy of the molecule in its cage is approximately equal to the intermolecular potential, $\phi(r)$, which is chosen to be the Lennard-Jones potential, equation 7. The total partition function for this model is then:

$$Z(N,V,T) = \left[\frac{v_f}{\lambda^3} e^{-\phi(r)/kT} \right]^N \quad . \tag{14}$$

If the procedure of equation 10 is used to derive the equation of state, one finds for the Free Volume Model:

$$PV = \frac{NkT}{1 - v_o/v} - NV \left(\frac{\partial \phi}{\partial V} \right)_T \quad . \tag{15}$$

2.1 (Continued)

In order to evaluate the partial derivative, we first note that:

$$NV\left(\frac{\partial\phi}{\partial V}\right)_T = N\ v\left[\left(\frac{\partial\phi}{\partial r}\right)\left(\frac{\partial r}{\partial v}\right)\right]_T \tag{16}$$

Further work with the Free Volume Model at Boeing has centered around the "lumped-parameter" assumption that the specific volume is directly proportional to the cube of the intermolecular separation with proportionality factor a_o:

$$v = a_o r^3 \quad . \tag{17}$$

This allows complete evaluation of the partial derivative in equation 15 to yield:

$$\frac{PV}{NkT} = \frac{1}{1-v_o/v} + 16\,\frac{\varepsilon}{kT}\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2\left[\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 - \frac{1}{2}\right] \tag{18}$$

where $a = a_o/N_o$ (N_o is Avogadro's number) and $b_o = (2/3)\pi\ N_o\sigma^3$. If equation 18 is solved for a^2, then:

$$a^2 = \frac{1}{4}\left(\frac{2\pi}{3}\right)^2\left(\frac{v}{b_o}\right)^2\left[1 + \sqrt{1 - \frac{kT}{\varepsilon}\left(\frac{1}{1-v_o/v} - W\right)}\ \right] \tag{19}$$

where W is the compressibility factor, PV/NkT. Thus a depends on temperature and pressure, but because of the form of this dependence, the variation of a from a constant value (for a given liquid) over certain ranges of T and P should be small. Table I gives a values and deviations for ten liquids over temperature and pressure ranges corresponding to the dense liquid phase.

Equation 18, then, is the equation of state for the Free Volume Model, and its accuracy is determined largely by the deviation of the a parameter over the range of T and P to which it is applied. Table I shows that this deviation is less than 20% for all liquids studied and is less than 1% for water. A 20% inaccuracy, while not desirable, is still normal for theoretical predictions of dense liquid properties.

TABLE I

APPLICABLE FREE VOLUME EQUATION OF STATE PARAMETERS FOR VARIOUS LIQUIDS

LIQUID MATERIAL	PRESSURE RANGE	TEMPERATURE RANGE	v_o [a]	b_o [b]	ε/k [b]	MEAN VALUE OF a^2	DEVIATION OF a^2
	ATMOSPHERES	K	cm^3/gm mole	cm^3/gm mole	K		
Ar	200-500	90-150	7.69	46.08	93.3	0.832	0.124
He	0.5-2.0	3.0-4.2	2.45	20.95	10.22	3.93	0.37
N_2	180-800	90-120	9.95	69.14	71.4	0.579	0.111
O_2	0.1-50	55-85	8.02	52.60	106.7	0.350	0.021
NH_3	800-1100	310-400	16.26	30.78	558.3	1.11	0.142
CO_2	500-1000	273-303	14.23	77.25	195.2	0.462	0.066
H_2O	1-1000	273-373	6.92	23.25	809.1	1.09	0.01
CH_3OH	1000-12000	293-353	20.19	60.17	481.8	0.971	0.081
C_3H_7OH	1000-12000	293-353	26.87	118.8	576.7	1.21	0.122
Hg	1000-7000	273-293	8.52	33.03	750	0.417	0.046

[a] References 8 and 9

[b] Reference 10

2.1 (Continued)

Since the derivative of intermolecular potential with respect to volume occurs often in calculating thermodynamic properties from the partition function, relation (17) has allowed the derivation of

$$\text{INTERNAL ENERGY:} \quad \frac{E}{NkT} = \frac{3}{2} + \frac{4\varepsilon}{kT}\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2\left[\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 -1\right] \tag{20}$$

$$\text{CHEMICAL POTENTIAL:} \quad \frac{\mu}{kT} = \ln\frac{\lambda^3}{v_f} + \frac{1}{1-v_o/v} + \frac{4\varepsilon}{kT}\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 \times\left[5\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 -3\right] \tag{21}$$

$$\text{ENTHALPY:} \frac{H}{NkT} = \frac{3}{2} + \frac{1}{1-v_o/v} + \frac{4\varepsilon}{kT}\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2\left[5\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 -3\right] \tag{22}$$

$$\text{FREE ENERGY:} \quad \frac{F}{NkT} = \ln\frac{\lambda^3}{v_f} + \frac{4\varepsilon}{kT}\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2\left[\left(\frac{3a}{2\pi}\right)^2\left(\frac{b_o}{v}\right)^2 -1\right] \tag{23}$$

$$\text{ENTROPY:} \quad \frac{S}{Nk} = \frac{3}{2} + \ln v_f/\lambda^3 \quad . \tag{24}$$

The Free Volume Model treats diffusion by assuming that random density fluctuations can open holes in the cages of individual molecules which are large enough to permit the translation of a molecule across this void created within its cage. Thus diffusion is viewed as the result of a redistribution of free volume within the liquid rather than as the result of an activation in the ordinary sense (Reference 5). If the free volume exceeds some critical value, v*, then diffusion can take place, the diffusion coefficient being:

$$D = \frac{1}{3}\,\delta u\left(v^* + \frac{v_f}{\gamma}\right) e^{-\gamma v^*/v_f} \tag{25}$$

where δ is the ratio of the mean-free-path to the "instantaneous" free volume, u is the velocity of the molecule as it diffuses (taken to be the gas kinetic velocity) and δ is an overlap factor, lying between 1/2 and 1, which accounts for the fact that more than one molecule can have the same value of the free volume.

Once the diffusion coefficient is known, several other transport properties become available. First, the viscosity is inversely related to the diffusion coefficient by:

2.1 (Continued)

$$\eta = \frac{kT}{3\pi R_o D} \tag{26}$$

where R_o is the molecular diameter. Crystallization is characterized by two rate functions: the frequency per unit volume at which crystals nucleate, I, and the crystal growth velocity, u_c. These functions are:

$$I = \left(\frac{ND'}{VR_o^2}\right) e^{-\frac{16\pi\sigma_1^3}{3F^2kT}} \tag{27}$$

$$u_c = D'' \frac{f_o}{R_o} \left(1 - e^{\frac{\Delta G}{kT}}\right) \tag{28}$$

where: σ_1 is a parameter identified with the liquid-crystal surface tension,

F is the free energy of crystallization per volume,

ΔG is the change in free energy at the crystal-melt surface,

and f_o is the fraction of lattice sites in the boundary to which molecules can be attached.

Strictly speaking, D' and D" are rate constants from nucleation theory, but Turnbull (Reference 2) finds that to a good approximation, D", D' and D can be considered identical.

It should be noted that definitions of the free volume other than equation 13 do exist (References 2, 7 and 11). However, they all involve some combination of the specific volume, which is a thermodynamic variable, and some reference volume which is approximately constant. Therefore, since v_o can be calculated from handbook data for various molecules, equation 13 is probably more practical than the other definitions. The critical volume for diffusion, v*, is not really specified by the theory. But it is found experimentally that the product, γv^*, is near the molecular volume, v_o, so that calculations of transport and kinetic properties in the Free Volume Model are greatly simplified.

The Guggenheim Dilute Solution Model

In his classic book (Reference 12), Guggenheim presents a general treatment of the dilute solution (or "doped" liquid) situation which leads to a simple partition function for the mixture when the P.F. for the solvent

2.1 (Continued)

is known. The initial assumption is that interactions between solute molecules can be neglected, so that these molecules are viewed as a perfect quasi-gas moving freely in a region of constant potential energy, χ_s. χ_s depends on the nature of the solute, the nature of the solvent, and the temperature. The partition function is thus:

$$Z = \frac{Z^0}{N_s!}\left(z_{kS}\, V\, e^{\frac{\chi_s}{kT}}\right)^{N_s} \qquad (29)$$

where N_s is the number of solute molecules, z_{ks} is the kinetic P.F. for the solute (including internal effects, as desired), and Z^0 is the P.F. for the one-component solvent. V is the total volume, as usual. From equation 29, the free energy is simply:

$$F = -kT \ln Z^0 - N_s\chi_s - N_s kT \ln \frac{z_{kS}Ve}{N_s} . \qquad (30)$$

Differentiating F with respect to N_s yields the chemical potential for the solute:

$$\frac{\mu_s}{kT} = -\frac{\chi_s}{kT} + \ln\frac{N_s}{N_1} - \ln\left(z_{kS}V_1\right) \qquad (31)$$

where N_1 is the number of solvent molecules and V_1 is the volume of the solvent. By using the Gibbs-Duhem relation (Reference 13), the chemical potential for the solvent is:

$$\frac{\mu_1}{kT} = \frac{\mu_1{}^0}{kT} + \ln\frac{N_1}{N_1 + N_s} \qquad (32)$$

where the subscript 1 refers to the solvent and the superscript o indicates a quantity for the pure solvent substance. The importance of the chemical potentials arises from the fact that in mixtures, the chemical potentials are identical to the partial molar Gibbs potentials of the components

$$\mu_1 = G_1 , \qquad \mu_s = G_s \qquad (33)$$

This is useful for two reasons:

(1) in any reversible isothermal process (such as the liquid - solid transition) the decrease in Gibbs potential is equal to the net work done by the system; and

2.1 (Continued)

(2) when a mixture undergoes a first order phase transition, the equilibrium distribution of the substance s between the two phases is determined by the condition that μ_s have the same value in each phase, since equal Gibbs potentials is the criterion for phase equilibrium.

Guggenheim considered only thermodynamic properties of dilute mixtures in his model, and neglected the transport properties. However, several other models (Reference 1), including the Free Volume Model, provide descriptions of transport properties of multi-component mixtures. Thus other models must be used in conjunction with the Guggenheim model to completely describe the liquid system. The thermodynamic functions for dilute solutions which have been derived from the Guggenheim model (expressed in terms of the pure solvent functions) are:

FREE ENERGY:

$$\frac{F}{N_1 kT} = \frac{F^0}{N_1 kT} - \frac{N_s}{N_1}\left(\frac{\chi_s}{kT} + \ln \frac{Ve}{N_s \lambda_s^3}\right) \tag{34}$$

EQ. OF STATE:

$$\frac{PV}{N_1 kT} = \frac{P^0 V}{N_1 kT} + \frac{N_s}{N_1} \tag{35}$$

ENTROPY:

$$\frac{S}{N_1 k} = \frac{S^0}{N_1 k} + \frac{N_s}{N_1}\left(\frac{3}{2} + \ln \frac{Ve}{N_s \lambda_s^3}\right) \tag{36}$$

INTERNAL ENERGY:

$$\frac{E}{N_1 kT} = \frac{E^0}{N_1 kT} + \frac{N_s}{N_1}\left(\frac{3}{2} - \frac{\chi_s}{kT}\right) \tag{37}$$

ENTHALPY:

$$\frac{H}{N_1 kT} = \frac{H^0}{N_1 kT} + \frac{N_s}{N_1}\left(\frac{5}{2} - \frac{\chi_s}{kT}\right) \tag{38}$$

SPECIFIC HEAT:

$$C_v = C_v^0 + \frac{3}{2} N_s k \tag{39}$$

The Curie Law Of Paramagnetism

The Curie law of paramagnetism was discovered experimentally by Pierre Curie in 1895 and derived theoretically by Paul Langvin in the early twentieth century. Langevin's procedure was to derive the average value of the molecular magnetic dipole moments in the direction of an applied field. The result is:

$$\overline{m \cos \theta} = \frac{m^2 H_{in}}{3kT} \tag{40}$$

2.1 (Continued)

where H_{in} is the resulting internal field, θ is the angle between the field and an individual dipole, and m is the permanent dipole moment of a molecule.

The volume magnetization of the bulk material is obtained by multiplying equation 40 by the density, n. The magnetic susceptibility of the material is then:

$$\chi_m = \frac{M}{H_{in}} = \frac{nm^2}{3kT} \tag{41}$$

Once the susceptibility of a liquid is known, the magnetic permeability is given by:

$$\mu = (1 + \chi_m)\,\mu_0 \tag{42}$$

where μ_0 is the permeability of free space. The magnetic induction, $\vec{B}$, which determines the force on a material in an external field, $\vec{H}$, is then related to the field by:

$$\vec{B} = \mu \vec{H} \quad . \tag{43}$$

The Curie Law model is important in materials processing because all natural liquids, that is those which are not suspensions of ferromagnetic powders, are paramagnetic or diamagnetic, with most materials of interest in space processing being paramagnetic. This means that equation 43 holds whereas it is invalid for ferromagnetic material. Equation 43 in turn allows straightforward calculation of the effect external magnetic fields have on liquids. This would not be possible if $\vec{B}$ were not a linear function of $\vec{H}$. In practical calculations, it is not always necessary to make use of equation 41. Since χ_m is on the order of 10^{-6} for paramagnetic materials (-10^{-6} for diamagnetic materials), it is often sufficient to use a constant value for μ, since it will change only slightly with varying temperature and density. In any event, it is the magnetic permeability of a liquid which couples the liquid directly to a static magnetic field and, with the electrical conductivity, helps couple liquid and field when motion is involved.

2.2 FIELD EFFECTS ON CONVECTION

To understand the effect external fields have on convection, one must first understand the general theory of fluid flow, which is derived from Kinetic Theory (Reference 14). The first step is the derivation of the Boltzmann transport equation which is a nonlinear integro-differential equation for the distribution function $f(\vec{r}, \vec{u}, t)$. f is defined so that

$$f\ (\vec{r},\vec{u},t)\ d^3r\ d^3u$$

is the number of molecules at time t which have positions lying within a volume element d^3r in the region about $\vec{r}$ and within a velocity-space element d^3u about $\vec{u}$. Needless to say, solution of the Boltzmann transport equation poses a tremendous mathematical problem. However, by combining approximations to the transport equation with the conservation theorems for mass, momentum and energy, the equations of viscous fluid dynamics may be derived. These are commonly called the continuity, Navier-Stokes and temperature equations and are usually combined with an equation of state which provides an independent relationship between temperature, pressure and density.

It should be noted here that density, rather than specific volume, is customarily used in discussing fluid flow problems. These variables are related by:

$$n = \frac{1}{v} = \frac{N}{V} = \frac{\rho}{m} \tag{44}$$

where N is the total number of molecules and V is the total volume of the system. n is sometimes called the number density to distinguish it from the mass density, ρ, and m is the molecular mass.

Boltzmann transport theory and the fluid dynamics equations derived from it might be considered as an additional model to those in Section 2.1. Or they might be considered an alternate approach to the problem of field effects on liquids in the sense that fluid dynamics is quite different from the models in Section 2.1. In this sense, transport theory may be considered as part of Task 2 of the contract, which was to "determine alternate approach(es) as required."

The Equations of Magnetohydrodynamics

If a liquid is placed in a magnetic field, the theory which describes the liquid-field system is called magnetohydrodynamics (MHD). For the description of such a system, one adds to the four fluid dynamics equations discussed above (modified to include magnetic forces) a fifth equation which governs the behavior of the field in the region of the liquid. The five simultaneous MHD equations are then:

2.2 (Continued)

CONTINUITY: $$\frac{\partial n}{\partial t} + \vec{\nabla}\cdot n\vec{u} = 0 \tag{45}$$

NAVIER-STOKES: $$\rho\left(\frac{\partial}{\partial t} + \vec{u}\cdot\vec{\nabla}\right)\vec{u} = \vec{f}_T - \vec{\nabla}\left(P - \frac{\eta}{3}\vec{\nabla}\cdot\vec{u}\right) + \eta\nabla^2\vec{u} \tag{46}$$

TEMPERATURE: $$\left(\frac{\partial}{\partial t} + \vec{u}\cdot\vec{\nabla}\right)T = -\frac{1}{c_v}(\vec{\nabla}\cdot\vec{u})\,T + \alpha\nabla^2 T + \eta\Phi_\eta \tag{47}$$

STATE: $$P = \frac{nkT}{1-v_o n} - A_3 n^3 + A_5 n^5 \tag{48}$$

FIELD: $$\frac{1}{\nu}\frac{\partial\vec{H}}{\partial t} = \nabla^2\vec{H} + R_m\vec{\nabla}\times\left(\frac{\vec{u}\times\vec{H}}{Lu}\right) \tag{49}$$

where: $\vec{u}$ is the velocity of a small liquid volume element,

$\vec{f}_T$ is the total body force (force per unit volume) due to external fields,

P is pressure

η is viscosity in poise (1 poise = $10^2 \frac{\text{dyne sec}}{\text{cm}^2}$)

T is absolute temperature

c_v is specific heat at constant volume

α is thermal diffusivity $\alpha = \frac{K}{\rho c_v}$

$\eta\Phi_\eta$ is a viscous heat dissipation term

v_o is the hard-sphere volume of a molecule $v_o = \frac{1}{6}\pi R_o{}^3$

ν is magnetic diffusivity $\nu = \frac{1}{\mu\sigma}$

R_m is magnetic Reynolds number ($R_m = Lu\mu\sigma$) .

A_3 and A_5 are constants related to the Free Volume model parameters (Section 2.1) by:

$$A_3 = 8\varepsilon\left(\frac{3ab_o}{2\pi}\right)^2 , \qquad A_5 = 16\varepsilon\left(\frac{3ab_o}{2\pi}\right)^4 \tag{50}$$

2.2 (Continued)

Thus, the models discussed in Section 2.1 enter the MHD equations at three points. Of course equation 48 comes from the Free Volume Model (it should be replaced by the equation of state from the Guggenheim model, when dealing with two-component liquids). The magnetic permeability occurs in both ν and R_m in the field equation (49), and also contributes to the external force term, f_T, in the Navier-Stokes equation. This body force term will now be discussed in some detail.

Explicit Terms and Approximations

In the case of interest, i.e., a liquid under the influence of both gravitational and magnetic fields, the force term can be considered the sum of three component terms:

$$\text{GRAVITATIONAL:} \quad \vec{f}_1 = \rho\vec{g} = -\vec{\nabla}\rho\psi \tag{51}$$

$$\text{STATIC MAGNETIC:} \quad \vec{f}_2 = -\frac{1}{2}H^2\vec{\nabla}\mu + \frac{1}{2}\vec{\nabla}\left(H^2\rho\frac{\partial\mu}{\partial\rho}\right) \tag{52}$$

$$\text{MAGNETODYNAMIC:} \quad \vec{f}_3 = \vec{J}^* \times \vec{B} \quad . \tag{53}$$

$\vec{f}_1$ is obviously proportional to the local gravitational acceleration, which can be expressed as the gradient of a potential function, ψ (or of $\rho\psi$ where density gradients are small). The static term, $\vec{f}_2$, is the body force which is applied to the liquid when the field is constant in time and when the liquid is at rest. Since μ has the form of equation 42, the derivatives of μ can be considered to be derivatives of the susceptibility, χ_m. For paramagnetic (or diamagnetic) liquids, χ_m is on the order of $\pm 10^{-6}$ and the derivatives of χ_m are correspondingly small. So to a good approximation we have:

$$\vec{f}_2 \simeq 0 \quad . \tag{54}$$

The magnetodynamic term really applies to two different cases depending on whether the magnetic field is constant in time or not. For the case of a static field with convection in the liquid, Maxwell's fourth equation states:

$$\vec{J} = \vec{\nabla} \times \vec{H} \quad . \tag{55}$$

2.2 (Continued)

Therefore equation 53 becomes:

$$\vec{f}_3 = \mu(\vec{\nabla} x \vec{H}) x \vec{H} = \mu[(\vec{H} \cdot \vec{\nabla}) \vec{H} - \frac{1}{2} \vec{\nabla} H^2] \quad . \tag{56}$$

by applying a vector identity (Reference 15). We can now write the entire external body force term as:

$$\vec{f}_T = \mu(\vec{H} \cdot \vec{\nabla}) \vec{H} - \vec{\nabla} [\rho\psi + \frac{1}{2} \mu H^2] \quad . \tag{57}$$

In simple geometries, such as those in which H_i is not a function of x_i, the first term of 57 vanishes. This allows a clear comparison of the gravitational and magnetic forces. The resulting expression:

$$\vec{f}_T = - \nabla[\rho\psi + \frac{1}{2} \mu H^2] \tag{58}$$

says that $\rho\psi$, which can be called a gravity-induced pressure, and $\frac{\mu}{2} H^2$, which is a magnetic pressure, are completely equivalent in a formal sense. That is, magnetic fields produce body forces the same as gravity. This means that if the magnetic field can be controlled so that:

$$-\vec{\nabla} (\frac{1}{2} \mu H^2) = + \vec{\nabla} (\rho\psi) \tag{59}$$

then the external body force can be minimized. The pressure gradient in equation 46 can also be interpreted as a body force, and the magnetic field can be used to balance this force as well. Conversely, if the liquid is in a low-gravity orbiting laboratory, and a net body force is desired, a magnetic field may be used to replace gravity by equation 58.

Of course, for a rigorous numerical solution of MHD problems, one must solve equations 45-49 simultaneously for the density, temperature and velocity distributions and for the equilibrium pressure and magnetic field values subject to the boundary conditions of the specific problem. However, the equations of state and continuity are basically constraint equations (if pressure is approximately constant). Therefore, qualitative information about fluid flow patterns, temperature distributions and magnetic field behavior can be obtained from the remaining equations if it is assumed that all other quantities in the respective equations (46, 47, 49) are known. This will be attempted in the following paragraphs.

2.2 (Continued)

Magnetic Field Representations

Before considering how magnetic fields affect liquids in more detail, it will be helpful to digress into how laboratory magnetic fields are represented mathematically.

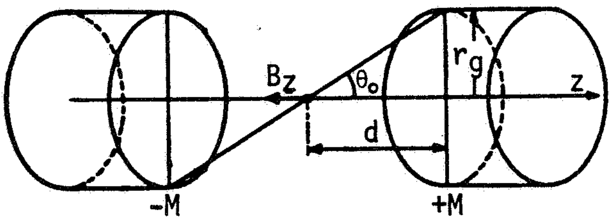

FIGURE 1: MAGNET GEOMETRY

Figure 1 depicts the two pole faces of a laboratory electromagnet. The equation for the magnetic induction between the faces (before a sample is introduced) is:

$$\nabla^2 B_z = 0 \quad . \tag{60}$$

The general solution in cylindrical geometry is:

$$B_z = \sum_k C_k I_0 (ikr) e^{ikz} \tag{61}$$

where k and C_k are constants determined by the boundary conditions, r is the radial distance from the central axis, and I_0 is the zeroth order Bessel function.

If the magnetic surface charge, M, is now calculated from the currents in the pole faces:

$$M = -\frac{1}{2} \vec{\nabla} \cdot (\vec{r} \times \vec{J}_0) \tag{62}$$

2.2 (Continued)

equation 61 may be expressed as an expansion in either r or z (Reference 16):

$$B_z = 4\pi M[F_0 + F_2(z/d)^2 + F_4(z/d)^4 + . . .],\ z^2 < d^2 \qquad (63a)$$

$$B_z = 4\pi M[F_0 - 1/2F_2(r/d)^2 + 3/8F_4(r/d)^4 - . . .], r < d \qquad (63b)$$

where the coefficients F_{2i} are:

$$F_0 = 1 - \cos\theta_0$$

$$F_2 = 3/2(\cos^3\theta_0 - \cos^5\theta_0) \qquad (63c)$$

$$F_4 = -5/8(3\cos^5\theta_0 - 10\cos^7\theta_0 + 7\cos^9\theta_0)$$

The explicit dependence of B_z on r and z shown here allows the calculation of vector derivatives of the field (on which the forces depend) if one recalls that $B_z = \mu H_z$.

Magnetic Diffusion

Equation 49, which is derived in Appendix A, relates the spatial dependence of the magnetic field in a moving fluid to the time dependence of the field. Problems involving dense liquids can be greatly simplified by considering the magnetic Reynolds number in this case, where, from equation A-8:

$$R_m = Lu\ \mu\sigma \quad .$$

For typical group III-group V elements, the properties μ and σ have the following orders of magnitude:

$$\mu \simeq 10^{-8}\Omega sec/cm$$

$$\sigma \simeq 10^3\ \Omega^{-1}cm^{-1} \quad .$$

If the experimental liquid sample has dimensions on the order of 10 cm and natural convection in the liquid produces a velocity on the order of 10^{-1} cm/sec, we have:

2.2 (Continued)

$$R_m \simeq (10\text{cm})(10^{-1}\text{cm/sec})(10^{-8}\Omega\text{sec/cm})(10^{3}\Omega^{-1}\text{cm}^{-1}) = 10^{-5}. \quad (64)$$

Since R_m is so small, the second term on the right hand side of equation 49 can be neglected. This equation then becomes:

$$\frac{1}{\nu}\frac{\partial \vec{H}}{\partial t} = \nabla^2 \vec{H} \quad (65)$$

which is a simple diffusion equation for the way the field penetrates the liquid. The time constant for this penetration will be:

$$\tau = \mu\sigma L^2 = \frac{L}{u} R_m \ . \quad (66)$$

Using the previously assumed values, this is:

$$\tau \simeq 10^{-3}\text{sec} = 1 \text{ msec.}$$

Thus for static fields or for oscillating fields with frequencies of less than 10^3 Hz there will be negligible screening of the field. However, for higher frequency fields, for instance RF fields at 10^6 Hz, the fields will be screened with a penetration or "skin depth" of:

$$\delta = \sqrt{\frac{2}{\mu\sigma\omega}} \ . \quad (67)$$

For the above values of μ and σ, RF fields have a skin depth on the order of 0.4 cm. This is the region in which eddy currents will be of greatest magnitude for such fields.

Eddy Currents

The screening, or exclusion, of external magnetic fields in a conducting medium is accomplished by the electric currents flowing in the region of the medium (liquid) defined by the skin depth. For a conducting liquid in a cylindrical container placed in a transverse magnetic field (see Figure 2), there will be no ordinary current flow, since the liquid is

2.2 (Continued)

not part of an electric circuit. However, if the magnetic field changes in time with a frequency ω, eddy currents will be induced which in turn will give rise to a magnetodynamic body force:

$$\vec{f}_3 = \vec{J}_e^* \times \vec{B} \quad . \tag{53}$$

Here $\vec{J}_e^*$ is the complex conjugate of the induced eddy current, $\vec{J}_e$.

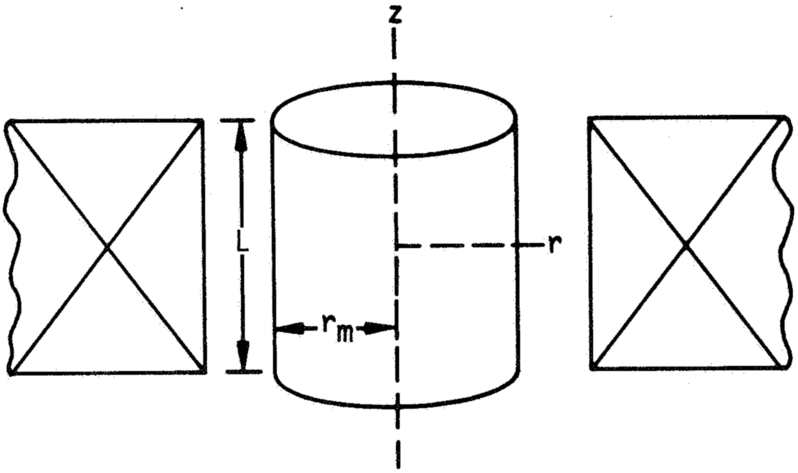

FIGURE 2: LIQUID CONTAINER-MAGNET GEOMETRY

Eddy currents are determined in the following manner. According to Faraday's law, a changing magnetic field gives rise to an induced electromotive force, $\mathcal{E}_e$, which is related to the field and the eddy current by:

$$\mathcal{E}_e = \frac{1}{\sigma} \oint \vec{J}_e \cdot d\vec{\ell} = -\iint_S \frac{\partial \vec{B}}{\partial t} \cdot d\vec{s} \quad . \tag{68}$$

This states that the line integral of the current around its circuit loop is equal to the surface integral of the rate of magnetic flux change through the surface enclosed by the loop. Equation 68 also assumes that Ohm's law:

$$\vec{J}_e = \sigma \vec{E}_e \tag{69}$$

2.2 (Continued)

is valid for the liquid material under consideration. The eddy current must also of course satisfy Maxwell's fourth equation which is repeated here:

$$\vec{J}_e = \vec{\nabla} \times \vec{H} \quad . \tag{55}$$

From these four equations (53, 68, 69 and 55), the shape and direction of the eddy current loops and the liquid flow patterns they cause will now be deduced.

First of all, for the geometry assumed in Figure 2, the magnetic field will have the form:

$$\vec{H} = [H_r(r,\theta,z)\,\hat{r} + H_\theta(r,\theta,z)\,\hat{\theta}]\,e^{i\omega t} \tag{70}$$

which yields, from equation 55, the current expression:

$$\vec{J}_e = \left[-\frac{\partial H_\theta}{\partial z}\,\hat{r} + \frac{\partial H_r}{\partial z}\,\hat{\theta} + \left(\frac{\partial H_\theta}{\partial r} - \frac{1}{r}\frac{\partial H_r}{\partial \theta}\right)\hat{z}\right] e^{i\omega t} \quad . \tag{71}$$

Equation 71 indicates that in the geometry of the liquid, the currents will have no simple symmetry. But from equation 68, we know that the current loops will lie in planes normal to the field direction (see Figure 3). Note that the direction of current flow will reverse when the oscillating field reverses its direction. Of course, the currents are much stronger in the skin depth region than they are outside this region, i.e., for $r < (r_m-\delta)$ there is practically no current. Thus, with the exception of those small loops which fit entirely in the skin depth region and are nearest the pole faces, the current is strongest in the $\pm z$ directions.

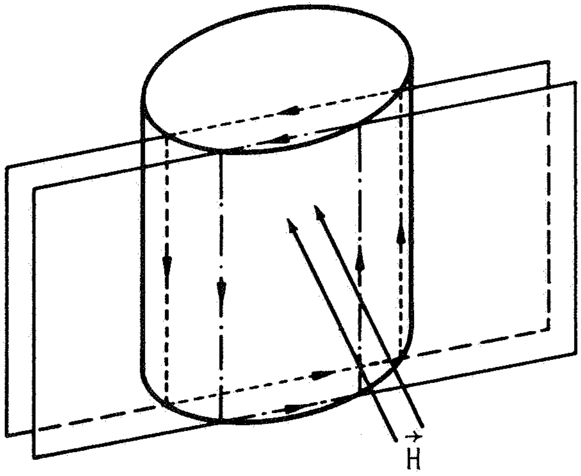

FIGURE 3: EDDY CURRENT LOOPS

2.2 (Continued)

The ±z components of the eddy current loops, then, produce the largest body forces. In the absence of all other external forces, equation 53 tells us that these eddy current-produced body forces will cause liquid flow patterns to be set up in the r-θ planes over the length of the liquid cylinder. It should be noted that the body forces produced by eddy currents are independent of time since the imaginary exponential time dependence vanishes upon performing the operation $\vec{J}^* \times \vec{B}$. This means physically that the field and current oscillate in phase to give a constant force.

Before determining liquid flow patterns, we first need to know what the skin depth configuration is. From the surface integral in equation 68, it is obvious that the net magnetic flux inducing the eddy currents is $\vec{B} \cdot d\vec{s} = \vec{B} \cdot \hat{r} ds = Bds \cos\theta$, since $\hat{r}$ is the unit vector normal to the cylindrical surface. The greatest contribution to the integral will then be near θ=0, that is, in the direction parallel to the field, while the contribution will fall off toward the direction transverse to the field, θ=π/2. Thus the skin depth region will assume the shape shown in Figure 4 where the liquid cylinder is viewed from the top.

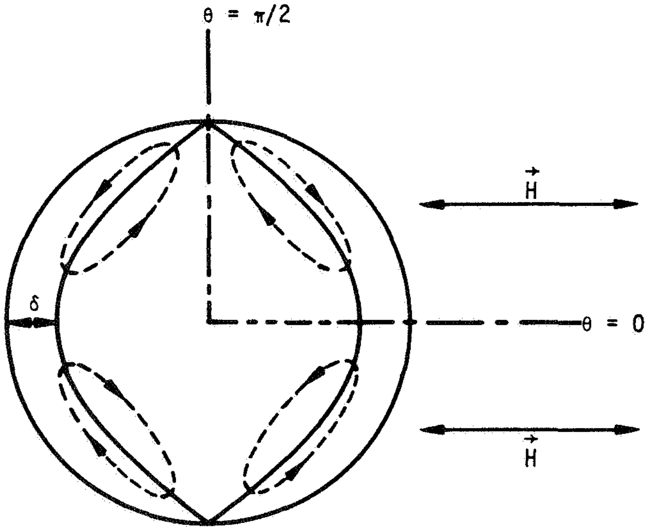

FIGURE 4: SKIN DEPTH CONFIGURATION AND LIQUID FLOW PATTERNS

From the current and field directions shown in Figure 3, equation 53 indicates the force (and therefore the liquid flow if no other forces are present) direction to be perpendicular to $\vec{H}$ and lying in the r-θ plane. Since the force will be most intense in the skin depth region, the net effect

2.2 (Continued)

is to produce a flow going from the $\theta = \pm\pi/2$ poles toward the $\theta=0$ or $\theta=\pi$ points, thus yielding the patterns illustrated in Figure 4. These patterns are repeated in each r-θ plane of the liquid cylinder.

In physical situations, there are always forces other than magnetodynamic forces present. Specifically, in a gravitational field, buoyancy-driven natural convection currents will be flowing. Whatever the shape of the convection flow patterns, they will have a large $\pm z$ component which will be disrupted by the eddy current-produced flow described above. In addition to breaking up convective flow, eddy currents produce heating in the region they inhabit with the heating rate having the proportionality:

$$Q(\text{watts}) \propto \frac{r_m}{\sigma} H^2 F_1\left(\frac{r_m}{\delta}\right) \tag{72}$$

where $F_1(r_m/\delta)$ is a function which depends on the geometry of the system (Reference 18). This heating produces a temperature rise in the liquid which has an effect to be discussed in Section 2.3.

Magnetic Viscosity

By using equations A-3 and A-4 from Appendix A, it can be shown that:

$$\vec{J} \times \vec{B} = \mu\sigma\,(\vec{E}_t \times \vec{H} - \mu H^2 \vec{u}_t) \tag{73}$$

where $\vec{E}_t$ and $\vec{u}_t$ are the electric and velocity field components transverse to the magnetic field. The Navier-Stokes equation [46] can be written as:

$$\rho\frac{d\vec{u}_t}{dt} = \vec{\Sigma}_t + \mu\sigma(\vec{E}_t \times \vec{H} - \mu H^2 \vec{u}_t) \tag{74}$$

where $d\vec{u}/dt$ is the total time derivative of velocity, and

$$\vec{\Sigma} = -\vec{\nabla}\,(\rho\psi + P - [\eta/3]\,\vec{\nabla}\cdot\vec{u}) + \eta\nabla^2\vec{u} \quad . \tag{75}$$

In liquids it is possible for $\vec{\Sigma}$ to be small, and when eddy currents are the largest currents present, $\vec{E}_t$ will be negligible. Under these conditions, induction drag will cause the motion across the field lines to decay with a time constant:

$$\tau = \frac{\rho}{\sigma\mu^2 H^2} = \frac{\rho}{\sigma B^2} \quad . \tag{76}$$

For a system of density 5 gm/cm^3 with $\sigma = 10^3\ \Omega^{-1}\text{cm}^{-1}$ and $B = 10^3$ gauss, the time constant is on the order of five seconds. This drag can be

2.2 (Continued)

interpreted as being due to a magnetic viscosity with an effective force comparable to:

$$F_m = \sigma\mu^2H^2u \quad . \tag{77}$$

This corresponds to an effective magnetic viscosity:

$$\eta_m = \sigma\mu^2H^2L^2 = \sigma B^2L^2 \tag{78}$$

which, for our example σ, L and B is roughly one poise. For comparison, the viscosity of mercury is 10^{-2} poise while molten glass at its working temperature is 10^6 poise (Reference 2). The Hartmann number is defined as:

$$h = \sqrt{\frac{\eta_m}{\eta}} \tag{79}$$

and is the parameter used to determine the importance of magnetic viscosity which dominates for $h > 1$.

For the case in which $\vec{E}_t$ is not negligible, the lines of force (always transverse to $\vec{H}$) will be frozen into the liquid and carried along with it. If the velocity of these force lines is called $\vec{w}$, we have for the current in the moving system:

$$\vec{J} = \sigma(\vec{E}_t + \mu\,\vec{w} \times \vec{H}) \tag{80}$$

so that: $$\vec{w} = \frac{\vec{E}_t \times \vec{H}}{\mu H^2} \quad .$$

This is the so-called "E cross B drift" which, when substituted into equation 74, shows that if $\vec{\Sigma} \approx 0$, the liquid motion approaches in a time τ a velocity such that $\vec{u}_t = \vec{w}$. Hence the transverse motion is still destroyed unless $u\tau/L \gg 1$.

If $\vec{\Sigma}$ is not negligible, then relative transverse motion is not destroyed but approaches a value $\vec{u}_t$ such that:

$$\vec{\Sigma}_t = \sigma\mu^2H^2\,(\vec{u}_t - \vec{w}) \quad . \tag{81}$$

The force $\vec{\Sigma}_t$ tends to push the lines of force past the field lines at such a velocity that the induced drag (viscosity) just balances $\vec{\Sigma}$. Thus there is always adjustment of the liquid motion (in a very short time) in such a way as to produce a balance of the viscous forces! The result is a steady-state Newtonian-type flow (after time $t > \tau$) with:

2.2 (Continued)

$$[-\vec{\nabla}\ (\rho\psi + P - \{\eta/3\}\vec{\nabla} \cdot \vec{u})]_t + \eta(\nabla^2\vec{u})_t = \sigma\mu^2H^2(\vec{u}_t - \vec{w})\ . \qquad (82)$$

Recapitulation

The point of these discussions of magnetic diffusion, eddy currents and magnetic viscosity is to provide a theoretical explanation of the effects which magnetic fields have on dense liquids and how they relate to the internal driving force, $-\vec{\nabla}P$, and the gravitational body force, $\rho\vec{g} = -\vec{\nabla}\rho\psi$. It is to be remembered that the major effects in counteracting gravity-induced convection are:

(1) eddy-current produced body forces which tend to disrupt convection flows, and

(2) a magnetic viscosity (equation 78) which increases viscous drag throughout the liquid and rapidly decays all motion transverse to the field lines for situations in which $\vec{\Sigma}$ and $\vec{E}_t$ are small.

2.3 (Continued)

2.3 FIELD EFFECTS ON DIFFUSION AND SOLIDIFICATION RATE

Diffusion Coefficient Increase

There are many liquid state models which derive expressions for diffusion coefficients from first principles (References 2 and 19). The major diffusion coefficient models fall into three categories, and these are the ones which are relevant to the present study. The first category contains the Free Volume Model in which the diffusion coefficient is primarily a function of free volume:

$$D = \frac{\delta u}{3\gamma} (\gamma v^* + v_f)\, e^{-\gamma v^*/v_f} \tag{25}$$

where as before δ in this expression is the ratio of molecular mean-free-path to the "instantaneous" free volume. In the second category are models which relate diffusion coefficient to the ratio of temperature to viscosity, as in the Stokes-Einstein model:

$$D = k_2 \frac{T}{\eta} \; . \tag{83}$$

In the third category, represented by Swalin's model (Reference 20), the diffusion coefficient is a function of T^2 only:

$$D = k_3 T^2 \; . \tag{84}$$

Based on the findings of Section 2.2, it is easy to derive the effect magnetic fields have on the diffusion coefficients in these last two categories. In Section 2.2 it was shown that both the temperature and viscosity of a conducting or semi-conducting liquid will increase when a magnetic field is applied. The result for the Swalin model is trivial. If D' is the diffusion coefficient in changed field conditions, it is obvious from equation 84 that $D' > D$.

Things are not as simple with the Stokes-Einstein type models, however. In this case, the field-induced diffusion coefficient may be written:

$$D' = k_2 \frac{T + \Delta T}{\eta + \Delta\eta} \tag{85}$$

where ΔT and $\Delta\eta$ are the field-induced terms. Therefore we have:

$$\frac{D'}{D} = \frac{1 + \Delta T/T}{1 + \Delta\eta/\eta} \tag{86}$$

Hence if $\Delta T/T > \Delta\eta/\eta$, D' will be greater than D. However, it is not obvious that this is always the case. Of course, $\Delta\eta/\eta$ is simply the square of the Hartmann number, but to date, no straightforward way of calculating $\Delta T/T$ has been developed.

Now consider the Free Volume Model. Here we have:

$$D' = \frac{\delta u}{3\gamma}\left(\gamma v^* + v_f + \Delta v_f\right) e^{-\frac{\gamma v^*}{v_f + \Delta v_f}} \tag{87}$$

and a little observation shows that D' is greater than D if one assumes that application of a magnetic field causes an increase in free volume. This will presently be shown to indeed be the case. At any rate, both the Free Volume Model and Swalin's model indicate that magnetic fields definitely increase the diffusion coefficient, and it is likely that Stokes-Einstein type models agree with this result for at least some classes of liquids. Henceforth, we will be concerned exclusively with the Free Volume Model, since the volume change mechanism allows us to compare magnetic and low gravity effects most directly.

<u>Volume Changes Due to Magnetic Fields and Low Gravity</u>

Let us begin by considering magnetic field effects. As usual, there are two ways to approach this problem, the first being through the theory of magnetostriction (Reference 21). This theory identifies three different components of magnetostrictive volume change occuring over different ranges of field strength (see Figure 5). The simplest of these components, and the one occuring at lowest values of H, is called the form effect. In the form effect the fractional volume change is given by:

$$\frac{\Delta V}{V} = \frac{N\chi_m^2 H^2}{2c\mu_0} \tag{88}$$

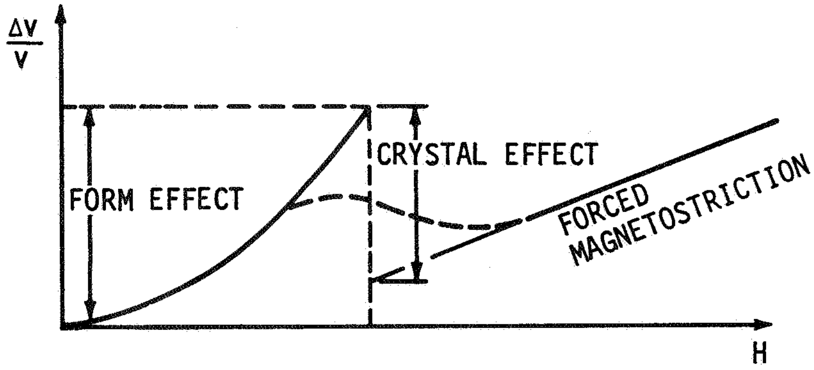

FIGURE 5: MAGNETOSTRICTION EFFECTS

2.3 (Continued)

where N is a demagnetizing factor

χ_m is magnetic susceptibility

c is the bulk modulus of elasticity, and

H is the field strength.

Although the other components are more complicated, it is obvious from the figure that $\Delta V/V$ is always positive and generally increases with increasing H.

The next approach to the problem of magnetic field-induced volume change is through the definition of isothermal compressibility, equation 12. Rewriting this equation in terms of finite volume and pressure differences, we have:

$$\left(\frac{\Delta V}{V}\right)_T = -\beta\Delta P \tag{89}$$

where β is the isothermal compressibility coefficient. It will be recalled that magnetic pressure was discussed in Section 2.2. The change in magnetic pressure for the situation of interest here may be expressed as (Reference 22):

$$\Delta P = -\left(\frac{1}{2}\right)\mu_0\,[H_0{}^2 - \chi_m H^2] \tag{90}$$

where H_0 is the initial field strength before the liquid was placed in the field, and H is the resulting steady-state of field after the liquid is placed in the field. Thus:

$$\left(\frac{\Delta V}{V}\right)_T = \left(\frac{1}{2}\right)\beta\mu_0\,[H_0{}^2 - \chi_m H^2] \tag{91}$$

which is always positive for $H \leq H_0$. This will occur in cases where eddy currents or viscous flow are balanced so that the electric currents in the liquid are negligible.

Now we consider the volume change resulting from removing a liquid quantity from the earth's surface and placing it in a region of low gravity. Once again we will use the compressibility equation, but first the pressure change must be found. Figure 6 depicts a container of liquid with a crystal being pulled from it. The crystal-melt system is initially on the earth's surface.

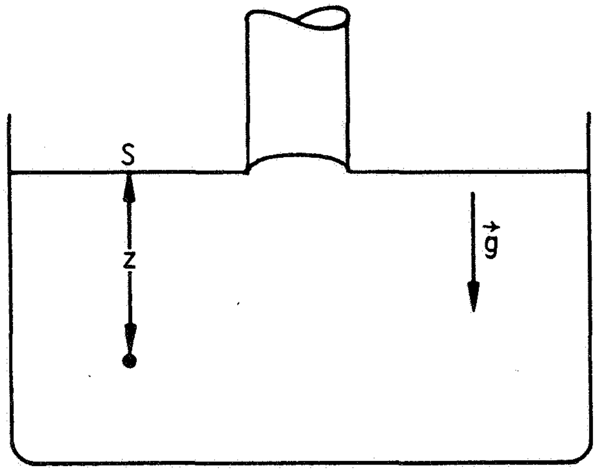

FIGURE 6: CRYSTAL-MELT ARRANGEMENT

If the equilibrium pressure at the surface is P_S, the pressure at a point a distance z below the surface is given by (Reference 23):

$$P_z^E = P_s + \rho g z \quad . \tag{92}$$

If the liquid is now taken into space where there is no gravitational contribution, the difference in pressure at the example point will be:

$$\Delta P = P_z^S - P_z^E = P_s - (P_S + \rho g z) = -\rho g z \quad . \tag{93}$$

Therefore, from equation 89:

$$\left(\frac{\Delta V}{V}\right)_T = \beta \rho g z \quad . \tag{94}$$

Since all terms in equation (94) are positive, it is evident that a decrease in hydrostatic pressure produces an increase in the volume of the liquid. This general result is of course confirmed by everyday experience with fluids at pressures above one atmosphere, and should be expected to apply between zero and one atmosphere as well. One must be careful, however, to interpret the factor g in equation (94) as the <u>difference</u> between the acceleration due to gravity at the earth's surface,

2.3 (Continued)

and the acceleration level in the space laboratory. This is due to the difficulty in obtaining absolutely acceleration-free environments even in an orbiting laboratory. But since acceleration levels are commonly on the order of 10^{-3}g to 10^{-5}g in orbiting spacecraft, taking g to be the same as the earth surface gravitational acceleration is a good approximation.

Thus the application of a magnetic field or the removal of a gravitational (acceleration) field will cause a positive increase in liquid volume, ΔV. From the definition of free volume (equation 13) it is obvious that this volume increase is the same as an increase in the total free volume, $\Delta(Nv_f)$. Therefore, according to equation (87), both magnetic fields and low gravity conditions will cause an increase in diffusion coefficient, i.e., $D' > D$.

Solidification Rate Dependence on Diffusion and Free Energy

In the Free Volume Model, the crystal growth velocity or solidification rate of a crystal growing from an undercooled melt (Reference 2) is given by equation 28 which is repeated here:

$$U_c = D \frac{f_o}{R_o} [1 - e^{\Delta G/kT}] \quad . \tag{28}$$

For fixed f_o and R_o, the now established fact that D increases in a magnetic field or low gravity conditions would indicate a corresponding increase in U_c if it can be shown that the exponential term decreases.

For the magnetic case it has already been shown that $T' > T$. The free energy change is (Reference 24):

$$\Delta G' = \Delta G - \vec{H} \cdot \vec{M} = \Delta G - \frac{c'}{T} H^2 \tag{95}$$

where c' is a constant. Since c', T and H^2 are positive, $\Delta G' < \Delta G$ so that:

$$e^{\Delta G'/kT'} < e^{\Delta G/kT} \quad .$$

Under low gravity conditions, there is no gravity field-dependent change in temperature to consider, only the change in free energy. This is:

$$\Delta G' = \Delta G + \Delta V \Delta P = \Delta G - \beta V(\Delta P)^2 \tag{96}$$

2.3 (Continued)

where V is the volume at the earth's surface. Since $(\Delta P)^2$ is positive as well as β and V, obviously:

$$\Delta G' < \Delta G \rightarrow e^{\Delta G'/kT} < e^{\Delta G/kT}$$

for the gravitational field case.

Hence the solidification rate, U_c, is increased by both the application of a magnetic field and by processing in a zero gravity field region. This is a purely formal and qualitative result, and a true comparison of solidification in space and solidification in magnetic fields must wait until the parameters required by equations 28, 87, 88, 91 and 95 can be obtained. However, it should be noted that a magnetic field-induced increase in crystal growth rate has already been observed in the laboratory (Reference 25). It is recommended that further research place emphasis on the quantitative comparison of solidification in space and solidification in the presence of magnetic fields, and on the comparison of the increased growth rate predicted by equation 28 and that observed by Schieber (Reference 25).

2.4 REFERENCES

1. R. I. Miller, A Summary of Liquid Models for Materials Processing in Space, Interim Report - Task 1, Contract NAS8-28664, The Boeing Company, August 15, 1972.

2. David Turnbull, Trans. Met. Soc., AIME, Vol. 221, p. 422, June 1961.

3. K. Huang, Statistical Mechanics, John Wiley and Sons, Inc., New York, 1967.

4. H. Eyring, D. Henderson, B. J. Stover and E. M. Eyring, Statistical Mechanics and Dynamics, John Wiley and Sons, Inc., New York, 1964.

5. M. H. Cohen and D. Turnbull, J. Chem. Phys., Vol. 31, No. 5, p. 1164, November 1959.

6. D. Turnbull and M. H. Cohen, J. Chem. Phys., Vol. 34, No. 1, p. 120, January 1961.

7. D. Turnbull and M. H. Cohen, On the Free-Volume Model of the Liquid-Glass Transition, Technical Report No. 24, Office of Naval Research, September 1969.

8. Handbook of Chemistry and Physics 46th ed., Chemical Rubber Co., Cleveland, 1965.

9. W. J. Moore, Physical Chemistry, p. 229, Prentice-Hall, Inc., Englewood Cliffs, 1963.

10. R. A. Svehla, NASA Tech. Rept. R-132, Lewis Research Center, Cleveland Ohio, 1962.

11. David Turnbull, "Free Volume Model of the Liquid State," in Liquids: Structure, Properties, Solid Interactions, T. J. Hughel, ed., Elsevier Pub. Co., New York, pp. 6ff, 1965.

12. E. A. Guggenheim, Mixtures, Oxford University Press, London, pp. 89ff, 1952.

13. Ibid., p. 5.

14. K. Huang, op. cit., Ch. 3 and 5.

15. J. D. Jackson, Classical Electrodynamics, Ch. 10, John Wiley and Sons, Inc., New York, 1965.

16. D. J. Kroon, Electromagnets, Philips Technical Library/Boston Technical Publishers, Cambridge.

2.4 (Continued)

17. H. E. Duckworth, Electricity and Magnetism, Ch. 5, Holt, Rinehart, & Winston, New York, 1961.

18. R. T. Frost, et. al., Field Management for Positioning and Processing of Free Suspended Liquid Materials, Contract NAS8-24683 Task IV Report, DCN 1-9-54-20055, S2, General Electric Company, May 15, 1970.

19. H. A. Walls and W. R. Upthegrove, Acta Met., Vol. 12, May 1964.

20. R. A. Swalin, Acta Met., Vol. 7, p. 736, 1959.

21. S. Chikazumi and S. Charap, Physics of Magnetism, John Wiley and Sons, New York.

22. E. S. Shire, Classical Electricity and Magnetism, pp. 187 ff., Cambridge University Press, 1960.

23. F. Sears and M. Zemansky, University Physics, Addison-Wesley Publishing Company, Reading, 1964.

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

25. M. Schieber, J. Crystal Growth, Vol. 1, p. 131, 1967.

APPENDIX A
DERIVATION OF THE MAGNETIC FIELD EQUATION (49)

The last two of Maxwell's equations of electrodynamics state that:

$$\vec{\nabla} \times \vec{H} = \vec{J} \tag{A-1}$$

$$\vec{\nabla} \times \vec{E} = -\mu \frac{\partial \vec{H}}{\partial t} \tag{A-2}$$

and Ohm's law for the case of a moving conducting liquid is:

$$\sigma \vec{E}' = \vec{J} \tag{A-3}$$

where σ is the electrical conductivity, the field $\vec{E}$ is referenced to the "fixed" frame of an observer and $\vec{E}'$ is the electric field moving with the liquid. Thus for a liquid of permeability μ and moving with velocity $\vec{u}$, we have:

$$\vec{E}' = \vec{E} + \mu \vec{u} \times \vec{H} \ . \tag{A-4}$$

Combining equations A-2, A-3 and A-4 yields:

$$-\mu \frac{\partial \vec{H}}{\partial t} = \frac{1}{\sigma} \vec{\nabla} \times \vec{J} - \mu \vec{\nabla} \times (\vec{u} \times \vec{H}) \tag{A-5}$$

or, substituting from A-1 and applying the vector identity $\vec{\nabla} \times \vec{\nabla} \times \vec{H} = -\nabla^2 \vec{H}$ when $\vec{\nabla} \cdot \vec{H} = 0$ (as is the case in electromagnetism), we find that:

$$\frac{\partial \vec{H}}{\partial t} = \frac{1}{\mu\sigma} \nabla^2 \vec{H} + \vec{\nabla} \times (\vec{u} \times \vec{H}). \tag{A-6}$$

If we now define the magnetic diffusivity to be:

$$\nu = \frac{1}{\mu\sigma} \tag{A-7}$$

and the magnetic Reynolds number to be:

$$R_m = Lu\mu\sigma \tag{A-8}$$

where L is a characteristic length for the liquid system and u is the magnitude of $\vec{u}$, equation A-6 becomes:

$$\frac{1}{\nu} \frac{\partial \vec{H}}{\partial t} = \nabla^2 \vec{H} + R_m \vec{\nabla} \times \left(\frac{\vec{u} \times \vec{H}}{Lu}\right)$$

which is equation 49.