# FRAZIL NUCLEATION MECHANISMS

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Abstract. Previously the author had suggested that frazil nucleation occurs by a mechanism analogous to spinodal decomposition, aided by turbulence. After further study the following points are made: (1) No critical point exists between solid and liquid; this rules out true spinodal decomposition. (2) Pure water can be supercooled to $-40°C$; at $-40°C$ the theoretical energy barrier to nucleation is about $10^{-19}$ J. Frazil forms after supercooling less than 0.1 deg; at this temperature the theoretical energy barrier is about $10^{-14}$ J. (3) Theory shows that turbulence increases the energy barrier. (4) Turbulence may aid dissipation of heat of solidification, but not sufficiently to account for observed frazil formation at small supercoolings. (5) The author's evidence that frazil can begin to form at supercoolings as small as 0.02 deg suggests that no nucleus except ice itself can account for "heterogeneous" nucleation of frazil.

Résumé. *Mécanismes de nucléation du frazil.* Nous avions auparavant, suggéré que la nucléation du frazil se produisait par un mécanisme analogue à la décomposition spinodale, aidée par la turbulence. Après une étude plus poussée les points suivants sont relevés. (1) Il n'existe pas de point critique entre le solide et le liquide; ceci rejette l'idée d'une vraie décomposition spinodale. (2) L'eau pure peut être surfondue jusqu'à $-40°C$; à $-40°C$ la barrière énergétique théorique est d'environ $10^{-19}$ J. Le frazil se forme après une surfusion de moins de 0,1 deg; à cette température la barrière énergétique théorique est autour de $10^{-14}$ J. (3) La théorie montre que la turbulence augmente la barrière énergétique. (4) La turbulence peut aider la dissipation de la chaleur de solidification, mais pas suffisamment pour tenir compte des formations de frazil observées pour des faibles surfusions. (5) L'observation suivant laquelle le frazil peut commencer à se former à des surfusions aussi faibles que 0,02 deg suggère qu'aucun noyau, sauf la glace elle-même, ne peut être à l'origine de la nucléation "hétérogène" du frazil.

Zusammenfassung. *Mechanismen für die Keimbildung freischwebender Eiskristalle.* Der Verfasser hat früher vorgeschlagen, dass die Keimbildung freischwebender Eiskristalle durch einen der spinodalen Entmischung ähnlichen Mechanismus erfolgt, der durch Turbulenz unterstützt wird. Nach weiteren Untersuchungen werden folgende Feststellungen getroffen: (1) Es gibt keinen kritischen Punkt zwischen fester und flüssiger Phase; dies schliesst echte spinodale Entmischung aus. (2) Reines Wasser kann bis $-40°C$ unterkühlt werden; bei $-40°C$ beträgt die theoretische Energieschwelle für die Keimbildung rund $10^{-19}$ J. Freischwebendes Eis entsteht nach Unterkühlung von weniger als 0,1 deg; bei dieser Temperatur ist die theoretische Energieschwelle rund $10^{-14}$ J. (3) Die Theorie zeigt, dass Turbulenz die Energieschwelle erhöht. (4) Turbulenz mag die Verteilung der Gefrierwärme fördern, aber nicht in ausreichendem Masse, um die beobachtete Bildung freischwebender Eiskristalle bei geringer Unterkühlung zu erklären. (5) Die Beweise des Verfassers für den Beginn der Bildung freischwebender Eiskristalle bei Unterkühlungen von nur 0,02 deg legt nahe, dass kein Keim, ausser Eis selbst, für die "heterogene" Keimbildung der freischwebenden Eiskristalle verantwortlich ist.

Of the several forms of ice found in Nature, frazil is interesting because of several unusual characteristics of its formation and because it leads to an annual world expenditure of millions of dollars (or pounds). Frazil formation has been reviewed by Michel (1971). One question which has received much attention is how frazil begins to form in water supercooled by less than one degree. Speculating that the process might differ from the usual nucleation mechanisms, Hanley considered the theoretical approaches used to explain spinodal decomposition, and suggested (Hanley, 1975) that such a study might also clarify the role of water turbulence in frazil production. This paper describes attempts made to attack the problem in five ways, by considering (1) the metastable states involved in the process and the possibility that some kind of critical point is associated with these states, (2) the energy barrier traversed during frazil formation, (3) the effect of turbulence on the energy barrier, (4) the effect of turbulence on the temperature gradient outside the nucleus, and (5) the possibility that heterogeneous nucleation may account for frazil initiation. Although none of these approaches has succeeded in identifying a new mechanism, it is hoped that further insight will be gained by bringing them together and applying them specifically to frazil formation, especially when the pertinent mechanisms become better understood.

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Frazil was defined by Kivisild ([1971]) as: "Fine spicules, plates, or discoids of ice suspended in water. In rivers and lakes it is formed in supercooled turbulent waters." In international ice terminology it is distinguished from the terms *frazil slush* and *frozen frazil slush*.

Spinodal decomposition has been discussed by Hillert (1961, unpublished) and further developed by Cahn (1961, 1968). It is a specific type of phase transformation which occurs in some binary or multicomponent systems (usually metals and glasses) when deeply quenched near a critical point. For example, an Al–Zn melt at a composition and temperature which place it near its critical point, when cooled at a suitable rate separates during solidification in such a way that one component gathers in small regions randomly distributed through a matrix of the other component. The term spinodal decomposition probably should not be extended beyond such transformations, but certain aspects of the theoretical treatment of spinodal decomposition may be useful to understand frazil formation. The most interesting of these aspects is that when the conditions for spinodal decomposition are fulfilled, the energy barrier to solidification seems to disappear. Frazil formation has been observed in water at temperatures less than 0.1 deg below the freezing point (Michel, 1963; Carstens, 1966; Hanley and Michel, 1975). Therefore this paper will discuss the energy barrier to solidification in an attempt to explain frazil formation at small supercoolings.

Hillert (1961) has approached spinodal decomposition by way of the metastable state of a substance approaching a phase change. While considering the use of metastable states as an explanation for frazil formation, two conclusions were reached.

A familiar example of metastable states involved in phase transitions is illustrated by the pressure–volume diagram for water (Fig. 1). If a sample of water vapour at 360°C is subjected to an increase of pressure at constant temperature, it moves along the isotherm from A to B.
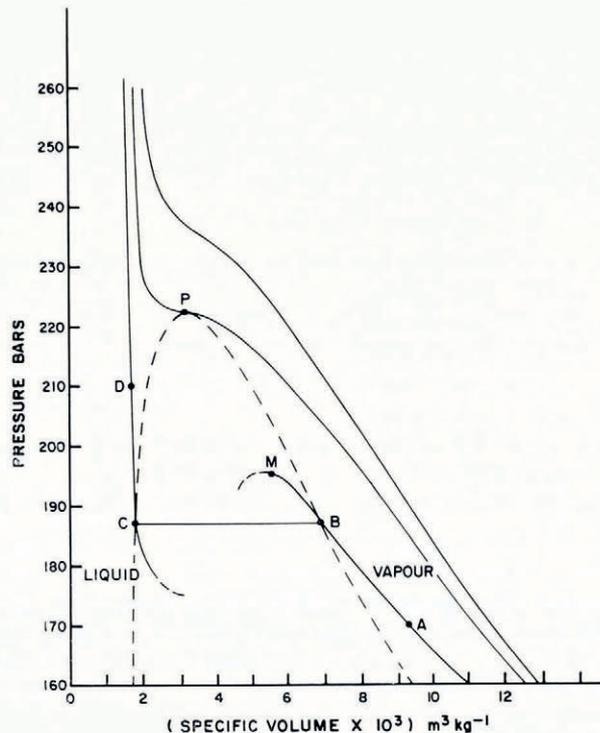


Fig. 1. *Pressure P versus specific volume v for water. Continuous lines represent isotherms; the dashed line encloses a region of metastable states.*

A further increase of pressure will move it toward point M through a succession of metastable states. Local fluctuations of pressure will eventually allow the vapour to liquefy and move to point c, from which with further increase of pressure it will traverse the path CD. The region for metastable equilibrium, enclosed by a dashed line in Figure 1, has a maximum at the critical pressure which corresponds to a unique critical point on a $P$, $V$, $T$ surface.

In a cooling process in which frazil is produced, the decrease in temperature involves an isobaric change as shown in Figure 2. Water cooled at the ambient barometric pressure passes along an isobar from A to B and, as it supercools, proceeds metastably toward M. When freezing begins, it tends to go to the state at c and then, with further cooling, toward D. Further advances to an explanation of frazil formation using fluctuations in the specific volume are hampered by the fact that no complete theoretical description has been produced for the volume–temperature relationship of water near the freezing point.

Figure 1 includes a region containing the metastable states possible during the phase transition. At its peak is a critical point. In presenting the curve shown in Figure 2, the possibility of a similar region and a critical point was considered. Bridgman (1931) discussed the possibility of a solid–liquid critical point for pure substances as raised by several investigators and concluded that, "the probability that there is a critical point between liquid and solid is so remote that it can be dismissed without further discussion".

Therefore it seems clear that spinodal decomposition does not provide an explanation for frazil formation. It is likely, however, that when we understand more completely the intermolecular mechanisms which govern the behaviour of water near 0°C, it will be fruitful to apply fluctuation theory to the isobaric transition from water to ice.

The next consideration is the height of the energy barrier. Several attempts have been made to develop an expression describing the energy barrier as a function of some kind of
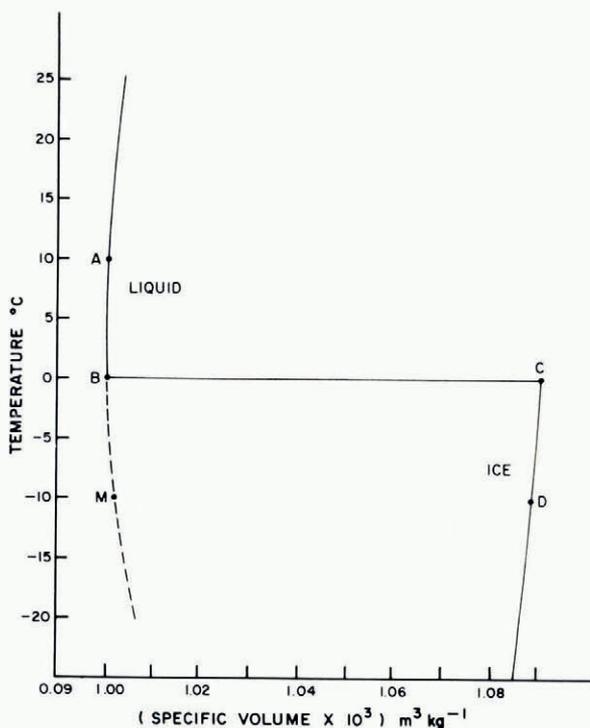


Fig. 2. *Temperature t versus specific volume v for water. The dashed line represents supercooled water.*

concentration. Némethy and Scheraga (1962) define a mole fraction which is a combination of five possible molecular structures, Jackson and others (1967) similarly use the fraction of possible sites on an interface, while Fletcher (1970) uses the number of molecules in an ice-like cluster. But attempts to express free energy as a function of any such concentration-like parameter will necessarily involve poorly known quantities until more is understood about embryo shapes and anisotropic surface energies. For the present we must work with approximate functions and average values. For example, the height $\Delta G^{\star}$ of the nucleation barrier can be expressed (Fletcher, 1970, equation 4.31) by the equation

$$\Delta G^{\star} = \frac{16\pi\sigma^3}{3(\langle \Delta S_v \rangle \Delta T)^2}, \tag{1}$$

where $\sigma$ is the surface free energy (approximately 0.022 J m$^{-2}$), $\Delta T$ is the temperature of supercooling, and $\langle \Delta S_v \rangle$ is the average entropy of fusion over the supercooling range $\Delta T$. For water,

$$\langle \Delta S_v \rangle \approx (1.13 - 0.004\Delta T) \times 10^6 \text{ J m}^{-3} \text{ deg}^{-1}. \tag{2}$$

Under optimum conditions water cannot be supercooled below about −40°C. This suggests either that the energy barrier for solidification becomes very low at −40°C or that fluctuations in the thermal energy of the water at −40°C enable it to surmount the energy barrier. Equations (1) and (2) indicate that at −40°C the height of the energy barrier is $1.2 \times 10^{-19}$ J (about 0.74 eV). But it has been observed that frazil forms in water at temperatures less than 0.1 deg below the freezing point (Michel, 1963; Carstens, 1966; Hanley and Michel, 1975). By the same equations the barrier at this supercooling is $1.4 \times 10^{-14}$ J (about 87 keV), five orders of magnitude higher than at −40°C.

Hanley (1975) suggested that turbulence could aid in surmounting the energy barrier to solidification. Upon further consideration it appears that turbulence, in fact, has the opposite effect. We must distinguish between turbulence produced by movement of water past a stationary object, in which case the boundary layer is thicker than a laminar boundary layer, and movement of an object along with a turbulent stream. Here we need only consider the second of these situations. In this case turbulence decreases the thickness of the boundary layer which separates the growing embryo from the surrounding water and hence increases in magnitude the gradients of temperature, cluster size, density, and so on. It is in the boundary layer that the clusters of water molecules become re-arranged into an orientation favourable to regular crystal growth. Thus increased turbulence might be expected to increase to some extent the supercooling required for successful frazil nucleation.

An increase in supercooling for frazil formation with an increase in turbulence was indicated in the results reported by Hanley and Michel (1975) and shown in Figure 3. The same conclusion is supported by the diffuse-boundary model for nucleation developed by Cahn and Hilliard (1958). If we apply Cahn and Hilliard's theory and their boundary conditions to a spherically symmetric nucleus, the Gibbs free energy of the nucleus can be written

$$\Delta G = 4\pi N_v \int_{r=0}^{\infty} \left[ \Delta g_v(\rho) + K \left( \frac{\partial \rho}{\partial r} \right)^2 \right] r^2 \, dr. \tag{3}$$

Here $N_v$ is the number of molecules per unit volume, $\rho$ is the density of the water at a distance $r$ from the centre of the nucleus, $\Delta g_v$ is the free energy per molecule of a solution of uniform density $\rho$, and $K$ is a constant for the condensing substance. The second term in the integrand represents the effect of the density gradient in the boundary layer. Because the square of the gradient is involved, a boundary layer made thinner by turbulence results in an increased free energy, whatever may be the sign of the gradient.
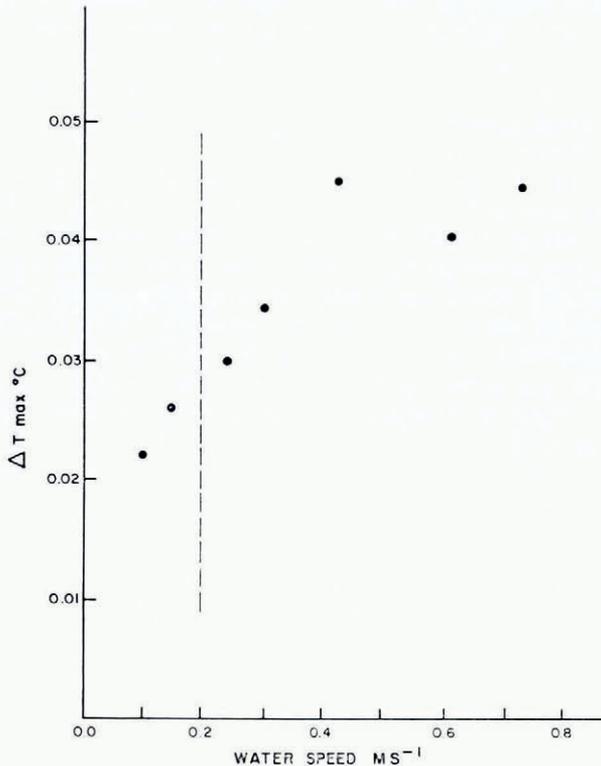
*Fig. 3. Experimental mean values for the maximum supercooling observed in a cold room tank at various water speeds. Frazil formed in all experiments at speeds of 0.24 m s⁻¹ or greater.*

But turbulence in the water, by making thinner the boundary layer surrounding the embryo, will also increase the magnitude of the temperature gradient outside the nucleus. This suggests that the heat of condensation is more readily conducted away in turbulent water, with a consequent enhancement of growth of the embryo. Lothe and Pound (1969) elaborated the effect of heat dissipation on nucleation, and concluded (p. 145) that the effect of slow heat dissipation is to retard the rate of nucleation slightly. If turbulence increases the temperature gradient and the heat dissipation by a reasonable factor, even an order of magnitude, the effect on nucleation is far from the five orders of magnitude needed to explain nucleation at $-0.1\,°C$. It should be noted also that, after the discussion referred to above, Lothe and Pound themselves (1969, p. 112), question the validity of the assumption that macroscopic thermodynamic properties such as surface tension and volume free energy may be applied in the description of small clusters.

It must be admitted, then, that the studies outlined above have revealed no mechanism which can explain homogeneous nucleation of ice in slightly supercooled water.

Heterogeneous nucleation must also be considered. However, we must remember that frazil has been observed to form after a bulk supercooling of less than 0.1 deg (Michel, 1963; Carstens, 1966; Hanley and Michel, 1975) and recent evidence suggests that it has begun to grow at about $-0.02\,°C$ (Hanley and Michel, 1977). This is considerably warmer than the nucleation threshold of $-4\,°C$ ascribed to silver iodide, the best-known inorganic ice-nucleating agent, or the $-1.3\,°C$ cited as the threshold for biogenic nucleators by Schnell and Vali (1972). These values, it should be noted, are for nucleation of ice from the vapour.

In discussing nucleation thresholds, Fletcher (1958, 1970) defines an interface parameter which is characteristic of the nucleating particle and by which he correlates the nucleation temperature and the size of the nucleating particle. Despite the deficiencies which he points out for this model, it shows clearly that nucleation at $-0.02°C$ or even at $-0.1°C$ requires almost perfect compatibility between the nucleating particle and the ice. This suggests that the nucleation is not truly heterogeneous.

If such a compatibility between the nucleating particle and the ice is necessary, one explanation for the formation of frazil is by means of tiny ice particles falling to the surface of the water from above, and drawn into the bulk of the flow by turbulence. This mechanism has been studied in considerable detail by Osterkamp and others (1974) and Osterkamp (1977). It appears plausible that in the cold room in which the study of frazil formation led to the conclusion that frazil began to form at a supercooling of 0.02 deg, tiny ice crystals may have been generated either in the air above the water tank or in the heat exchanger. Another mechanism which might explain the onset of frazil formation is surface nucleation, as proposed by Michel (1967). He is now attempting to describe this mechanism in a quantitative manner (private communication from B. Michel).

The study of frazil formation as possibly analogous to spinodal decomposition has led to the following conclusions which have been presented in this paper: (1) No critical point exists between ice and water; this rules out true spinodal decomposition. (2) Pure water can be supercooled to $-40°C$ at which temperature the theoretical energy barrier to nucleation is about $10^{-19}$ J. Frazil forms after supercooling less than 0.1 deg; at this temperature the theoretical energy barrier is about $10^{-14}$ J. (3) Theory shows that turbulence increases the energy barrier. (4) Turbulence may aid dissipation of heat solidification, but not sufficiently to account for observed frazil formation at small supercoolings. (5) The author's evidence that frazil can begin to form at supercoolings as small as 0.02 deg suggests that no nucleus except ice itself can account for "heterogeneous" nucleation of frazil.

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## DISCUSSION

W. B. KAMB: In your laboratory experiments on frazil formation in moving water, can you not control the input of ice particles from the atmosphere, and hence test Osterkamp's hypothesis?

T. O'D. HANLEY: Unfortunately, I am now far removed from the laboratory in which the experiments were done. If I had access to that laboratory, I would want to look carefully for ice crystals coming from the heat exchanger in the cold room when the room was in equilibrium at −2°C. I have not been able to make this search elsewhere, and I would be glad to hear the result if anyone else has done it.

J. HALLETT: Would it be a fair assumption to say that nucleation of a few crystals in the cold analysing air could give crystals which could then propagate in the liquid by secondary ice production, by collision of the walls or with each other in the turbulent flow?

HANLEY: Ice literature reports studies of collision breeding—for example Garabedian and Strickland-Constable (1974). I am not sure that we have reliable values for the rate at which crystals multiply by collision. I was willing to assume that breeding could occur if any crystals were present in the water, but I was concerned about how the first crystals come to be in the water.

F. PRODI: As a possible nucleation mechanism for frazil I suggest the sedimentation on the water surface of radiatively cooled aerosol particles. Radiation cooling may lower the temperature of the aerosol particle by a remarkable amount. If so, we should notice higher frazil frequencies by night, with clear sky.

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