THERMAL CONTROL BY FREEZING AND MELTING

INTERIM REPORT
ON
SPACE THERMAL CONTROL STUDY

March 1968

Contract NAS8-21123

(NASA-CR-120641) THERMAL CONTROL BY
FREEZING AND MELTING Interim Report
(Lockheed Missiles and Space Co.) 85 p

N76-71225

Unclas
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HREC-1123-1
LMSC/HREC A791342

LOCKHEED MISSILES & SPACE COMPANY
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FOREWORD

This report presents the results of a theoretical study of the operation of melting-freezing processes under space boundary conditions and the relation of these processes to efficient thermal control devices. The report essentially fulfills Task 1 as set forth in Contract NAS8-21123, to wit,

> Perform meaningful theoretical studies (including laboratory studies which are necessary to support the theoretical studies) on the scientific aspects involved in the use of phase-change materials in the boundary conditions of space. (This study will not be directed toward specific applications of phase-change materials in space.) Specific considerations will include the study of solidification, crystallization, and nucleation as affected by space conditions of weightlessness, void formation due to thermal contractions and other means, high energy radiation (which penetrates the phase-change material container) and other boundary conditions. These studies should be appropriate for all types of potential materials. The term "nucleation" is used here to mean "the initiation of a new phase within a given phase."

This study program is sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama. Mr. T. C. Bannister, MSFC Space Sciences Laboratory, is the director of the study. Dr. P. G. Grodzka, Research Specialist, Thermal Control Systems Group, Lockheed Missiles & Space Company, Huntsville Research & Engineering Center, Huntsville, Alabama, is the principal investigator.

This report was prepared by Dr. Grodzka with Dr. C. Fan, Research Specialist, Aero-Physics Group, Lockheed Missiles & Space Company, Huntsville Research & Engineering Center, as a major contributor.

SUMMARY

The operation of melting-freezing processes in the boundary conditions of space are examined theoretically. From this consideration, possible problems unique to space operation of thermal control devices based on solid-liquid phase change are isolated and evaluated. Also examined are the roles of various rate processes in net freezing and melting. The limitations these rate processes place on efficient PCM* operation and ways in which the limitations can be overcome are covered in detail. Conclusions reached in regard to the influence of space boundary conditions on PCM performance are:

- Gravity in the zero to 1-g range has no direct, significant influence on any of the microscopic processes involved in phase change.
- The influence of gravity will have an effect on phase change indirectly through convection currents. (Convection currents affect temperature and/or concentration distributions which, in turn, affect freezing, melting, and nucleation rates.)
- Although the general nature of convective currents in zero-g conditions can be predicted, complex coupling effects between phase-change kinetics and various possible modes of convective motion cannot be predicted accurately without actual flight test data.
- The magnitudes of magnetic and electric fields likely to be encountered in earth orbit are expected not to alter phase-change behavior significantly from that observed on the earth surface.
- Radiation fields encountered in earth orbit are expected to have little effect, except perhaps in the case of organic PCM where long-time exposures will result in buildup of impurity.

From the consideration of the rate processes, it became evident that PCM candidate materials, chosen on the bases of high heat of fusion and low melting temperature, are likely to have phase-change kinetics which are

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*Abbreviation for Phase Change Material

detrimental to efficient PCM operation. A thorough understanding of the nature of the rate processes, however, can expedite isolating the non-equilibrium effect causing the problem and indicate solution by design and material alterations. The problems arising from non-equilibrium effects judged most likely to cause unpredictable PCM performance are:

- Dependence of melting and freezing rates on the freezing conditions under which the solid was formed or is being formed.
- Destruction of nucleating catalysts by repeated thermal cycling.
- Production of concentration non-equilibrium in multi-component PCM.

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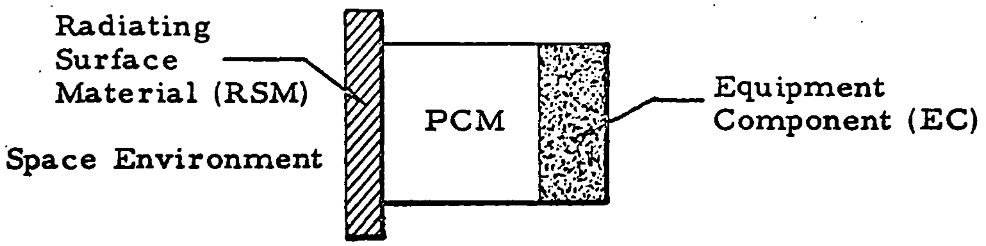
Section 1
INTRODUCTION

The need for passive means of thermal control of satellite and spacecraft becomes more demanding as the length and sophistication of space missions increases. Passive thermal control based on solid-liquid phase change offers several attractive features for many envisioned future space missions. Among these are: no power requirements, no moving parts, maintainance of equipment within narrower temperature limits than is possible with commonly used coatings, and dissipation of externally and internally generated heat pulses. Thus, phase-change material (PCM) thermal control is a simple, reliable technique adaptable to a broad field of application. One disadvantage of the technique which can be minimized by PCM selection is a greater weight penalty than with other means of passive thermal control such as coatings. Compared to louvered or forced-circulation systems, however, which may be classified as active thermal control systems, the weight penalty is much less. Use of PCM thermal control, therefore, in combination with coatings and/or other thermal control devices offers complementary capabilities which can increase system versatility, lifetime, and dependability.

The principle of PCM thermal control is very simple. Basically, it consists of a core of PCM between the equipment component whose temperature is to be controlled and an outer radiating surface, as shown in the following figure.



Ideally, when the heat fluxes from the space environment or the internal environment cause the RSM (Radiating Surface Material) - PCM or EC (Equipment Component) - PCM interface temperatures to reach the PCM melting point, the PCM will melt, absorbing an amount of heat equivalent to its latent heat of fusion. The RSM-PCM or EC-PCM interface temperatures will not rise appreciably above the PCM melting point as long as both solid and liquid PCM phases are present. Should the RCM-PCM or EC-PCM interface temperatures begin to fall as the result of external or internal cooling, the PCM solidifies liberating latent heat. Again, the RSM-PCM or EC-PCM interface temperatures do not appreciably depart from the PCM melting point as long as both solid and liquid PCM phases are present. Once the PCM is completely converted to solid or liquid, further heat absorption or liberation is determined by heat capacity considerations. It must be emphasized that the preceding description of PCM thermal control is highly idealized. One very important deviation from this ideal behavior, which is likely to occur unless precautions are taken, is that once the PCM is completely liquid the initiation of solid phase formation by cooling can be extremely difficult. Some materials can be cooled far below their solid-liquid equilibrium temperature without any appearance of solid. In this state the liquid is said to be supercooled. The initiation of a solid phase from a liquid phase is called nucleation and is discussed in the main body of this report. Other factors which work against ideal PCM behavior and ways in which they can be mitigated also are considered in the main body of this report.

Research and development of PCM application is fairly extensive at present. Design considerations using PCM thermal control for various space applications are considered briefly in References 1 and 2. Analytical and experimental feasibility studies of PCM thermal control in space environments are reported in References 3 and 4. In addition to these studies, the Russians have been carrying out experimental investigations, apparently since 1954, of PCM thermal control of instruments, gravity meters in particular (Reference 5).

The use of PCM primarily for storage of thermal energy which can then be converted to electrical energy is considered in Reference 6. Solar home heating and heat pump applications of PCM are considered in References 7, 8, 9 and 10.

The preceding studies indicate that the use of PCM for satellite spacecraft thermal control or for heat storage is definitely feasible, but a number of questions and problems regarding PCM performance in space and various thermal environments require further research and development. In particular, more attention to the basic physical processes controlling phase change, heat transfer, and their operation in space environment is needed. The past studies have oversimplified these processes and, as a result, may be inaccurate indicators of PCM performance behavior in space or under a variety of imposed thermal conditions. In the first part of the present study, therefore, these physical processes are considered and their operation and importance in space environments are evaluated. The rest of the report deals with the various rate processes involved and their pertinence to efficient PCM performance.

Only solidification of melts or solvents is considered in this report in contradistinction to crystallization from solution or growth of solute particles. The fact is mentioned here to avoid possible confusion in regard to the term "solid-liquid phase change" which is used extensively throughout this report.

Section 2

EFFECTS OF GRAVITY, ELECTRICAL, AND MAGNETIC FIELDS ON SOLID-LIQUID PHASE CHANGE

2.1 GENERAL CONSIDERATIONS REGARDING PHASE CHANGE AND FORCE FIELDS

The problem of predicting solid-liquid phase change under space boundary conditions has two aspects. First is the question of the effect of imposed gravity, electrical and magnetic fields on the phase-change thermodynamic parameters of fusion temperature and latent heat of fusion. Then the question of how the imposed boundary conditions influence the rates of nucleation, melting and freezing must be answered. These two aspects will be considered in following paragraphs. Before this consideration is undertaken, however, it is worthwhile to consider the nature of gravity, electric and magnetic fields. These fields exert long-range forces or body forces proportional to $1/r^2$; intermolecular or interatomic forces are short-range forces by comparison and generally proportional to $1/r^s$ where s is some power greater than 3 and the term r is the distance between two masses (Reference 11). The terms intermolecular and interatomic are used here in a generic sense for forces between atomic or molecular particles. Specific forces describing coulombic attractions between ions, metallic bonds, covalent bonds, etc., need not be considered for the purpose of the present discussion. The acceleration caused by a given gravity field is independent of the mass accelerated because the gravity force is strictly proportional to inertial mass. Gravitational fields do not neutralize one another, and the gravitational force does not depend on the relative velocities of the bodies or their temperatures. Electric and magnetic fields, on the other hand, can be neutralized by their interaction with matter. Thus, it is possible to construct a shield for electric and magnetic fields, but there is no way to shield an object from a gravitational field.

The thermodynamic parameters of fusion are directly related to the intermolecular forces, so that the question of how gravity, electric and magnetic fields affect the thermodynamic properties of fusion requires a consideration (Section 2.2) of the interaction between the long-range forces of gravity, electric and magnetic fields and the short-range intermolecular forces.

The question of how the rates of nucleation, freezing and melting are affected by force fields necessitates the recognition that the overall, net macroscopic rate of nucleation, freezing, or melting — that is, the rates at which nuclei, solid, or liquid actually are observed to form — are determined by two coupled rate processes. (This coupling is discussed in detail in Section 4.2.2). One of these processes is the rate of solid-liquid phase transition on a microscopic scale and the other is the rate of heat transport through the solid and liquid phases. The microscopic phase kinetics are determined by local conditions, taken on a small scale, of temperature and pressure and the thermodynamic parameters of phase change. Once the question of how force fields affect the thermodynamic parameters, temperature fluctuations, and the heat transport mechanisms has been answered, the effect of force fields on the macroscopic kinetics of phase change can be considered (Section 2.3).

2.2 EFFECT OF FORCE FIELDS ON THE THERMODYNAMIC PARAMETERS OF PHASE CHANGE

2.2.1 Gravitational Field Effects on Intermolecular Forces

Gravitational fields are very weak compared to intermolecular forces or interatomic forces. For example, the gravitational energy between two CO_2 molecules when they touch each other is -1.1×10^{-44} erg, while their potential energy as the result of intermolecular attraction is 14.0×10^{-14} erg (Reference 12). If two coupled CO_2 molecules are considered in an earth gravity field, it can be seen at once that this field would have an infinitesimal effect on the intermolecular force, because the earth gravity force would act on all of the molecules. Consideration of the interaction between the gravitational fields of individual CO_2 molecules with that of earth and each other, i.e., a three-body problem, hardly seems necessary.

Gravity fields, nevertheless, can indirectly affect intermolecular forces through pressure. As discussed in any physics textbook, the pressure of air is greater near the surface of the earth than at higher altitudes, but the temperature would be constant and not change with altitude for an equilibrium atmosphere. Thus, for a long column of material in solid-liquid equilibrium in the earth's gravity field, the equilibrium temperature would be different for different levels of the solid-liquid interface because of the varying pressure. For the amount of material which would be used for PCM thermal control, however, this effect would be negligible in the zero to 1-g range.

2.2.2 Effect of Magnetic and Electrical Field on Thermodynamic Parameters

Magnetic and electric fields can cause internal changes in the state of matter if the material has permanent or induced electric or magnetic moments. But, as in the case of earth gravity, the magnitude of magnetic fields necessary to produce any observable effect on thermodynamic parameters would appear to be much greater than the 0.5 to 0 gauss range variation (Reference 13) from earth surface to space. Electric fields in space will arise from the potential taken up by the spacecraft, and this again is not expected to cause any large internal potential differences in the body of the spacecraft. Although nothing as yet has been found in the literature directly pertaining to the effect of magnetic or electric fields on melting points, heats of fusion, etc., the following effect on other properties are pertinent. The effect of a magnetic field on the boiling point is given by

$$\delta T = T \chi H^2 / 2 \ell_e \rho_\ell \tag{2.1}$$

where χ = magnetic susceptibility, H = field strength, ℓ_e = latent heat of evaporation, and ρ_ℓ = density of liquid. However, experimental results have not been in good agreement with the equation (Reference 14, p. 376). Also, the application of magnetic fields up to 18,000 gauss produced no effect on the surface tensions of pure liquids and solutions (Reference 15). On the other hand, electric voltage may produce changes in the surface tension of liquids; the experimental results are inconclusive (Reference 15).

2.2.3 Conclusions Regarding Effects of Force Fields on Thermodynamic Parameters

The gravity, electric and magnetic field environments likely to be encountered in earth orbit are expected to have negligible influence on the thermodynamic parameters of phase change.

2.3 EFFECTS OF GRAVITATIONAL, MAGNETIC AND ELECTRIC FIELDS ON RATES OF NUCLEATION, FREEZING AND MELTING

The initiation of a solid crystalline phase within a completely liquid phase which contains no solid impurities does not occur at the equilibrium temperature, T_e. A definite, and in some cases an appreciable, undercooling of the liquid is required before any observable solid forms (see Section 4). For present purposes it is sufficient to note that the appearance of solid phase within a homogeneous liquid is governed by configurational fluctuations within the liquid. Particle clusters that reach a certain critical size as the result of these fluctuations can continue to grow and are called nuclei. Particle clusters of subcritical size are called embryos. Embryos change their size continuously at finite rates by losing or gaining atoms one at a time from the surrounding medium. The mechanism by which embryos become nuclei at constant temperatures and pressure may be represented as (Reference 16)

$$X + X \rightleftarrows X_2$$

$$X_2 + X \rightleftarrows X_3$$

$$X_{j-1} + X \rightleftarrows X_j$$

$$X_j + X \rightleftarrows X_{j+1}$$

where X represents a single atom or molecule and X_j a critical nucleus which will continue to grow on the average. The steady-state rate of nucleation is proportional to the equilibrium number of critical size embryos (Reference 17).

Somewhat similar considerations apply to further growth of critical nuclei and larger crystal particles. As will be discussed later, the microscopic rates of crystallization and melting depend on the temperature difference $T_e - T_i$ (T_i = actual interface temperature). Since these rates are on a microscopic scale, it stands to reason that gravity would exert an influence only if the average temperature and density fluctuations on the microscopic scale were appreciably gravity dependent. Although no specific discussion of the effect of gravity on fluctuations has been found, there appears to be no reason to believe that gravity has any direct effect on them. This belief finds support in the following consideration. A relative density fluctuation can be given by (Reference 18)

$$\delta = -\frac{kT}{V_s \left(\frac{\partial P}{\partial V_s}\right)_T} \tag{2.2}$$

where V_s is a small volume element. There are no directly dependent gravity terms in the above equation, so that no direct gravity effect would be predicted. An indirect gravity effect through pressure [the compressibility term $\left(\partial P/\partial V_s\right)_T$ is pressure dependent] is possible, but, for the amounts of material which would be used for PCM, this would be negligible in the 0 to 1-g range.

Although gravity is expected to have insignificant direct effects on nucleation rates or crystallization and melting rates, gravity fields can significantly influence the rates of nucleation, melting or freezing by means of still another, other than pressure, indirect mechanism. This mechanism arises because convective currents caused by buoyancy forces can be different in different g fields. To amplify: the microscopic rate of freezing or melting is determined mainly by the difference between the equilibrium temperature and the actual interface temperature (pressure has much less influence). If this difference is the same in a gravity field and a nongravity field, the rates will be the same. In other words, in a system which transported heat purely by conduction in a 1-g field, the rate of freezing or melting observed in this field would remain the same when the system was operated in a zero-g field under the same conditions of input-output heat flux. In a 1-g field, however, heat transport by free convection is possible. Therefore, if free convection exists in our system in a 1-g field, the rates of freezing and melting would certainly be different in a zero-g field. The coupling of the phase-change kinetics to heat transport is discussed in Section 4. The point to be made here is that the phase-change kinetics are not influenced directly by gravity fields, but only indirectly through convection currents and pressure.

Two other aspects of nucleation should be mentioned. When a liquid is suddenly quenched to a temperature below its equilibrium temperature, a definite time lag may occur before the rate of nucleation attains its steady-state value. Also, macroscopic flow and mechanical vibrations enhance the rate of nucleation (Reference 16). The effect of gravity on these phenomena is expected to involve no new considerations other than those which have already been discussed, so that again we predict negligible direct gravity effects but possible indirect effects.

The action of electric and magnetic fields on nucleation, freezing and melting rates is less understood at present. It has been established that electric and magnetic fields can cause marked changes in the rates of nucleation in materials having permanent or induced electric or magnetic moments (Reference 19), but again the strengths of the fields used to obtain noticeable effects with organic materials appear to be much larger (~ 3,000 volt/cm and ~ 18,000 gauss) than we would expect to encounter in the space vicinity of earth. Even with metals, it was concluded that field strengths up to 1135 gauss do not influence nucleation directly (Reference 20).

2.4 CONCLUSIONS REGARDING FORCE FIELD EFFECTS ON SOLID-LIQUID PHASE CHANGE

Gravity in the zero to 1-g range is predicted to have negligible direct effects on the microscopic processes involved in phase change, but significant indirect effects through convection currents. The magnitudes of magnetic and electric fields likely to be encountered in earth orbit are expected to exert insignificant influence on the microscopic rates of phase change.

Section 3
ROLE OF CONVECTIVE CURRENTS IN SOLID-LIQUID PHASE CHANGE

3.1 GENERAL CONSIDERATIONS

Convective currents affect melting or freezing processes by their effect on temperature distributions and/or concentration distributions. The driving forces for these currents, i.e., gravity, acceleration, inertia, and surface or interfacial tension, are usually all present to some degree on earth. In space orbit, gravity, although not absent, is conteracted by centrifugal force, so that an effective zero-g environment prevails. The extrapolation of freezing or melting behavior observed on earth to zero-g environments must be considered carefully because complex coupling effects between the various mechanisms driving fluid flow can occur. For example, if a long thin layer of liquid contained in a boat is heated on one vertical side, one might expect only some circulation near the heated wall because of buoyancy effects. But temperature fluctuations throughout the whole length of the liquid can and do occur because of coupling between various forms of natural convection and/or between natural convection and surface tension driven flows. Such convection currents during horizontal solidification are of great concern to metallurgists. The recent paper by Carruthers (Reference 21) considers the topic in detail. Peculiar convection currents during vertical solidification or melting also can occur, again, undoubtedly, because of coupling between various convection modes. The interface of ice-water during both net freezing and net melting was actually observed to oscillate under certain vertical temperature gradients (Reference 22, p. 88).

In the following discussion, the types of convective motion possible in solid-liquid phase change and their effects on freezing and melting rates are considered. From this discussion it will be evident that:

- Convective mode couplings can result in convection where none would be predicted if the coupling were ignored.
- Convection driven by surface tension gradients will undoubtedly be present to some extent in zero-g environments since it is unlikely that all liquid-gas interfaces can be eliminated by package design.
- Certain couplings can be very sensitive to operation-parameters.
- There is a possibility that not all the driving forces for convection are recognized at present; i.e., solid-liquid interfacial tension gradients can perhaps drive fluid flow.
- Present analytical models are complex, approximate, and unyieldly to calculate accurately.

For these reasons, it would appear that only actual flight test data can indicate accurately the actual coupling between various convective motions in space and between convective heat transfer and solid-liquid phase change.

The effect of magnetic fields on convection motion was not considered in this report. From indications in the literature, it would appear that magnetic fields start to dampen convective motions of metals significantly at about the 200 gauss level. Much greater field strength undoubtedly would be required to affect convective motions in non-conductors.

Briefly, the possible convective modes are:

- Convective motion in the liquid phase of a freezing or melting system caused by density gradients in the liquid in a gravity field. This type of convection, known as natural convection, will be discussed in detail in Sections 3.2 and 3.3.
- Convection induced by unbalanced surface traction forces as a result of temperature variations on a free surface. The stability problem of this type convection motion and its general influence on solidification or melting will be discussed in Section 3.4.
- Convective motion caused by density change on solidification (Reference 23). In such a case, the motion will be directed toward or away from the solidification front depending upon whether the density of solid is greater than or less than the density of the liquid. According to Chambre (Reference 23), the maximum velocity of this convective motion occurs at the interface and

is equal to $(\Delta\rho/\rho)(dX/dt)$, where $\Delta\rho$ is the difference in density between solid and liquid, ρ is the density of liquid, and dX/dt is the rate of growth. This means that the magnitude of this motion is usually very small, and its effect on solidification rate insignificant except in the case of very fast growth rate (solidifying into a highly supercooled liquid) and large density difference between the solid and its melt. However, this motion may have significant effects on the interface morphology of a phase-change system.

- Liquid motion during a phase-change process caused by growing or collapsing of bubbles. Bubble formation is discussed in Section 4.4.

3.2 MELTING OR FREEZING WITH NATURAL CONVECTION

Although the mathematics of the solid-liquid phase change has been extensively treated in the literature, few treatments include the possible effect of buoyancy forces in the liquid phase. The cause of natural convection in freezing and melting is readily seen from the following simple example (Reference 24). Consider a finite column of liquid situated vertically in an earth gravity field. Let freezing be initiated at the top surface. There will be positive temperature gradient existing in the liquid column from top to bottom surface. Consequently, for most substances, the liquid layer will experience buoyancy forces caused by decreased density near the bottom surface, as the temperature is higher there. The assumption of only conductive heat transfer in the liquid phase is valid only if the system remains stable, i.e., when the Rayleigh number remains below a critical value (Reference 25).

The only attempt to mathematically describe the solid-liquid moving boundary problem including buoyance force was made by Tien and Yen (Reference 26). They considered a semi-infinite solid extending from $x = 0$, where x is taken opposite to the direction of the gravitational force. Initially, only solid phase was present at a constant temperature. At time $t = 0$, a step change in temperature was imposed at $x = 0$ to induce melting. This is described as the classical Stephen's problem, discussed further in Section 4.2.4 where a schematic diagram of the system is given. (See Figure 4-1, p. 30.)

The exact pure conduction solution (Neumann's solution) presented in Section 4.2.4 is valid as long as the liquid phase remains stable. Instability, or natural convection, sets in when a critical Rayleigh number, R_c, is reached. Tien and Yen used

$$R_c = \frac{g\beta X^3}{\nu_l\ \alpha_l}(T_S - T_e) = 1720 \tag{3.1}$$

where g is the acceleration due to gravity, β is the coefficient of expansion of the liquid, and ν_l is the kinematic viscosity of the liquid. The other parameters appearing in Equation (3.1) are defined in Section 4.2.4, p. 29. The critical Rayleigh number of about 1720 was derived theoretically and verified experimentally for normal fluids (density decreases with increasing temperature) confined between two parallel horizontal plates, infinite in extent. More discussions on the instability problem for the onset of natural convection will be given in Section 3.3.

Utilizing Equation (3.1), a critical liquid layer thickness X_c beyond which natural convection started was defined and a critical time t_c was determined from the Neuman solution. Then, the problem was restated for times greater than t_c by assuming that the rate at which the temperature distribution reaches its steady state in the liquid phase is much greater than the melting rate. Consequently, Tien and Yen assumed that the change in geometry due to melting can be ignored as far as heat transfer in the liquid is concerned. Under this assumption, the problem was reduced to a simpler melting problem in which a prescribed heat flux was imposed at the solid-liquid interface. The heat flux was evaluated by using the correlations developed by O'Toole and Silveston (Reference 27) for natural convection of normal fluids confined between two parallel horizontal plates. The problem was then solved using Goodman's integral technique (Reference 28). Numerical calculations were made for a water-ice system. But the peculiar property of density inversion of water (density increases from 0°C to 4°C and then decreases with increasing temperature) was neglected. Thus, the calculated results reported in Reference 26 can only be viewed as approximate. However, the authors should be commended for attacking such a long neglected problem. Their technique is more valid for a normal fluid than water.

Boger (Reference 24) conducted careful experiments and reported extensive data on the phase-change process of an ice-water system, with and without natural convection. He also developed a mathematical model for a finite slab melting and freezing problem with the inclusion of possible occurrence of natural convection. The agreement between his theoretical results and experimental data is claimed to be excellent. Boger also observed, on both theoretical and experimental grounds, that the effect of natural convection in the liquid phase during phase change is to enhance melting and to retard freezing. It is noteworthy that Boger's work was done under the supervision of Professor J. W. Westwater, who is considered a leading expert on phase-change processes. Boger's measured melting and freezing rates were obtained under conditions which were detrimental to extensive supercooling in the liquid phase. In crystallization from supercooled water, natural convection was found to increase growth rates (Reference 29).

The problem of hydrodynamic instability or onset of convection needs to be investigated next. (See the following section.)

3.3 RAYLEIGH CONVECTION DUE TO GRAVITY FORCE

The problem of hydrodynamic instability of a fluid layer heated from below has been a subject of intensive study since the turn of this century. As early as 1900, Bénard (Reference 30) reported his observation of a type of cellular motion in a thin layer of liquid heated from below. Bénard experimented with several liquids of differing physical properties. He was particularly interested in the role of viscosity, and, for liquids of high viscosity, he used melted spermaceti and parafin. In all cases, Bénard found that when the temperature of the lower surface was gradually increased, at a certain instant the layer became reticulated and revealed its dissection into cells. The initial cells formed consisted of convex polygons with four to seven sides and vertical walls. Then, after a short duration, the cells became regular hexagonals. He further noticed that there were motions inside the cells: of ascension at the center and of descension at the boundaries with the adjoining cells. Bénard himself was more interested in the emergence of the hexogonal cells. He did not give the conditions necessary for the onset of instability.

Later, Lord Rayleigh (Reference 25) made a theoretical analysis of convective motion of the type observed by Bénard. Rayleigh explained the motion in terms of buoyancy force caused by density gradient in a gravity field.* He also arrived at a certain instability criterion, which is now commonly referred as the critical Rayleigh number, for the onset of convective motion.

Consider a horizontal layer of fluid having a thickness d and a vertical temperature gradient dT/dy when heat is supplied uniformly from the lower surface. Let ν, α and β be the kinematic viscosity, thermal diffusivity and coefficient of expansion of the liquid, respectively. Then, the Rayleigh number is defined as

$$R = \frac{g \beta \frac{dT}{dy} d^4}{\nu \alpha} \tag{3.2}$$

This number is a measure of the ratio of gravity force to viscous force. The onset of convective motion occurs when a critical value of Rayleigh number, R_c, is reached; that is, when the buoyancy force is large enough to overcome the viscous force.

Rayleigh's work was later generalized and also extended to a broader range of boundary conditions by Jeffreys (Reference 32), Pellew and Southwell (Reference 33), Roberts (Reference 34) and others. In the meantime, experimental investigations on heat transfer and hydrodynamic instability were conducted by Chandra (Reference 35), Silveston (Reference 36), O'Toole and Silveston (Reference 27), Schmidt and Silveston (Reference 37), Globe and Dropkin (Reference 38), Boger and Westwater (Reference 22), and Tritton and Zarraga (Reference 39). It has now been conclusively established that the stable cellular motion in the form of hexagonal shape does occur in most

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*Recently, there has been some doubts as to whether the convective motion observed by Bénard were actually caused by gravity force (Reference 31).

carefully controlled experiments. Also, the onset of hydrodynamic instability due to buoyancy force occurs at a critical Rayleigh number which varies according to imposed boundary conditions. This critical Rayleigh number takes a value of about 600 for two free bounding surfaces; about 1100 for one rigid and one free boundary surface; and about 1700 for both rigid bounding surfaces. The above are for a layer of fluid either uniformly heated from below or uniformly cooled from above. When heat is produced internally in a fluid layer with one rigid wall below and free surface above, the critical Rayleigh number takes a value of approximately 2770 (Reference 39).

Some typical experimental results reported by various investigators are shown in Figures 3-1 to 3-4. Figure 3-1 is a reproduction of Silveston's data in the neighborhood of instability in various fluids confined between two rigid parallel plates and heated from below. The data consistently indicate that, in all of these liquids, instability sets in at the Rayleigh number 1700 ± 50. This is in very good accord with the theoretical value 1708 obtained by Chandrasekhar (Reference 40). The data in Figure 3-1 also indicate that for Rayleigh numbers R below its critical value, R_c, the Nusselt number Nu (a dimensionless heat transfer parameter) remains constant; but as R is increased above R_c, Nu increases almost linear with R.

Boger and Westwater (Reference 22) conducted experiments on the phase change of water into ice and vice versa. Their results are shown in Figure 3-2. The ratio of k_{eff} to k_L represents the ratio of actual heat transfer rates to the heat transfer rates if conduction is the only mode of energy transfer in the liquid. It is seen that, for Rayleigh numbers less than about 1700, no natural convection occurs ($k_{eff} = k_L$). But when R exceeds about 1700, k_{eff}/k increases greatly with R. Boger and Westwater's results agree with other experimental data, which were also shown in the figure.

Figure 3-3 is a reproduction of one of Bénard's original photographs. This picture shows the regular convection cells observed when a thin layer

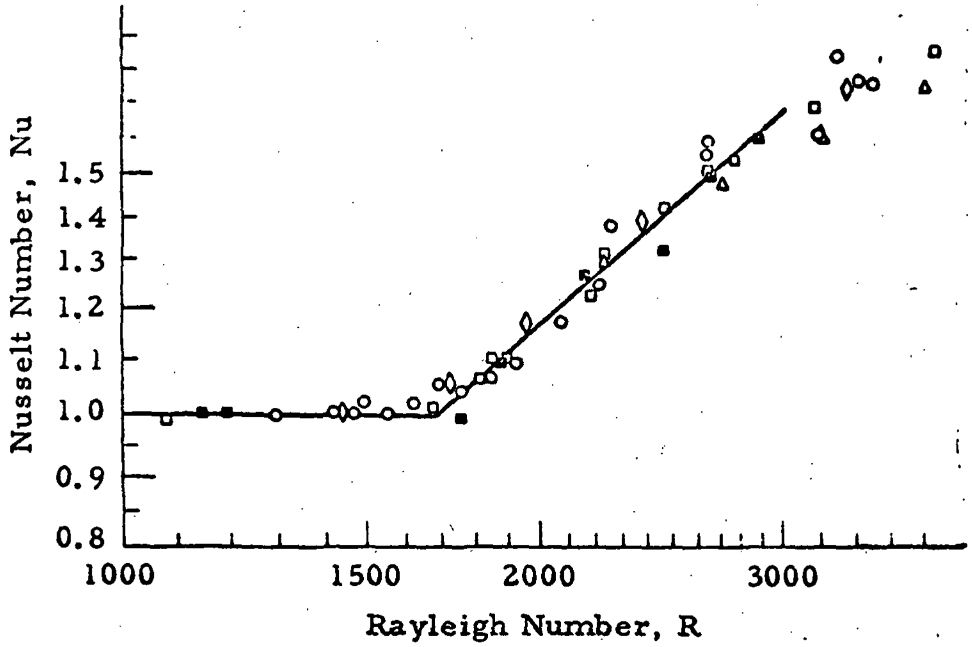


Figure 3-1 - Silveston's Experimental Results in the Neighborhood of Instability in Various Liquids (■ silicon oil AK 350; ◊ silicone oil AK 3; □ ethylene glycol; △ heptane; ○ water)

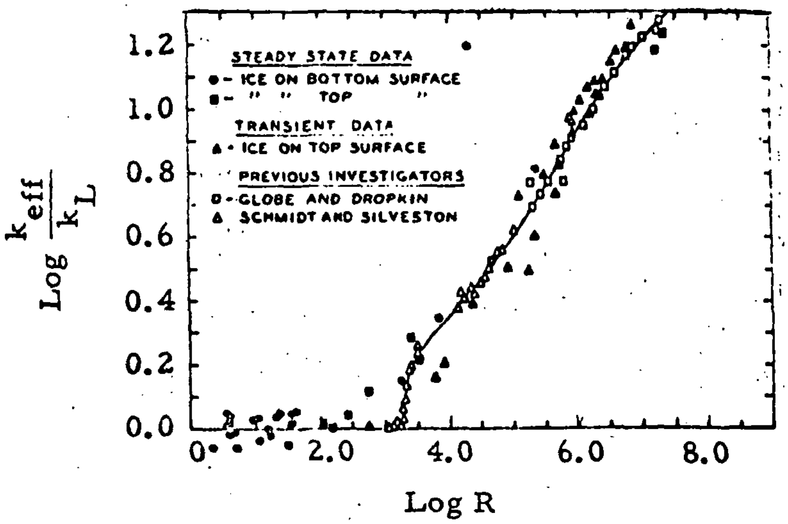


Figure 3-2 - Correlation of Effective Thermal Conductivity and Rayleigh Number (Reference 22)

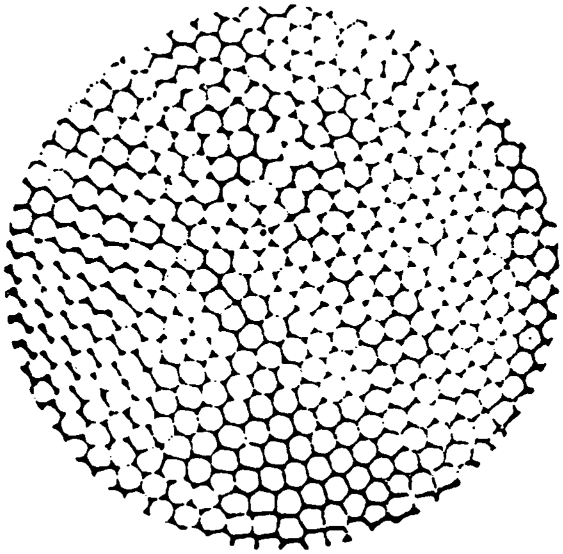


Figure 3-3 - Bénard Cells in Spermaceti

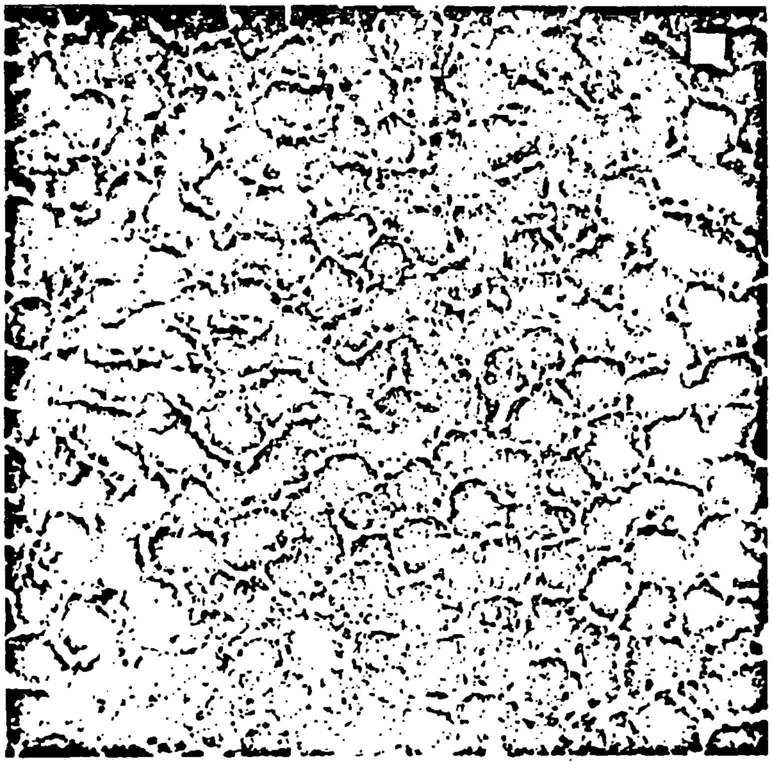


Figure 3-4 - Convection Pattern at $R/R_c \sim 7$, Showing Principally Beads Deposited on the Bottom (Reference 39)
(The scale is indicated by a white square in the top right-hand corner. The side of this is equal to twice the depth of the layer.)

(about 1 mm thick) of spermaceti is uniformly heated from below. No Rayleigh number was given by Bénard. It is possible that the Rayleigh number for the heated fluid system at which the picture was taken was less than the critical value, and the observed convective motion may be due to causes other than buoyancy force. Further discussions will be made on this point in the following section.

Figure 3-4 is another photograph of convection cells reported by Tritton and Zarraga (Reference 39). Aqueous zinc sulphate solutions were used as the experimenting fluid, and heating was produced internally by an electrolytic current. Note that in Figure 3-4 the Rayleigh number is about seven times as large as the critical value. Tritton and Zarraga observed in their experiments that the fluid was rising at the peripheries of the cells and falling at the centers. This is exactly the opposite way around from Bénard's observations in his experiment with water and spermaceti. This is another evidence that the cellular motion observed and photographed by Benard might be caused not by buoyancy or gravity force but by other physical properties, such as surface tension. The later property was neglected by Rayleigh and others in their theoretical analysis of hydrodynamic instability.

3.4 MARANGONI CONVECTION DUE TO SURFACE TENSION FORCE

Recently, Pearson (Reference 31) made a pioneering study of cellular motion in terms of surface tension. He suggested that cellular motion of the type observed by Bénard can also be induced by surface tension forces. When a thin layer of fluid is heated from below, the temperature gradient is such that small variations in the surface temperature lead to surface tractions which cause the fluid to flow and thereby tend to maintain the original temperature variations.

Pearson was able to come up with a stability criterion based on a dimensionless number B. This number expresses the ratio of surface tension to viscous force. It is known as the Marangoni number and is defined as

$$B = \frac{-\frac{d\sigma}{dT}\frac{dT}{dy}d^2}{\rho\nu\alpha} \tag{3.3}$$

where dT/dy, d, ν and α are the same as those appearing in Equation (3.2) $d\sigma/dT$ represents the rate of change of surface tension with temperature and ρ is the density of the fluid. Note the acceleration of gravity, g, is absent in Equation (3.3). The critical value of B for the onset of cellular flow, in the case of one free and one rigid bounding surface, has been determined to be approximately 80.

From Equations (3.2) and (3.3), one may derive a critical thickness of the fluid layer for instability due to gravity force and surface tension force. This critical thickness is

$$d_c = \left[\frac{-\frac{d\sigma}{dT}}{\rho g\beta}\frac{R_c}{B_c}\right]^{1/2} \tag{3.4}$$

For most liquids (such as water and spermaceti) at laboratory temperature, Equation (3.4) leads to values of d_c of the order of 1 cm. For thicknesses less than d_c, then, we expect surface tension to be more effective than buoyancy force in producing instability; and, for values of d as small as 1 mm, the onset of cellular motion could confidently be attributed to surface tension rather than buoyancy force (Reference 31). The same conclusions may be drawn through direct comparison of R and B. As the ratio of R to B is proportional to d^2, it is more likely that, for a very small d, surface tension is the major cause of cellular convection.

Just as Rayleigh neglected surface tension in developing his theory of hydrodynamic instability, so Pearson neglected gravity force in offering a new explanation for the cause of cellular motion. Usually in practice, however, both buoyancy and surface tensions are operative. A combined theory, which takes into account both buoyancy and surface tensions effects, was given by Nield (Reference 41). In his analysis of the generalized problem of cellular motion, the author utilized Fourier analysis in conjunction with a linear perturbation technique. It was found that the two agencies (buoyancy and surface tensions) causing instability reinforce one another and are strongly coupled. Nield also developed a criterion of instability under maximum reinforcement as

$$\frac{R}{R_c} + \frac{B}{B_c} \geq 1 \tag{3.5}$$

Equation (3.5) shows that if surface tension effect is absent, i.e., B = 0, the instability criterion becomes the same as that formulated by Rayleigh; while in the absence of gravity (R = 0), the onset of cellular motion occurs as B exceeds B_c, as suggested by Pearson's theory. In general, R and B reinforce each other in such a manner that cellular convection may occur at a Rayleigh number R and a Marangoni number B smaller than their corresponding critical values, R_c and B_c.

Nield stated in his paper that "buoyancy must, of course, be the sole agency responsible when there is no free surface." This is probably true for a liquid confined between two perfectly rigid walls. However, in the case of a solid in contact with its melt at or near its melting temperature, the solid-liquid interface probably cannot be considered as a rigid boundary for the liquid. This interface is somewhat "soft," as the molecules at the surface possesses great mobility at or near the equilibrium temperature. Hence, interface tension gradients could be the cause of cellular motion. On the other hand, there might be voids formed under certain conditions which accumulate at either the interface or at the liquid-container surface This would, of course, create a real "free surface" where cellular motion of the Marangoni type is definitely possible.

A possible evidence of the appearance of cellular motion during phase change is that cellular structures are sometimes formed on melting or freezing solid surfaces when the liquid layer is rapidly decanted. It is observed that the cellular structure of interface growth assumes almost the same form as those of Bénard cells. It is quite conceivable that the formation of interface cellular structure might be due to hydrodynamic instability occurring near the solid-liquid interface.

3.5 CONCLUSIONS REGARDING PROMINENT CONVECTIVE MODES IN SPACE

From the foregoing discussions, it may be concluded that, in a gravity field, both Rayleigh and Marangoni convection are possible; while in the absence of gravity force, a cellular motion of the Marangoni type is still possible. The existence of both would greatly influence the surface morphology in the phase-change process. Further, the presence of convective motion of either type during phase change would enhance or retard freezing or melting depending on the circumstances. The melting (freezing) rate can be increased (decreased) by as much as 30% in a water-ice system, and presumably more for a normal fluid (Reference 42).

Section 4

PHYSICAL ASPECTS OF PHASE-CHANGE BEHAVIOR IMPORTANT TO OPTIMUM PCM PERFORMANCE

4.1 GENERAL CONSIDERATIONS

In Section 3 the influence of convection currents on phase-change behavior was considered. In this section, the role of heat transfer in phase-change behavior will be considered in more detail, because this aspect of phase change is of paramount importance to optimum PCM performance and usually overlooked in the literature.

Other topics pertinent to PCM performance, such as nucleation catalysis, bubble and void formation, effect of thermal cycling on nucelation, impurities, crystal morphology, and material selection are discussed in this section. The topic of crystal morphology is included because the shapes of crystals are related to temperature conditions under which they are formed.

4.2 ROLE OF HEAT TRANSFER IN PHASE-CHANGE BEHAVIOR

4.2.1 Modes of Heat Transfer in Solid-Liquid Phase Change

There are three basic modes of heat transfer, namely, radiation, conduction and convection. Convective heat transfer processes involve mass motion (convective currents) and can only occur in a fluid. Convective heat transfer may or may not occur in a fluid system experiencing convective motion. The mechanism of heat transfer in convection is actually the same as that of conduction in fluids when explained in microscopic terms.

It is a physical fact that radiation always exists in every heat transfer system as long as there are temperature differences. However, the effect of thermal radiation within a body is usually not considered in most systems operating at ordinary temperatures. This is because, at ordinary temperatures, the amount of heat transferred due to radiation is usually negligible as compared with that of convection or conduction. If a heat transfer system is exposed to a radiation source or sink, then the amount of radiant energy received or lost by the system can be treated as a boundary condition, specifying the energy flux at the boundary of the system. Only one paper has been found which indicates that radiative heat transfer may play a role in solid-liquid phase change (Reference 43, p. 531). Apparently for metals, radiative heat transfer becomes a factor at high growth rates. Radiative heat transfer is not considered further in this report.

In a solid-liquid phase-change system, conduction may or may not be the only mode of heat transfer, depending on whether or not convective motion appears in the liquid phase. The pure conduction heat transfer problem of a freezing or melting system in the absence of any convection current is to be discussed in Section 4.2.4.

4.2.2 Solid-Liquid Interface Temperatures and Controlling Rate Processes

At a given pressure, the solid and liquid phases of a pure, single component material can co-exist in equilibrium at only one temperature. In this equilibrium condition, there is no macroscopic melting or freezing. On a microscopic scale, however, the solid is continuously melting and the liquid is continuously freezing, but the rates at which these two processes are occurring at the equilibrium temperature are equal so there is no net macroscopic change of solid or liquid.

If heat is added or taken away in a <u>reversible</u> manner from a system that contains both solid or liquid phases, a net macroscopic change of solid or liquid occurs at the equilibrium temperature. The amount of heat causing the reversible change at T_e is called the latent heat of fusion and is related to T_e by the relationship

$$T_e = \frac{\Delta H_f}{\Delta S_f} \tag{4.1}$$

where ΔH_f is the latent heat of fusion and ΔS_f the entropy of fusion.

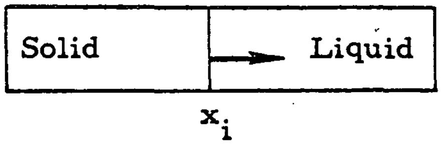
Any actual macroscopic melting or freezing, of course, will occur irreversibly, so that the solid-liquid phase change will occur at temperatures which may be considerably removed from T_e. To appreciate the physical significance of this statement, consider the following situation. A small seed crystal is added to a batch of melt of the same substance, maintained at a constant temperature by means of a thermostated bath. If the temperature of the melt is T_e, no net crystallization or melting will occur when the seed crystal is introduced into the melt. In other words, at T_e, the solid and liquid are in equilibrium and no driving force for net crystallization or melting exists. If a seed crystal is added to a melt maintained at some temperature, T_∞, below T_e, crystallization will proceed. The solid-liquid interface temperature T_i will be almost T_e or almost T_∞ or someplace inbetween. The relative rates of heat transport to or away from the solid-liquid interface and of solid-liquid phase change will determine the interface temperature. For example, when a seed crystal is introduced into a melt of temperature T_∞ (T_∞ below T_e), crystallization will proceed and the interface temperature will initially be at T_∞. If, as crystallization proceeds, heat is liberated faster than it can be removed, the interface temperature will rise. Obviously, if the interface temperature were exactly T_e there would be no driving force for crystallization. Nor can T_i be exactly T_∞, for then there would be no driving force for heat removal (Reference 44). However, if the rate of phase change is fast in comparison to the rate of heat removal, T_i will be very close to T_e. If, on the other hand, the rate of heat removal is fast in comparison to the rate of phase change, T_i will be very close to T_∞,

In any sequence of consecutive, coupled rate process, the overall net rate is determined or said to be controlled by the slowest rate in the sequence. Thus, in the preceding situation where the rate of heat transport is fast and the microscopic rate of phase kinetics slow, the overall, macroscopic rate of phase change can be said to be "kinetic controlled". Conversely, where the heat transport rate is slow and the phase kinetics fast, the macroscopic rate may be called "heat controlled" In a heat controlled phase change, T_i will be close to T_e, while in a kinetically controlled phase change, T_i will be close to T_∞. In cases where neither heat nor kinetic control predominate, T_i will be somewhere between T_e and T_∞.

Heat controlled phase change will be relatively sensitive to heat flow parameters and hence to such things as dimension of the container and the thermal conductivities. Kinetic controlled phase change will be relatively insensitive to heat flow parameters and determined mainly by material nature and interface undercooling.

4.2.3 Coupling Between Phase-Change Kinetics and Heat Transport Processes

The heat transport and kinetic processes of phase change are both dependent on the interface temperature. The driving force for phase change is determined by the temperature difference $\Delta T_i = T_e - T_i$, while that for heat transport by $\Delta T_H = T_i - T_\infty$. For example, consider a plane solid front crystallizing steadily from liquid under the driving force of an imposed temperature gradient, shown as follows



If conduction were the only mode of heat transfer, the one-dimensional equation for the velocity of the interface can be written as

$$K_S \left(\frac{\partial T_S}{\partial x}\right)_{x_i} - K_L \left(\frac{\partial T_L}{\partial x}\right)_{x_i} = \Delta H \rho v \tag{4.2}$$

where K_L and K_S are the thermal conductivities of the liquid and solid phases, respectively. The terms ρ, ΔH, and v are the average density of the system, the latent heat of phase change (equal to latent heat of fusion if the phase change is occurring close to T_e), and the velocity of the interface. The terms

$$\left(\frac{\partial T_L}{\partial x}\right)_{x_i} \quad \text{and} \quad \left(\frac{\partial T_S}{\partial x}\right)_{x_i} \tag{4.3}$$

are the temperature gradients at the phase interface. If the crystallization were heat controlled, it would be sufficiently accurate to set the temperature at x_i equal to T_e and the velocity to dx/dt. Even so, the solution of this problem is complex (see Section 4.2.4).

In cases where the phase kinetics have to be considered, the velocity of the interface, v, may in general be represented as some function of $T_e - T_i$. For present purposes, it is sufficient to represent the velocity of the interface kinetics as (Reference 45).

$$v = A(T_e - T_i)^n \tag{4.4}$$

where A and n can be taken as constants. In later sections the details of the interface kinetics and their dependence on mechanism and crystallographic planes will be discussed. Also, the latent heat of fusion has a slight dependence on temperature, but this can usually be ignored.

It is well to mention at this point that the change of phase from liquid to solid invariably requires some significant degree of supercooling, but the change from solid to liquid is accomplished with very little superheating in nearly all cases. The explanation for this (Reference 46, p. 84) is that the free energy of a solid-vapor interface is more than the sum of the solid-liquid and liquid-vapor free energies. Hence, there is no increase in free energy in the early stages of melting as there is in the early stages of nuclei formation in freezing. If the solid is heated internally by radiation or extremely rapidly, or if the solid has a surface of negative curvature and stabilized edges, superheating becomes possible. The first of these two phenomena is not expected to occur to any great extent in PCM operation because very little internal radiative heating is anticipated. (See Section 4.2.1.) The second phenomenon is relevant to nucleation (see Section 4.5).

4.2.4 Heat Conduction with Melting or Freezing

The conduction heat transfer involving a change of phase has been studied extensively in the past because of its scientific and practical importance. A typical example would be the classical Stephen problem of melting which describes the physical situation of a semi-infinite solid initially at a uniform temperature T_0 ($T_0 < T_e$ melting or equilibrium temperature) and subject to a surface temperature T_S higher that T_e. (See Figure 4-1.)

The unsteady temperature distributions T_1 and T_2 in, respectively, the liquid and solid phase satisfy the following set of differential equations (Reference 47).

$$\frac{\partial T_1}{\partial t} = \alpha_1 \frac{\partial^2 T_1}{\partial x^2} , \qquad x < X(t) \tag{4.5}$$

$$\frac{\partial T_2}{\partial t} = \alpha_2 \frac{\partial^2 T_2}{\partial x^2} , \qquad x > X(t) \tag{4.6}$$

where α_1 and α_2 are the thermal diffusivity of the liquid and solid phases, respectively, and X(t) is the time-dependent distance of the solid-liquid interface measured from the surface of the system.

Let H be the latent heat of fusion of the material, ρ be the density of the liquid and solid ($\rho = \rho_1 = \rho_2$), and k_1 and k_2 be the thermal conductivities of the liquid and solid phases, respectively. Then, for the foregoing specified problem, T_1 and T_2 must also satisfy the following initial

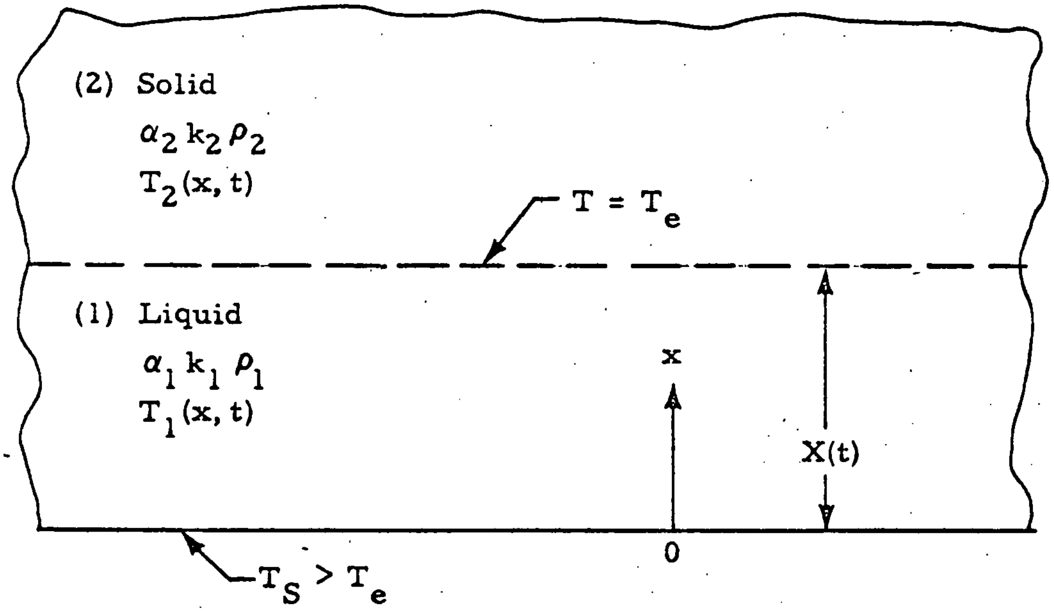


Figure 4-1 - Schematic Diagram of Stephen's Problem of Melting

and boundary conditions:

$$T_2 = T_0 \quad \text{for all} \quad x \geq 0 \quad \text{and} \quad X = 0, \quad \text{at } t = 0 \tag{4.7}$$

$$T_1 = T_2 = T_e \qquad \text{at } x = X(t) \tag{4.8}$$

and

$$-k_1 \frac{\partial T_1}{\partial x} = -k_2 \frac{\partial T_2}{\partial x} + \rho H \frac{dX}{dt} \qquad \text{at } x = X(t) \tag{4.9}$$

$$T_1 = T_S \quad \text{at} \quad x = 0 \tag{4.10}$$

$$T_2 = T_0 \quad \text{at} \quad x \to \infty \tag{4.11}$$

It should be noted that in the above formulation of the problem, the change of volume on melting has been neglected, and no superheating or undercooling at the interface is considered.

Equations (4.5) and (4.6) with the initial and boundary conditions (4.7) to (4.11) may be solved to give the following results

$$\frac{T_1 - T_0}{T_S - T_\infty} = 1 + \left(\frac{T_S - T_e}{T_0 - T_e}\right) \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_1 t}}\right)}{\operatorname{erf}(\lambda)}, \quad 0 \le x \le X(t) \tag{4.12}$$

$$\frac{T_2 - T_0}{T_e - T_0} = \frac{\operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_2 t}}\right)}{\operatorname{erfc}\left(\lambda\sqrt{\frac{\alpha_1}{\alpha_2}}\right)}, \quad x \ge X(t) \tag{4.13}$$

and

$$X(t) = 2\lambda(\alpha_1 t)^{1/2} \tag{4.14}$$

In the above equations, λ is a numerical constant to be determined from the following implicit equation

$$\frac{e^{-\lambda^2}}{\operatorname{erf}(\lambda)} \frac{k_2}{k_1}\sqrt{\frac{\alpha_1}{\alpha_2}}\left(\frac{T_e - T_0}{T_S - T_e}\right)\frac{e^{-\lambda^2 \alpha_1/\alpha_2}}{\operatorname{erfc}\left(\lambda\sqrt{\alpha_1/\alpha_2}\right)} = \frac{\sqrt{\pi}\,\lambda H \alpha_1 \rho}{(T_S - T_e)} \tag{4.15}$$

For a given material with given boundary temperatures, λ may be calculated numerically from Equation (4.15). Then, the temperature fields, T_1 and T_2, and the melting rate, dX/dT, can be determined by Equations (4.12), (4.13) and (4.14). Other nonsteady unidimensional solutions of melting and freezing problems under various initial and boundary conditions may also be found in Reference 47.

Recently, Muehlbauer and Sunderland (Reference 48) published a survey on "Heat Conduction with Freezing or Melting" in which a total of 146 references were listed. The vast amount of papers in relation to a single subject problem is the result of newly developed techniques for the solutions of the problem. These are: the variational technique, the heat-balance integral technique, the Riemann-Mellin contour integral technique, the analogue technique, and other analytical and numerical techniques. Interested readers on the subject of pure conduction with a phase change should refer to the papers cited in Reference 47.

4.2.5 General Summary of Phase-Change Behavior as Function of Imposed Thermal Conditions

Phase change kinetics have been discussed in some detail because the role of phase-change kinetics has been generally overlooked, dismissed or ignored in previous heat transfer work on PCM thermal control. The interface temperature has been assigned invariably the equilibrium value, i.e., heat control assumed. Although this is a reasonable assumption for melting, its validity must be tested for the freezing process, especially for PCM candidate materials, for which, as will be discussed later, there is every reason to anticipate slow freezing kinetics. Comparisons of theoretically calculated interface velocities, using the heat controlled solution for both freezing and melting of n-octadecane, have been in poor agreement with experimental results (Reference 49). The measured velocities were as much as 100% higher than predicted by heat controlled solution. Although convection currents and wall effects may account for this discrepancy, it is obvious from the motion pictures taken in the study of the interface during melting and freezing (References 49 and 50) that the influence of phase kinetics cannot be lightly dismissed (see Section 4.6 for discussion of relationship between interface morphology and phase kinetics). Also, because of this lack of recognition of the role of phase kinetics, some suggestions for packaging modifications to improve thermal diffusivity, such as packing with aluminum wool, fail to take into account that these modifications may be compounding supercooling problems.

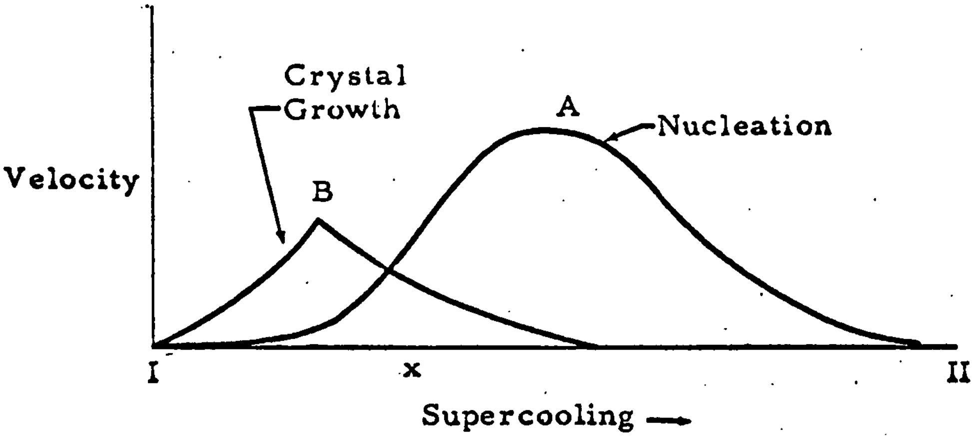
To illustrate some possible roles of phase kinetics in solidification, Flow Charts I and II have been drawn. These charts serve a twofold purpose.

First, they emphasize the dependence of freezing behavior on a large number of adjustable variables and on the nature of the material itself and thereby illustrate the interplay of heat transport rates and phase kinetics. Secondly, these charts indicate some of the supercooling problems that can be encountered with some materials and warn that supercooling problems are to be anticipated with PCM. Two of the most important requirements of PCM are that they possess high fusion latent heats and low fusion temperatures. From the relationship (4.1) i.e.,

$$T_e = \frac{\Delta H_f}{\Delta S_f}$$

it follows that, on a gram basis and usually on a molar basis also, the entropies of fusion of PCM will be high. Therefore, as indicated in the charts, supercooling problems are to be anticipated with such materials.

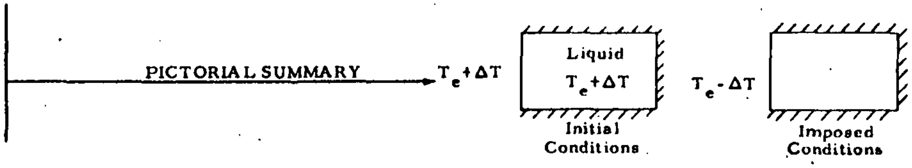
To illustrate the considerations that went into formulating Charts I and II, consider the following graphical representation which can be taken, for present purposes, as generally representing the dependence of nucleation and crystal growth rates on the liquid and interface supercooling (Reference 19, p. 420 and Reference 51, p. 366).

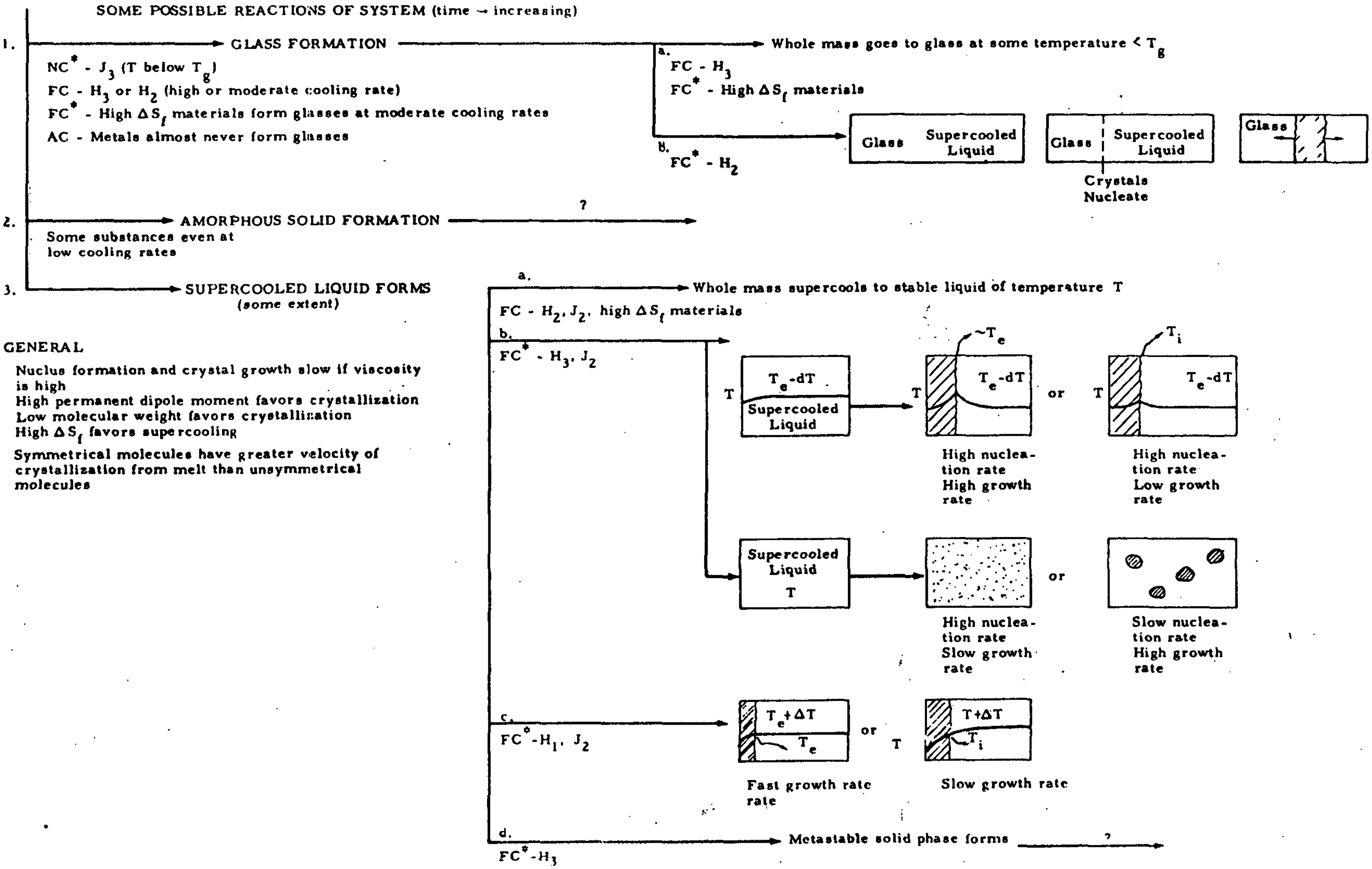


Following flow chart indicates some possible responses of phase-change material in zero-g condition as a function of cooling rate, final imposed temperature, and material class.

Variables:
H, J, A

Fixed Parameters:
$M_1, B_1, D_2, E_1, F_1, I_1, K_1, L_1, O, P, Q$





GENERAL

Nucleus formation and crystal growth slow if viscosity is high
High permanent dipole moment favors crystallization
Low molecular weight favors crystallization
High ΔS_f favors supercooling
Symmetrical molecules have greater velocity of crystallization from melt than unsymmetrical molecules

CHART I*

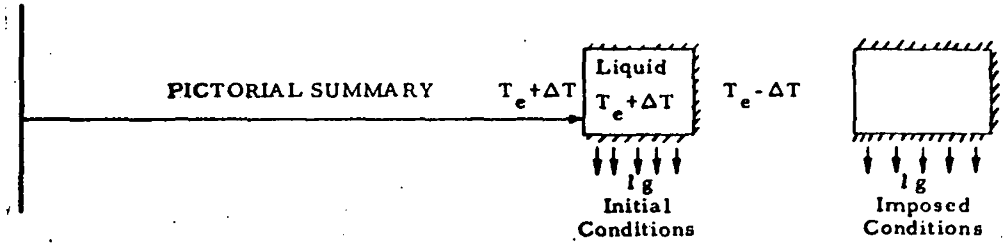
FREEZING IN ZERO-G CONDITION

*Key to symbols for Charts I and II are on pages 36 through 38.

Following flow chart indicates some possible responses of phase-change material in 1-g condition as a function of cooling rate, final imposed temperature, and material class.

Variables:
H, J, A

Fixed Variables:
$M_2, B_1, D_2, E_1, F_1, I_1, K_1, L_1, G_1, N_1, O, P, Q$



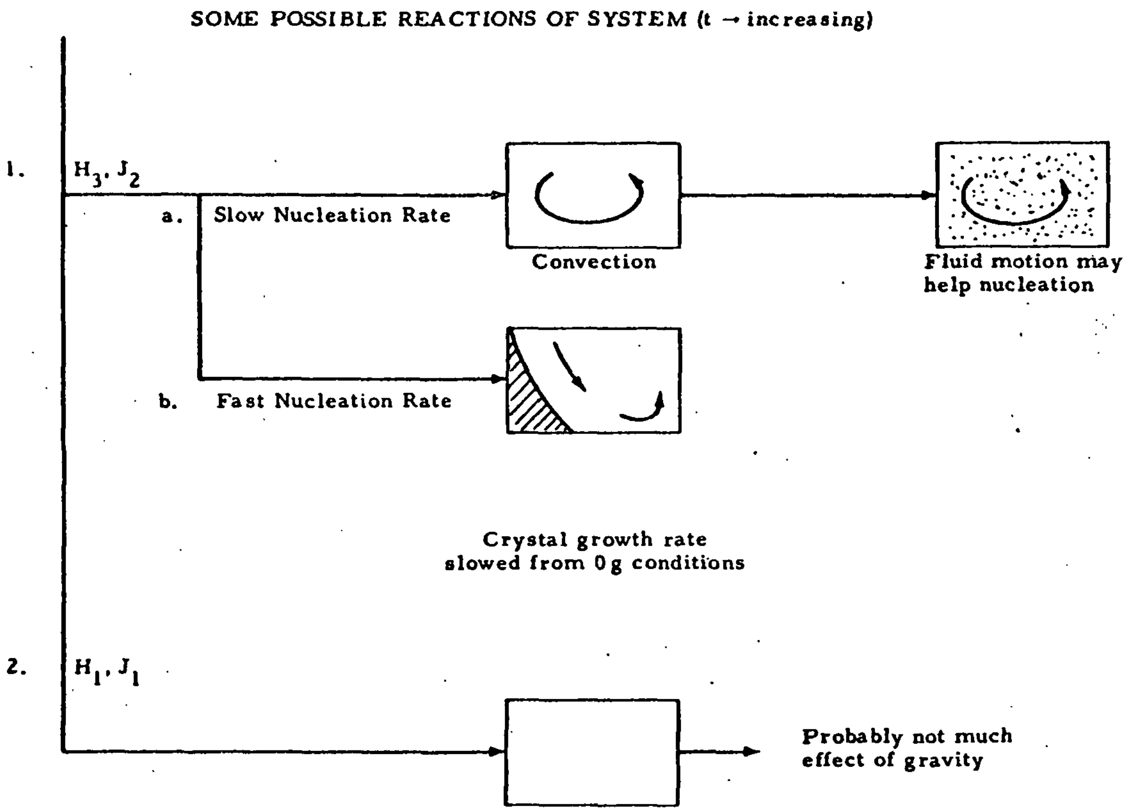


CHART II - FREEZING IN 1-G CONDITION

KEY TO SYMBOLS FOR CHARTS I AND II

NOTATION

FC - favorable condition
SC - sufficient condition
NC - necessary condition
AC - adverse condition
* - educated guess

T_e - solid/liquid equilibrium temperature
T_g - glass temperature
P - pressure

INDEPENDENT PARAMETERS

A. Material Class

- A_1 Metal
- A_2 Molecular
- A_3 Covalent
- A_4 Ionic
- A_4 Hydrogen Bonded

B. Number of Components in Material

- B_1 One
- B_2 Two
- B_3 Three

C. Concentration of Components

- C_1
- C_2
- C_3

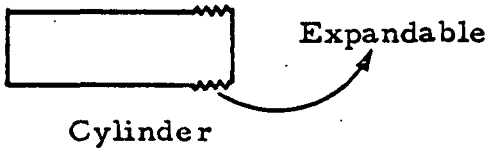
D. Relative Sample Size

D_1 Small

D_2 Large

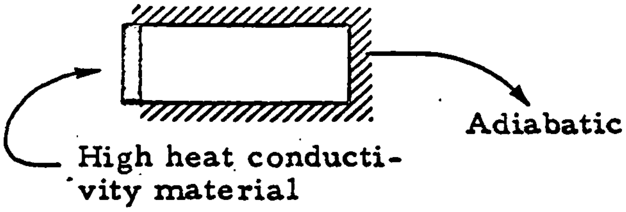
E. Container Configuration

E_1



F. Nature of Container Walls

F_1



G. Pressure Outside Container

G_1 One atm

H. Rate of Cooling or Heating

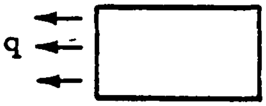
H_1 Low

H_2 Moderate

H_3 High

I. Symmetry of Cooling or Heating Conditions

I_1



J. Temperature Range/Ranges to which Sample is Subjected ($\Delta T = T_e - T$)

J_1 ΔT Small

J_2 ΔT Large

J_3 ΔT Large and T below T_g

K. Condition of Inside Wall of Container

K_1 Non-Catalytic

K_2 Catalytic

L. Initial T, P, and State of Sample

L_1 $P = 1$ atm, $T = T_e + \Delta T$, State-liquid

M. Magnitude of Gravity

M_1 0

M_2 1 g

N. Direction of Gravity in Relation to Solid/Liquid Interface or Container Faces

N_1 Parallel to Advancing Solid-Liquid Interface

O. Electric Field - Magnitude and Direction

P. Magnetic Field - Magnitude and Direction

Q. Radiation Field

If the temperature is in the range just below I, (see figure on p. 33), the rate of nucleation is very low, while the rate of crystal growth is also rather low. Thus, a few crystals will form and will grow slowly. As the undercooling increases, the probability of forming more nuclei increases, as does the growth rate. Thus, many small crystals can be expected. At extreme undercoolings the rate of nucleation and growth both decreases, and in this region glass formation is likely.

With a given material, quantitative prediction of its response to cooling conditions would be possible if the time-dependent and steady-state rates of nucleation and of crystal growth as a function of undercooling (T_e - T_i) were available. Such data are extremely scarce. Nucleation and crystal growth kinetic data are very difficult to generate experimentally. Extraneous heat flows and other difficulties usually complicate the results. On the basis of experience it may be predicted that, within a class, materials will show similar behavior, but sufficient exceptions exist so that only experiment can answer how a particular material actually does respond to cooling.

It appears that the behavior indicated in 3c, Chart I, would give the best PCM performance. Certainly, Cases 1, 2, 3a and 3d are undesirable. A case where small crystals form throughout the liquid might also be desirable if accompanied by interfacial tension-driven convection currents. As yet, however, there is little evidence that fluid flow can result by such a mechanism; although, as discussed in Section 3, there is reason to suspect that it may be possible.

The main problem foreseen in ensuring that PCM react to cooling as in Case 3c is that of nucleation. This will require materials which show rapid nucleation response. Otherwise effective nucleation catalysts must be sought. Another important consideration in regard to PCM performance are the absolute rates of crystallization. Because PCM are likely to exhibit slow phase kinetics, it must be ascertained that the absolute crystallization velocities are high enough to accommodate the imposed cooling fluxes.

In other words, even though nucleation begins, the rates of crystal growth may be so slow that the interface temperature falls enough to stop crystallization altogether even after nucleation. An understanding of the rates of kinetics and heat transfer in solid-liquid phase change can expedite efficient container design and identification of problem causes in practice.

4.3 SOLIDIFICATION OF BINARY COMPONENT MIXTURES AND IMPURITY EFFECTS

4.3.1 Solute Segregation

When more than one component is present in the liquid phase, a variety of effects can be expected, depending on the kind of component interaction that can occur in both the solid and liquid phases and on the concentrations of each of the components. Just the simplest of cases will be discussed here. Consider the following idealized phase diagram of a binary mixture (Figure 4-2).

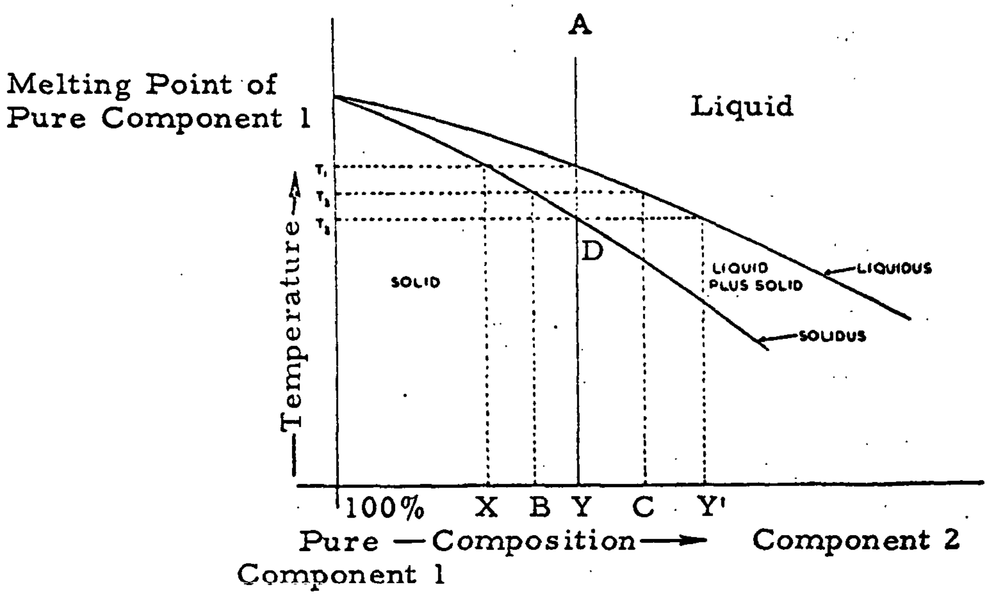


Figure 4-2 - Portion of Equilibrium Phase Diagram of Binary Component Material (Solid Solution Formed on Freezing). Reference 52, p. 27.

In a reversible solidification (equilibrium freezing) of a liquid of composition A, the following would happen. On lowering the temperature to T_1, solid of composition X would form. On further lowering of the temperature, more solid would form and its total composition would vary along the solidus line until point D is reached. At D, the solidification would be complete and the final solid composition would be Y throughout. In an actual or irreversible – in the thermodynamic sense – freezing of the same mixture, the first solid to form has the composition X as the temperature is lowered to T_1. Since the solid X has less Component 2 than does the liquid at T_1, the excess Component 2 is rejected into the solid-liquid intergace. Now the time required for diffusion is slower than temperature change, so concentration non-equilibrium results as the temperature is being lowered. Thus, the next portion of liquid adjacent to the solid and in line for solidification has a concentration greater than Y, say concentration C, and, as the temperature falls, solidifies to give a solid of composition B, rejecting additional Component 2 into the interface. At any given time during the solidification, the composition of the liquid will be generally as follows (Figure 4-3):

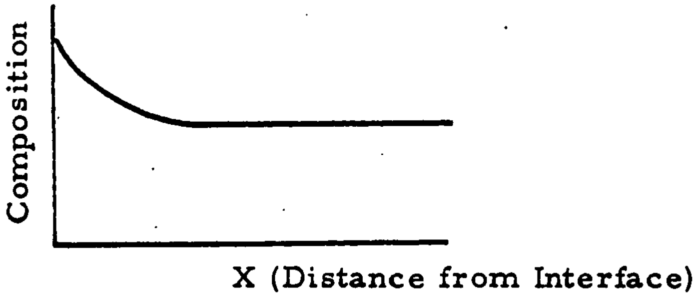


Figure 4-3 - Distribution of Solute in Liquid (Reference 53, p. 528)

The final composition of the solid will thus be heterogeneous as opposed to homogeneous in the equilibrium case. Depending on the freezing conditions, a number of concentration distributions can be obtained in the final solid. These are shown in Figure 4-4. Case (a) in Figure 4-4 is for equilibrium freezing. This would require an extremely slow freezing rate and is never realized. Case (b) is for freezing rates slow enough for mixing to erase all concentration gradients in the liquid but insufficiently slow for any diffusion to occur in the solid. In Case (c) the freezing is rapid enough for only diffusion in the liquid to be possible. Case (d) is where the solute concentration is affected by both diffusion and convection. The preceding types of segregation are called normal. See Reference 55, p. 281, for a full discussion of other types of segregation.

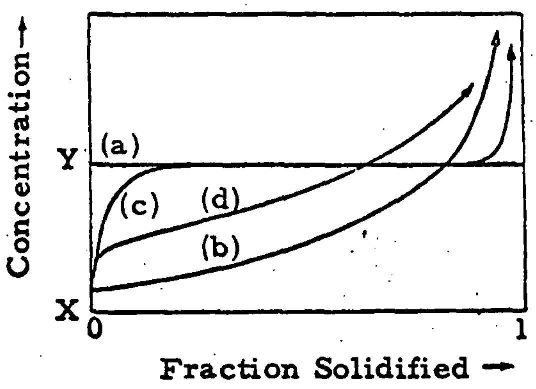


Figure 4-4 - Solute Distribution in a Solid Bar as a Result of Freezing a Liquid of Initial Concentration Y for the Cases (a) Equilibrium Freezing, (b) Complete Mixing, (c) No Mixing, and (d) Partial Mixing (Reference 54, p. 395)

The above is pertinent to PCM operation on a number of points. First, we can expect that even small concentrations of soluble impurities can lead not only to lower or higher equilibrium temperatures, but more important can lead to sliding freezing and melting points because of the squeezing-out effect. Secondly, because of this squeezing-out effect, local liquid areas will have greater densities, so we should expect more convection or even solute segregation in gravity fields than in nongravity fields. Thirdly, eutectics are contemplated as having possibilities for PCM application. Ideally, eutectics should crystallize like a pure one-component material.

Because eutectics are multi-component materials, however, we can expect some unique nonequilibrium effects. A common problem with eutectics seems to be that of non-simultaneous nucleation of both components. Thus, one component will start to crystallize before the other. This, of course, would disturb the liquid composition, especially if the crystals were segregated from the main body of liquid by gravity. Also, see Reference 55, p. 263, for a discussion of how the squeezing-out effect lowers the eutectic freezing point somewhat below its equilibrium value.

4.3.2 Constitutional Supercooling

As discussed in the preceding section, a buildup of solute concentrations will be present in the interface region during freezing of a binary component melt. Since the concentration is greater in this region, the freezing point may be lower than the actual temperature distribution. For example, Figure 4-5 shows the variation of the liquidus temperature, T_L, with distance from the interface. The actual temperature, T, may vary in such a way that it is below T_L in some regions.

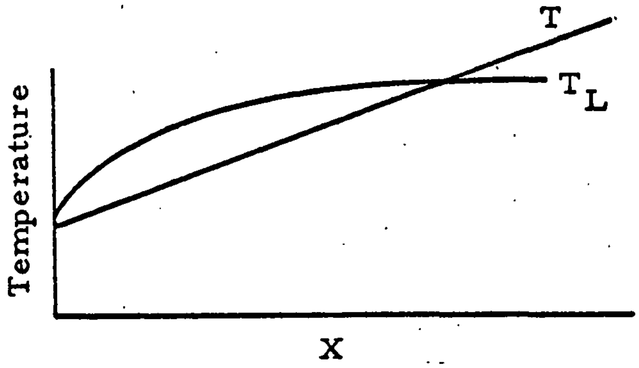


Figure 4-5 - Constitutional Supercooling (Reference 53)

The region where the actual temperature is below the liquids temperature is said to constitute a region of constitutional supercooling. Three consequences can occur (Reference 53). First, a smooth interface becomes unstable, and a cellular interface results. (A very small amount of impurity (~0.01%) can cause this effect to appear.) Secondly, dendritic growth can appear in a direction of rising temperature. (Morphology as a consequence of conditions of growth is discussed more fully in Section 4.6). The third consequence is that new crystals may be nucleated in this region of constitutional supercooling.

4.3.3 Impurities

Many of the effects of impurities on crystallization can be understood in terms of the preceding two sections. In addition to segregation and supercooling effects, impurities can profoundly influence nucleation crystal growth rates and morphology by surface effects or electrical effects (Reference 56, p. 28). It is difficult to define the latter type of impurity effects because even the smallest amounts that can escape the attention of the investigator can exert profound influences. Invariably, every material, no matter how carefully purified, will have some impurities. Because such small amounts of impurities can have such a strong influence, experimental study is difficult. Theoretical study is also difficult because many of the parameters such as interfacial tensions needed to evaluate a theory are unavailable. Some theories employ concepts which are doubtful on a microscopic scale. Any general conclusions from the literature, therefore, must, of necessity, be qualified with a "maybe." In general, in a practical situation, the influence of impurities which can act through surface effects would be predicted to decrease nucleation and growth rates. The growth rates can be decreased by absorption of impurities on crystal surfaces, thus blocking free passage of atoms or molecules of the parent material. As far as PCM operation is concerned, the real problem with impurities is that, over long periods of time and especially for organic materials in an intense radiation field, their composition or concentration may be altered sufficiently to cause problems.

4.4 BUBBLE AND PORE FORMATION DURING PHASE CHANGE

4.4.1 Mechanisms of Bubble and Pore Formation

The formation of bubbles and/or pores during freezing or melting is important in considering PCM behavior, because such formation can have a great influence on the heat transfer rates. Bubbles in the liquid phase will cause stirring actions. In a zero-g gravity field, they would migrate toward the hot side of the liquid because of Marangani flow (Reference 57) and seriously interfere with heat transfer. A vast amount of literature exists on the subject of bubbles, for it is basic to the mechanisms of heat transfer in boiling. Trapped in the solid phase, bubbles or pores will alter the effective thermal conductivity. Since bubbles are frequently seen to form spontaneously in liquids well below their boiling points and during freezing and melting of many compounds, it is important to understand under what conditions they are formed during melting and freezing and their likely behavior and influence once formed.

The formation of a bubble within a liquid phase at a given pressure requires a definite amount of superheat, i.e., an excess of temperature above the saturation temperature. For liquids whose boiling points are on the order of that of water, the heat fluxes required to attain this superheat are so large ($\sim >1 \times 10^5$ Btu/hr-ft^2, Reference 58, p. 63), compared to heat fluxes taken as typical in PCM operation (~ 6 to 400 Btu/hr-ft^2, Reference 3), that this mechanism of bubble formation can be dismissed at once. Vapor bubbles can also be nucleated at local points if the pressure falls so low that the saturated vapor pressure at the local temperature is reached, i.e., cavitation. This mechanism would lead to bubbles that would persist for a length of time sufficient for them to float around awhile or to be overgrown by solid only if extremely rapid fluid flow were present. Either forced convective currents or currents generated by extremely rapid rates of freezing by materials which experience a large volume change on freezing could cause rapid fluid flow. The first possibility of forced convection currents can be dismissed for PCM operation. The second is also unlikely. The change in volume on rapid freezing, however, can cause short-lived cavities which nucleate more solid phase when they collapse. This phenomenon has been analytically analyzed for the case of small crystals growing into an undercooled liquid (Reference 59). The conclusions of the cited analysis apparently are in agreement with the experimental observation that growing nickel nuclei, at large undercoolings, cause a shower of crystals (Reference 60). What the effect of volume shrinkage on freezing will be in the case of a liquid freezing with heat transfer through both the solid and liquid phases is unknown, for very little work on the whole subject has been done. Sekerka and Tiller briefly considered the convection arising from volume shrinkage for the preceding case (Reference 61) and concluded that convection arising from volume shrinkage could be neglected if

$$(\rho_S - \rho_L)/\rho_L \ll 1 \tag{4.16}$$

where ρ_S and ρ_L are the densities of the solid and liquid phases.

More analytical and experimental work is needed in this area of volume change on freezing or melting, for it may explain some peculiar experimental observations, for example, "ripples" on growing crystal faces and a slight, unexplained motion in the liquid phase during freezing and melting of some organic materials in an experimental set-up designed to eliminate natural convection (Reference 49).

For PCM operation, all of the preceding effects can probably be dismissed as unimportant, unless some experimental anomaly encountered in a PCM test warrants further consideration.

The most likely cause of persistent bubbles in PCM is dissolved gases. During solidification, dissolved gases can be rejected at the solid-liquid interface, just as any other solute (see Section 4.1.2). Chalmers (Reference 46, p. 187) gives an excellent discussion of bubble formation by this mechanism as well as possible relative rates of bubble growth and interface advance. During melting, bubbles overgrown by solid can be liberated.

Only one further aspect of the subject will be considered here. In a 1-g field, buoyancy forces would tend to remove bubbles before they can be overgrown by solid. In a zero-g field, therefore, a greater concentration of bubbles trapped in the frozen solid would be expected than in a 1-g field. In a 1-g field, the bubbles would be more likely to float to the top and coalesce. The preceding is, of course, only a generalization. Accurate prediction of the distribution of bubbles would necessitate a more detailed examination of inertial and surface forces acting on the bubbles.

Finally, voids or cavities may form in the solid phase from a number of other reasons. The mere fact that most liquids shrink on freezing means that a cavity or pores will have to be formed someplace, unless the container is collapsable. Chalmers (Reference 46, p. 286) lists the following five ways a solid may finally look (Figure 4-6).

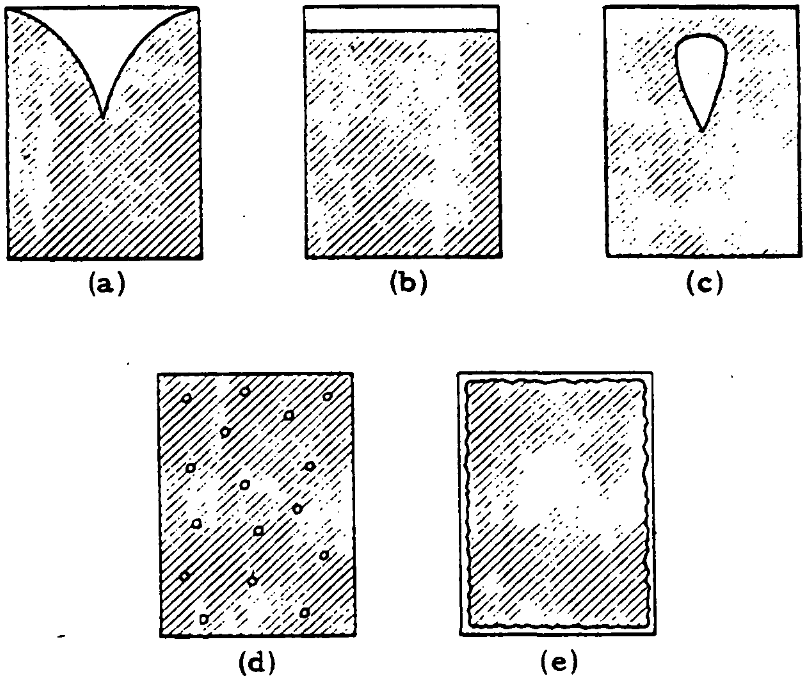


Figure 4-6 Shrinkage Effects [(a) Pipe, (b) Unidirectional Shrinkage, (c) Cavity, (d) Distributed Porosity, and (e) Surface Porosity]

Obviously, Cases a, b and e would interfere seriously with heat transfer. Case c results when cooling occurs on all sides, while Case d results from liquid solidifying in a small solid cavity, such as produced in dendritic growth (Figure 4-7).

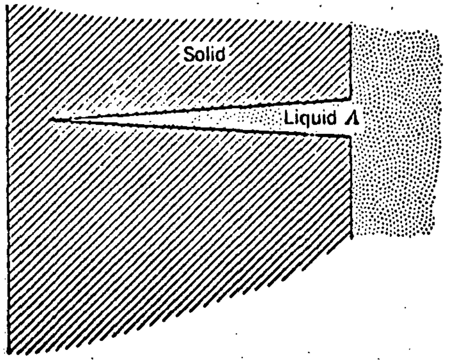


Figure 4-7 - Origin of Microporosity (Reference 46, p. 288)

In Figure 4-7, the liquid at A has too high a viscosity to feed the cavity, as it is solidifying. In such a freezing mechanism, a large gas content will encourage many small pores, while in a low gas content few, large pores.

In addition to bubbles and pores, various other defects can occur in the solid. Since these are expected to have lesser influence on thermal conductivity than pores, further consideration will be forgone. (See Reference 54, p. 416, for a review of these defects.)

4.4.2 Bubbles in PCM Operation

A large amount of dissolved gas would obviously be undesirable for PCM operation, for it would lead to a large number of bubbles which would interfere with heat transfer and also perhaps cause some unpredictable effects. A small amount of bubbles may be desirable for a number of reasons. First, if the bubbles are small and overgrown by solid, they can take up some of the volume shrinkage on freezing and ensure good thermal contact of solid with the wall, thus avoiding big center holes or separation of the solid from the wall. Secondly, some bubbles in the liquid phase could serve to stir up the liquid and increase heat transfer. Thirdly, the vapor-liquid interface would perhaps attract the soluble impurities and thus lower their concentration in the bulk of the liquid. The formation of bubbles coupled with heat transfer and solid-liquid phase change is so complex that only by experiment can their effect be studied.

A large amount of dissolved gas can be avoided by sample preparation. The liquid could be boiled and while still hot put into the container and sealed. Or a less soluble gas can be used to purge the liquid. For example, the bubbles that form when water is frozen are apparently caused by the dissolved oxygen (Reference 54, p. 424). Since oxygen is usually more soluble than nitrogen, especially in organic compounds, a purging with nitrogen would probably decrease the bubbles formed considerably. As a matter of fact, it would be highly desirable to get rid of the oxygen anyway because it is rather reactive with some materials and more apt to be a problem after some period of time, especially in radiation fields.

4.5 NUCLEATION AND NUCLEATION CATALYSIS

Excellent reviews and articles on the theory of nucleation will be found in References 62, 63 and 64. We will confine ourselves to the practical aspects of the subject.

A very pure liquid (assuming no catalytic wall effects) can be cooled far below its equilibrium temperature. Experimental studies on very small liquid drops have shown that there appears to be a definite limit to which the liquid can be cooled before spontaneous crystallization occurs. The spontaneous generation of crystallization sites within the liquid itself is called homogeneous nucleation. The homogeneous nucleation temperature is approximately 0.8 T_e for a wide variety of materials (Reference 62). In

PCM devices, of course, substantial samples will be used and impurities which can act as a catalysts will invariably be present, so that only a small degree of supercooling would be expected. Some materials, even though impure, however, exhibit extraordinary resistance to nucleation, while others show very little. Some materials can be cooled even below their homogeneous nucleation temperature, if the cooling rate is high, without any crystallization occurring at all; i.e., glasses are formed. The reason for this is most probably because both the nucleation rate and/or the crystal growth rate are such that at a high enough cooling rate either few nuclei form or, if they have formed, the growth rates are so slow that crystallization for all practical purposes does not proceed. For example, the following formula is given for x, the fraction of original liquid which has crystallized in time t after the beginning of crystallization (Reference 65).

$$x = 1 - \exp\left[-\frac{\pi}{3} I u^3 t^4\right] \tag{4.17}$$

where I is the nucleation rate and u the velocity of crystal growth. For a particular liquid if Iu^3 were 10^{-2} $\sec^{-4}$ and if the glass transition temperature were 100° below the melting point, the liquid would form a glass if cooled at a rate greater than 10° a minute. Another factor to be considered is that of nucleation time lags. The nucleation rates are based on steady state or quasi-equilibrium states. There may be significant time lags before the equilibrium nucleation rates can be attained. The general concensus in the literature seems to be that time lags are negligible. As pointed out in Reference 65, p. 46, however, this conclusion is based on rather serious, untested approximations. That the nucleation time lag does play a role in nucleation phenomena is discussed in References 66, 67, 68 and 69. Also, in Reference 69, the possibility that "memory" effects in phase change may be explained by nucleation time lags is discussed. Because the theory of time lags is still tentative, definite statements about its importance in a practical situation are unwarrented. Since nucleation catalysts will be sought in any case for PCM devices, negligible nucleation time lags will be assumed. As indicated by the previous discussion, nucleation is a very complex phenomenon. Repeated melting and freezing cycles have been found to decrease the crystallizing tendency of benzophenone (Reference 19, p. 402). Also, various heat treatements of the liquid, such as heating to too high a temperature or maintaining the liquid too long in the liquid state, can increase the difficulty of subsequent crystallization (Reference 19, p. 402). This sort of behavior probably arises from thermal destruction of impurities which were acting as crystallization catalysts, but causes previously discussed may also be responsible. Therefore, even though a catalyst has been found which appears to work for a few thermal cycles, it cannot be taken for granted that thermal cycling over long periods of time, with perhaps a few cycles that deviate from the usual pattern of heat input-output, will not affect nucleation behavior.

Accordingly, one of the most important problems anticipated in PCM performance is repeatable nucleation of crystalline phase at low subcooling — a maximum supercooling of 3^{o} below equilibrium temperature is required. Full testing of any potential PCM will be imperative to ensure that nucleation is really being induced by a deliberately introduced impurity and not by one unknowingly introduced or present already which can be destroyed by thermal cycling, or that other nucleation phenomena have become operative when unusual heating and/or cooling have been experienced.

Present theories of nucleation can perhaps indicate necessary but not sufficient conditions for nucleation catalysis. One commonly held theory is that potent nucleation catalysts have low index planes in which the atomic arrangement is similar to that in certain low index planes of the forming crystals. The order of potency of a nucleation catalyst, by this theory, is identical with the order of the diregistry (mismatch) between catalyst and forming crystals. Sundquist and Mondolfo, on the other hand, in a couple of papers (References 70 and 71) disagree with this conclusion; they hypothesize that nucleation takes place on an absorbed layer (of solid being nucleated) at the catalyst-liquid interface. Sundquist and Mondolfo also dispute the cavity theory of nucleation mentioned earlier, (see Section 4.2.3).

The present discussion indicates that an element of luck is probably involved in finding a catalyst. Once found, its effectiveness, undoubtedly, can be rationalized in terms of one of the theories.

4.6 INTERFACE MORPHOLOGY

4.6.1 Pertinence of Interface Morphology to PCM Operation

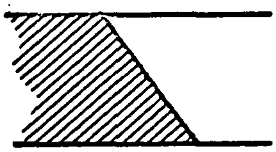
The thermal conductivity of the solid produced during freezing is a very important parameter in determining the overall operation of PCM devices. For PCM operation, both the thermal conductivity of solid and the shape of the interface will be important to the net rate of heat transfer. For example, a planar interface will have different heat transfer characteristics from one which consists of needle-like crystals protruding for perhaps considerable distances into the liquid. The thermal conductivity depends on the crystalline substructure comprising the solid; i.e., the solid may be a single crystal or polycrystalline. The arrangement of the small crystals within the main body of solid is also important, because, as is well known, many solids exhibit anisotropic thermal conductivity. Literally volumes in the field of metallurgy have been written on the relationship of the thermal environment to the type of crystals produced so that control over the final structure can be achieved. The growing of single crystals for electronics applications has also attracted considerable study. In view of the complexity of the phase-change kinetics, prediction of crystal habit from a knowledge of the thermal environment under which it was formed is still far from any quantitative solution.

It is difficult to make definite, general statements on the interface morphology of a wide range of materials because work in this area has been so specialized. The metallurgists concentrate on metals where the phase kinetics are usually fast and are given scant attention. Theoretical studies, on the other hand, have been concentrated on phase kinetics with rates of heat transport given little attention. Also, working against an accurate knowledge of morphological-thermal environment relationships is the fact that no suitable experimental means of measuring interface temperatures exists at present. For the most part then, it may be said that the whole topic is considerably confused. The recent work of Cahn and of Jackson, however, has made significant contributions concerning some of the discussed difficulties.

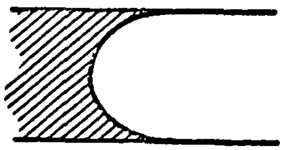
In the following subsection a brief summary is presented of those theories found most helpful in gaining a picture of the role of phase kinetics in determining interface morphology and judged most amenable to practical situations. This is not to slight the other theories, but a thorough review and evaluation is beyond the scope of the present study. In subsection 4.6.3 are presented what definite statements as can be made about the subject.

4.6.2 Macroscopic and Microscopic Morphology

The overall shape of a solid-liquid interface when viewed with the eye may take several shapes; e.g.,



(a)



(b)

The gross features of the interface reflect the relative, overall temperature distribution resulting primarily from heat flow characteristics. Case (a) could result when natural convection sets up a circulation pattern in which hotter liquid is near the top and colder liquid near the bottom. In Case (b), the heat extraction near the walls is greater than near the center of the liquid. If the interface is viewed more closely (a microscope may be necessary), a variety of substructures such as needles, cells, feathery crystals, large crystals, steps, spirals, etc., will usually be seen. These types of substructures may be termed macroscopic morphology in distinction to morphology on an atomic scale where the interface is said to be smooth, rough, or diffuse. The macroscopic morphology is determined by the local temperature and concentration distribution and, of course, the nature of the material itself. More precisely, the macroscopic morphology is a function of (Reference 54):

1. All those variables which influence the free energy of the phases; i.e., temperature distribution, solute distribution, and interface curvature;
2. Mechanical equilibrium with surfaces; i.e., grain boundaries, external surfaces and internal phase boundaries; and
3. Atomic kinetics of the freezing process and the anisotropy of the atomic kinetics.

Several morphologies may satisfy the listed factors. One, however, will respond most rapidly to the thermodynamic driving force and will predominate. To predict the expected macroscopic morphology, the equations for the time-dependent shapes need to be solved to find the one producing the highest rate, consistent with the growth conditions. Tiller (Reference 54) points out that it is extremely difficult to solve for time-dependent shapes, so the steady-state solution is preferable. In the steady-state, the stable interface morphology is the one which satisfies the following equation for growth velocity at every point on the surface,

$$\begin{aligned} V(\varphi) &= \mu(\varphi)\, \delta T(xyz) \\ &= \mu(\varphi) \left\{ T_e \left[C(xyz) \right] - T(xyz) - \left[\gamma(xyz)/\Delta S \right] K(xyz) \right\} \end{aligned} \tag{4.18}$$

where

$V(\varphi)$ = growth rate at any point of the interface whose surface-normal makes an angle with a primary crystallographic direction

μ = atomic kinetic coefficient which may also be a function of the supercooling at the interface

δT = supercooling at interface

$T_e \left[C(xyz) \right]$ = equilibrium freezing temperature for the liquid of concentration C

K = curvature at the point (xyz) on the surface
γ = the solid-liquid interfacial energy
ΔS = entropy of fusion per unit volume

Also, the normal thermal and solute boundary conditions everywhere on the surface and an optimization condition must also be satisfied. The optimization conditions states that the surface, S, should adopt that morphology, S_{opt}, which allows its extremities to penetrate a maximum distance into the nutrient phase in unit time, or

$$\left(\frac{d\,V_{ext}}{d\,S}\right)_{S_{opt}} \longrightarrow 0$$

In other words, the freezing velocity of the crystal extremities decreases as the interface shape changes from the optimum shape.

Tiller (Reference 54) goes on to consider four important examples of interface morphology (layer, cell, dendrite, and eutectics) observed in growth from melt and gives prediction criteria for the first three cases. This approach would allow, in principle, the complete calculation of all the temperatures involved.

The preceding discussion on morphology has been restricted and is by no means exhaustive. It was introduced to show the factors which determine the macroscopic morphology and the general approach presented in the literature to its accurate prediction under a given set of circumstances.

Because the macroscopic morphology is so strongly dependent on the atomic kinetics, a simple approach to the atomic kinetics will be given. This will be followed by a review of Jackson's theory of the role of atomic kinetics in determining interface morphology.

A simple, yet informative way of looking at atomic kinetics of phase change is that presented by Jackson and Chalmers (Reference 72). In their presentation, the net rate of a freezing process is given by the difference between the rate of freezing and the rate of melting; i.e.,

$$\overline{R} = R_F - R_M \tag{4.19}$$

The dependence of R_F and R_M on temperature is shown in Figure 4-8 below.

In terms of the geometry and crystallography of the interface, the above rates can be written

$$\overline{R} = N_L A_F G_F \nu_L \exp(-Q_F/RT) - N_S A_M G_M \nu_S \exp(-Q_M/RT) \tag{4.20}$$

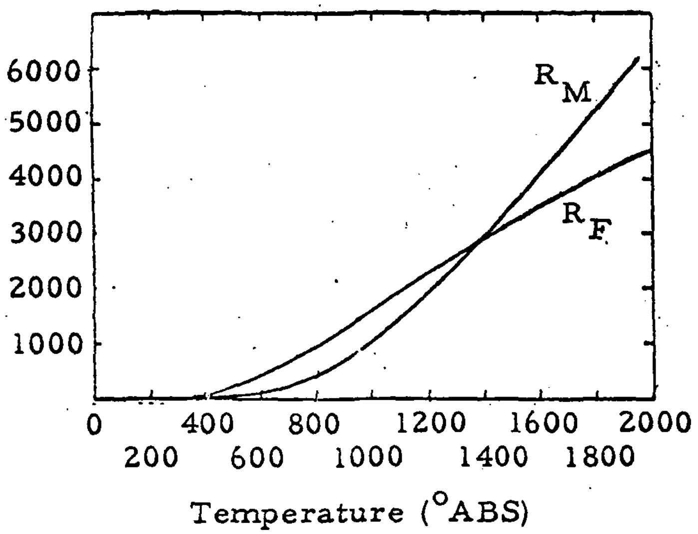


Figure 4-8 - Rates of Melting and Freezing for Copper

where

N_L, N_S = number of atoms per unit area of liquid and solid phases at the interface, respectively

A_F, A_M = accommodation coefficients for freezing and melting, respectively

G_F, G_M = geometric factors

ν_S, ν_L = frequency of atomic vibrations in solid and liquid phases, respectively

Q_F, Q_M = activation energies for freezing and melting, respectively

Excellent discussions of the significance of the above factors are given in References 65 and 46. The significance of the accommodation coefficients, however, deserves further consideration. The accommodation coefficient is defined as the probability that an atom is accommodated in the other phase. The coefficient A_F should be the same for all solid-liquid interfaces having the same arrangement of atoms at the surface and should be lowest for more closely packed planes (Reference 53, p. 521). Thus, different faces with different accommodation coefficients will have different equilibrium temperatures and different melting and freezing rates. This is illustrated in Figure 4-9.

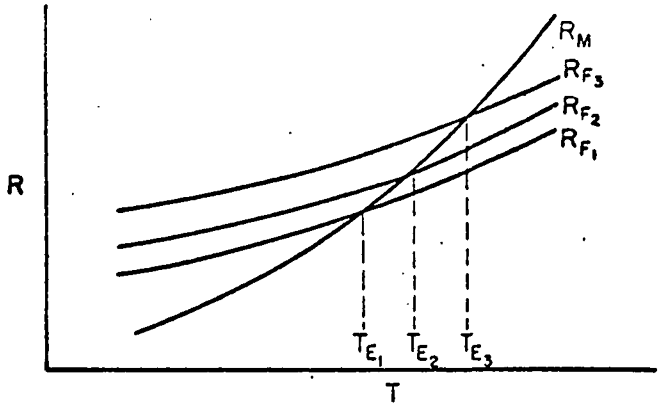


Figure 4-9 - Freezing and Melting Rates for Different Faces of a Face-Centered Cubic Crystal (R_{F_1} and T_{E_1} refer to the (111) face, R_{F_2} and T_{E_2} to the (100) face, and R_{F_3} and T_{E_3} to the (110) face.)

A crystal in equilibrium with its melt can have only one crystal face exposed, the one with the lowest accommodation coefficient. If the crystal is growing into the melt, however, the shape of the interface adjusts itself in various ways according to the temperature gradient which exists in the liquid near the interface, as discussed previously. The result is that in some cases certain faces grow faster than others, leading to a variety of interface morphologies and to phenomena such as orientated growth.

When experimental data are available on the velocity of crystal growth under kinetic controlled conditions, a mechanism by which atoms attach themselves to an interface can be inferred. The four most common mechanisms given (Reference 73) are:

1. At random sites on the surface,
2. At a step created by a screw location,
3. At a step created by two-dimensional nucleation, or
4. At a step created by a stocking fault or twin lamellae.

The growth velocity as a function of temperature for the first three mechanisms can be expressed as:

a. $V_1 = \mu_1 \delta T$

b. $V_2 = \mu_2 \delta T^2$

c. $V_3 = \mu_3 \exp[-(\mu_4 / \delta T)]$

where δT is the interface undercooling ($\delta T = T_e - T_i$). For small undercoolings the μ's can be taken as constant.

As Jackson (Reference 74, p. 9) points out, there is a striking paucity of meaningful kinetic data, so that other means of inferring a growth mechanism is desirable. Two other approaches exist, that of Cahn and that of Jackson. Jackson's approach, which is a statistical-mechanical in nature, is the one, it is felt, which gives most simply information about growth mechanisms. Also, on the basis of Jackson's critique (Reference 74), the applicability of Cahn's theory to first order phase transitions is doubtful. Jackson's theory permits general qualitative prediction of atomic growth mechanism and thus qualitative statements about macroscopic crystal habit, but quantitative results at present are not possible. Jackson's theory will be briefly outlined in the following paragraphs.

When additional molecules are added randomly to an initially plane surface at its equilibrium temperature T_e, the change in free energy is given by

$$\frac{\Delta F}{N k T_e} = \alpha x(1 - x) + x \ln x + (1 - x) \ln(1 - x)$$

where

$$\alpha = \frac{L}{R T_e} \xi \qquad (4.21)$$

The terms in the above expressions are identified as:

x = fraction of the N possible sites on an initially plane face

k = Boltzman constant

L = latent heat of transformation

R = gas constant

ξ = fraction of the total binding energy which binds a molecule in a layer parallel to the plane face to other molecules in the layer. The factor ξ is always less than unity and is largest for the most closely packed planes. For these it is invariably greater than or equal to 0.5.

A plot of $\Delta F/N k T_e$ vs x for different values of α is shown in Figure 4-10 on the following page.

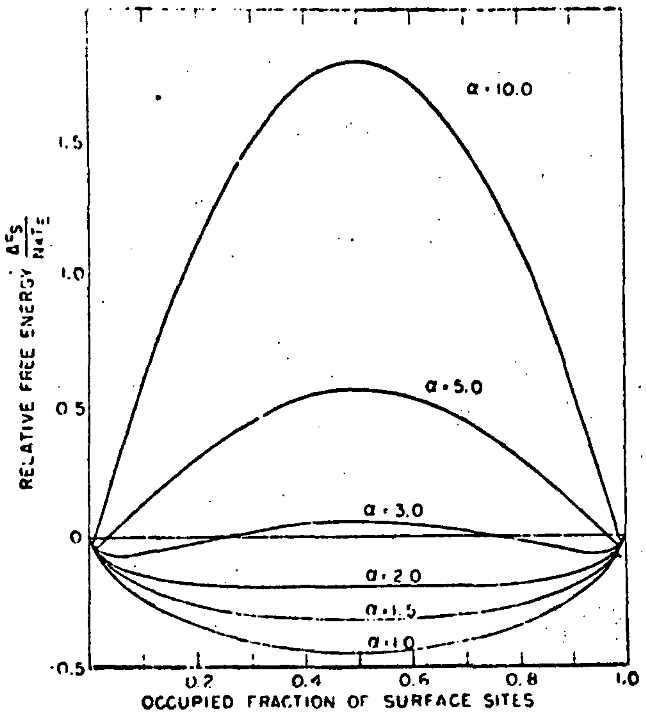


Figure 4-10 - Free Energy of an Interface vs Occupied Fraction of Surface Sites (after Jackson)

For $\alpha < 2$, the lowest free energy configuration corresponds to half the available sites filled and thus may be taken as a rough interface on an atomic or microscopic scale. For $\alpha > 2$, few molecules are missing from the completed layer, and thus this case may be taken as a smooth interface.

The effect of undercooling is to change the curves so that faces which are smooth at equilibrium may become rough at some large undercooling. For most materials, however, the effect of undercooling is to shift the maxima slightly.

For materials with $L_f/R\,T_e < 2$, even the most closely packed planes should be rough, and the initiation of new layers relatively easy. On an atomic scale, the interface will be rough. For $L_f/R\,T_e > 4$, the most closely packed faces should be smooth, and the initiation of new layers difficult. Less closely packed faces are expected to be rough.

On the basis of the preceding statements, it is deduced that for those materials of $L_f/R\,T_e < 2$ growth rate anisotropy should be small, while for materials of $L_f/R\,T_e > 4$ sizable growth rate anisotropy is anticipated.

4.6.3 Generalizations Relating Interface Morphology to Growth Conditions and Material Nature

The following generalizations found in the literature should prove useful in predicting and interpreting PCM solidification behavior.

1. A rounded crystal is evidence of heat controlled solidification (Reference 75, p. 1428).
2. In pure metal melts, dendritic growth is evidence for a negative temperature gradient in the melt; i.e., the supercooling increases with distance from the interface. Dendritic growth in pure metals produces preferred orientation. Terraced or plane interfaces occur in a positive temperature gradient; i.e., temperature increases in the melt with distance from the interface (Reference 76).
3. Cellular interfaces in metal alloys result from minor amounts of superconstitutional supercooling. As the supercooling increases, dendrites form (Reference 76).
4. In metals slow freezing tends to yield polyhedral crystals; fast freezing rods, filaments, and dendrites. Directed heat flow leads to columnar crystals with the crystallographic direction of maximum growth rate parallel to the direction of heat flow (Reference 77). Or, the preferred orientation is the one that allows heat to be conducted away most readily (Reference 43).
5. Low entropy of fusion materials will show plane or dendritic morphologies under moderate or fast cooling conditions. High entropy of fusion materials will show faceted growth over a wide range of cooling conditions. Very high entropy of fusion compounds like tristearin show spherulite morphology (Reference 72). With the high entropy of fusion materials, where the growth rates tend to be highly anisotropic, the interface temperature can vary considerably at different parts of the interface, all of which are advancing at the same rate.

In reviewing the literature on the relationship of morphology to material nature and growth conditions, it became apparent that much of the confusion could most likely be cleared up if more consideration is given to whether a particular crystallization is "heat controlled" or "kinetic controlled". For example, it is not clear from the discussions on the mechanisms of orientated growth whether anistropic growth exhibited in many crystallizations is caused by different equilibrium freezing points of the different crystal faces or, assuming that they all have the same equilibrium freezing point, different growth velocities, or both these causes. A consideration of "kinetic control" or "heat control" should clarify the matter.

Finally, it must be mentioned that the interface morphology observed in the last adhering layers of liquid is complicated by surface tension effects and should not be used as indicative of bulk solid-liquid growth without prior consideration.

PENETRATING RADIATION EFFECTS IN SOLID-LIQUID PHASE CHANGE

5.1 GENERAL CONSIDERATIONS

The effect of penetrating radiation on matter depends on a number of factors, such as the energy and type of radiation, exposure time, radiation intensity, and the nature of the material irradiated. Particle radiation produces damage mainly by (Reference 78): (1) production of displaced and excited electrons, i.e., ionization; (2) displacement of atoms by direct collision; and (3) production of fission and thermal spikes. Ionization effects are not significant in metals, and fission and thermal spikes are important in materials of high atomic number irradiated with massive particles. In addition to particle radiation, electromagnetic radiation from solar sources or from primary particle-matter interactions (bremsstrahlung) will be encountered in space. Photons of energies above 10^5 ev (wavelengths below 10^{-1} Å) can cause atomic displacements. Those of energies above 12 to 25 ev (1000 to 500 Å) can cause ionization, while photons of larger wavelengths can cause electronic excitation (Reference 79).

Because these interactions are so complex, the quantitative basis for studying the effects of radiation on matter is usually given in dose terms. The dose unit is given by the RAD, defined to be the amount of any kind of radiation which deposits 100 ergs per gram. An approximate idea of the dose levels causing damage can be gained from Table 1.

Depending on the intensity, energy and kind of radiation and also on the material irradiated, the RAD dose will be different in different depths of material. The range of penetration of radiation is given in terms of grams per square centimeter through which the radiation penetrates. A summary

Table 1

RADIATION DAMAGE THRESHOLDS FOR CERTAIN CLASSES OF MATERIALS
(Reference 80, p. 137)

Electronic components	10^1-10^3 rad
Polymeric materials	10^7-10^9 rad
Lubricants, hydraulic fluids	10^5-10^7 rad
Ceramic, glasses	10^6-10^8 rad
Structural metals, alloys	10^9-10^{11} rad

of the dose rates for various space radiations in different depths of material is given in Reference 79. From the tables in this reference, it can be concluded that, since PCM will be surrounded by a container, low energy particles and ultraviolet radiation will not be of significance.

The flux producing a certain dose rate depends on the energy and type of radiation and the material considered. Figure 5-1 shows the flux-to-RAD conversion factors for different types of radiation. Apparently, the material to which these conversion factors apply is tissue.

From Figure 5-1, it is apparent that alpha particles are the most destructive for a given flux, if we consider the RAD dose to be an indication of damage. An excellent summary of particle fluxes and energies in space environments is given in Reference 81. The dose rates in various space environments and the doses producing appreciable change in engineering properties of various materials are summarized in Reference 79.

The preceding mentioned reviews, along with less comprehensive ones (References 81 through 85) are concerned mainly with radiation effects on engineering properties of matter and do not discuss in any detail the kind of

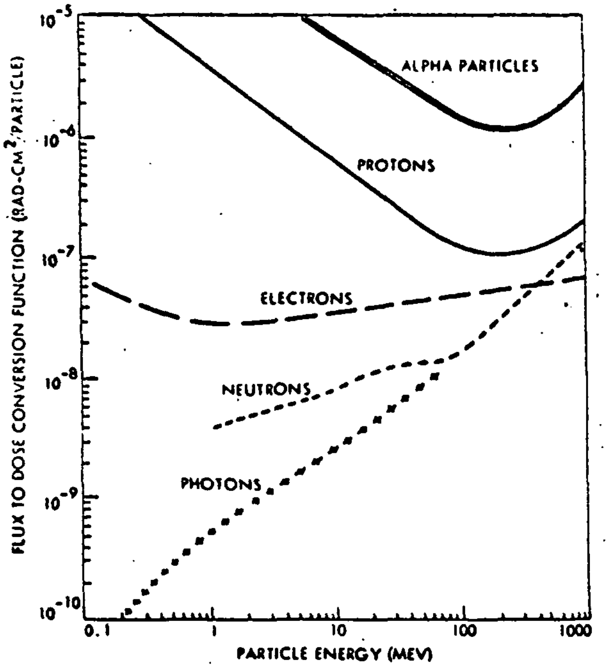


Figure 5-1 - Flux-RAD Dose Conversion Factors (Reference 80, p. 114)

damage done; i.e., whether the effect is permanent or temporary relative to the type of mission and under what conditions certain of these effects can be annealed out of the system. Therefore, it will be convenient, for consideration of radiation effects on PCM performance, to classify radiation effects as transient, temporary or permanent (Reference 81, p. 31). For temporary and permanent effects, the material properties are not the same before and after exposure to a radiation field. Temporary effects, however, persist only a matter of hours or minutes; i.e., the material spontaneously relaxes back to original state in a short time. Permanent damage effects persist for much longer periods of time, if not forever. Transient effects are manifested only while the material is in the radiation field and are not observable when the material is removed from the field. Transient effects are predominately electrical in nature.

We will further break down the permanent classification into annealable permanent and forever permanent. By annealable permanent, we mean those damages which, though they persist for long periods of time at low temperatures, are annealable when the temperature is raised. Forever permanent means that chemical bonds have been broken or fission has occurred. Forever permanent effects cannot be annealed by temperature rise.

Many of the damage effects which affect engineering properties are annealable permanent. In PCM thermal devices, the solid-liquid phase change will provide an annealing mechanism usually not considered. Therefore, temporary and annealable permanent effects, such as increased dislocation density or trapped ionic charges in ionic materials, should not be of much significance in PCM operation, because they will be annealed out of the system after a few cycles of melting and freezing before any appreciable buildup of them can occur. Thus, one of the great advantages of PCM thermal control devices will be their short-time, self-annealing ability to temporary and annealable permanent damage. This would mean greater reliability over longer periods of time than offered by some other thermal control devices which have no built-in annealing mechanism.

Forever permanent effects caused by chemical bond breakage are most likely with organic materials; fission can be neglected, for high atomic number materials are not contemplated for PCM. Forever permanent damage effects on phase change can be understood in terms of impurities. (See Section 4.3.)

The most probable transient effect of radiation is that of nucleation of crystals in supercooled liquid or bubbles in superheated liquid. It is well known that ionizing radiation can cause the nucleation of small bubbles in superheated liquid or of small liquid drops in supercooled vapor. These phenomena are basic to bubble chamber or Wilson cloud chamber ionization detectors. Thus, supercooled liquids would also be expected to be nucleated by ionizing radiation. In fact, the nucleation of crystal nuclei has been suggested as a basis for a radiation detector (Reference 86).

Because PCM are required to supercool only to a small extent before crystallization proceeds, it is unlikely that the whole mass of PCM will be supercooled at any given time, but local regions of supercooling may exist. Supercooled regions of any significant extent would exist only near growing crystal surfaces whose growth is controlled by the phase-change kinetics (see Section 4.2), so that nucleation of new crystals in these regions would be unimportant. Much the same kind of considerations apply to the nucleation of gas bubbles. The subject of bubble formation is covered in Section 4.4. Again, it is expected that ionizing radiation will cause only tiny, momentary local disturbances.

Only one report has been found (Reference 87) which is specifically concerned with the transient effects of radiation on the crystallization process itself. Its pertinence to the present study is doubtful because the γ-radiation dosage rates in the reported study (2400 rads/min or 240,000 ergs/gram-min) are far above any expected to be encountered in space. (See Reference 79.) However, because this was the only report found that dealt specifically with radiation effects on solid-liquid phase change, its results are of interest. Under irradiation and with no added $PbC\ell_2$, the crystallization of $KC\ell$ from aqueous solution was found to yield crystals with less dislocations than the same crystallization not irradiated. At certain levels of lead concentration, irradiation decreased the growth rate at the (100) faces. This is attributed to enhancement of the diffusion of lead in the crystal by γ-rays.

It may also be mentioned that many solids undergo solid-solid transitions before the melting point is reached. Radiation can affect these transitions in various ways, but information on the subject is scarce so that general statements are out of order at present. However, these effects can be classed as annealable permanent effects as far as PCM behavior is concerned.

5.2 CONCLUSIONS REGARDING RADIATION FIELDS

For time periods of about a year, and in the space vicinity of earth, only insignificant radiations effects on PCM behavior are generally expected, except perhaps in the case of organic materials where a small amount of chemical impurity content buildup may be expected which may present real problems. More precise definition of amount and kind of container material, PCM, and mission are required before more specific statements can be made.

Section 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The conclusions arrived at in regard to the influence of space boundary conditions on PCM performance are summarized briefly as:

- Gravity in the zero to 1-g range has no direct, significant influence on any of the microscopic processes involved in phase change.
- The influence of gravity will have an effect on phase change indirectly through convection currents.
- Although the general nature of convective currents in zero-g conditions can be predicted, complex coupling effects between phase-change kinetics and various possible modes of convective motion cannot be predicted accurately without actual flight test data.
- The magnitudes of magnetic and electric fields likely to be encountered in earth space orbit are not expected to alter phase-change behavior significantly from that observed on earth surface.
- Radiation fields encountered in earth orbit are not expected to have much effect, except perhaps in the case of organic PCM where long-time exposures will result in impurity build-up.

From the consideration of the rate processes involved in solid-liquid phase change, it became evident that PCM candidate materials, chosen on the basis of high heat of fusion and low melting temperature, are likely to have phase-change kinetics which are detrimental to efficient PCM operation. However, a thorough understanding of the nature of the rate processes involved can expedite isolation of the non-equilibrium effect causing the problem and indicate design and material alteration approaches to a solution.

The problems, caused by non-equilibrium effects, judged most likely to cause unpredictable PCM performance are:

- Dependence of melting and freezing rates on the freezing conditions under which the solid was formed or is being formed.
- Destruction of nucleating catalysts by repeated thermal cycling.
- Component concentration non-equilibrium in multicomponent PCM and its dependence on freezing and melting rates.

6.2 RECOMMENDATIONS

6.2.1 PCM Package Design

On the basis of the considerations discussed in the main body of the report, a logical sequence of experimental steps evolves for development of an efficient PCM design for space applications and testing. These steps are briefly summarized as follows:

(a) Preliminary materials selection and screening. This step, which is already in progress as part of the present study and will be documented in the final report, involves a literature search for thermodynamic parameters of fusion and heat transfer characteristics. Where lacking in the literature, necessary data is experimentally determined. Freezing response of compounds is checked by a simple procedure. Nucleation catalysts are sought.

(b) Further materials evaluation by quantitative studies of freezing and melting rates for materials chosen in step (a). The effect of operational variables such as thermal cycling, different heating and cooling loads, cell dimensions, etc., are checked.

(c) Effect of gravity is checked by tests with test cell orientated in different directions with respect to gravity field. Freezing and melting rates so obtained are checked with analytical heat-conduction or other theoretical convection solutions.

(d) Prototype package testing in space simulation facility.

(e) Prototype package testing in actual space flight.

The recommended experimental program is based on present information. It can, of course, be modified as work proceeds and additional information becomes available. A material may be found in steps (a) and (b), for example, that appears so ideal that immediate design of prototype metal containers is called for. Or, the response to radiation of the final PCM material chosen may be well known so that an actual radiation test may be unnecessary.

6.2.2 General Basic Research Needed

The present review and evaluation of melting — freezing processes is based on information found in papers dealing with such diverse and specialized areas of research as metallurgy, growing single crystals for electronic applications, water desalination, cloud seeding, ceramics, glass technology, theoretical kinetics, engineering melting-freezing heat transfer, etc. A number of areas of needed basic research suggested themselves as a result which would be of benefit to all fields concerned with melting and freezing. These are:

- Development of an experimental DTA (Differential Thermal Analysis) apparatus in which linear cooling rates could be as easily attained as linear heating rates presently are.
- Further development of mathematical techniques for calculating quantitative kinetic data from DTA data.

If DTA experimental and mathematical techniques were presently available which could perform the preceding functions, the materials search and development effort for PCM devices would be greatly simplified and reduced. Undoubtedly, such benefits will accrue to all fields of technology based on solid-liquid phase change with further development of DTA techniques.

Other areas of needed basic research are:

- Further development of analytical models of freezing with heat removal through the solid which would allow calculation of freezing velocities, or alternately from observed freezing velocities allow calculation of interface temperatures.
- Investigation of the possibility that gradients of solid-liquid interfacial tension can drive fluid flow.

- Further investigation of the role of volume change during melting and freezing in causing fluid flow and nucleation phenomena.

- Further research on correlating crystal morphology with thermal growth environment. In particular, more consideration should be given to whether the growth occurs under "heat controlled" conditions or "kinetic controlled" conditions.

- Further research on nucleation catalysis. In particular, a systematic experimental program is needed which would evaluate, under strictly controlled conditions, nucleation effectiveness of catalysts for a large variety of materials.

Section 7

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