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Crystal nucleation given rise by fracturing or by mechanical shock

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With 3 figures and 3 tables

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Introduction

It is well known that supercooling and supersaturation are broken by agitation of liquids, by irradiation with super-sonic wave or by rubbing glass wall of the vessel. It has been reported that supercooled water nucleates ice under various mechanical or electric actions. Reproducibility of these experiments, however, is not always good and the conclusion is frequently doubtful. We carried out somewhat systematic studies on nucleation of crystals given rise by fracturing of solids or by mechanical shock in various supercooled liquids and supersaturated solutions, and a theory covering these phenomena was proposed.

I. Nucleation given rise by fracturing of solid substances*I.1. Experimental results*

Self-nucleation accompanied by crystallization takes place frequently in the liquids shown below (A ~ D) when solids (table 1) immersed in them are fractured or injured mechanically, if the degree of supercooling (ΔT) or supersaturation (S) is large enough.

Mechanical methods employed were as follows:

i) to rub strongly, grind, injure or cut solids with harder ones such as diamond, carborundum, quartz, corundum, knife, glass and porcelain. Crystallization took place much more easily than by rubbing glass wall with a glass rod (table 2), and the growth velocity of ionic crystals nucleated in this way was larger than that of self-nucleated crystals.

ii) to deform plastically, or tear soft plastics or metals, e. g. sudden nucleation occurred in a supersaturated solution of Na_2HPO_4 when copper wire immersed in it was twisted to the extent of considerable plastic deformation.

The chance of nucleation increases with increasing ΔT as shown in table 2.

Table 1. Solids which give rise to nucleation in liquids (A ~ D) when fractured mechanically

Solids	Examples
ionic solid	calcite, fluorite, (glass)
valence crystal	graphite, red phosphorus, quartz
metal	Cu, Al, Fe, Sn, Pb, Pt
molecular crystal	soft crystals of substances with low molecular weight (paraffin, stearic acid etc.) do not nucleate. Sulfur frequently nucleates.
high polymer	rubber, polyethylene, paper, wool, starch
Liquids	
A) supersaturated aqueous solutions of ionic compounds	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$
B) that of polar organic compounds	sucrose
C) supercooled polar liquids	water, acetic acid, nitrobenzene (salol, thymol and mandelic ester do not nucleate)
D) supercooled nonpolar liquids	benzene, carbon tetrabromide

Table 2. Nucleation of supercooled acetic acid (mp = 17°) by fracturing of solids (++ easily nucleate, + rarely nucleate, - do not)

Temp. °C	rubbing		fracturing of		
	glass with glass	glass with corundum	paper	poly- ethylene	rubber
13.8	-	++	-	++	-
12.0	-	++	-	++	+
8.2	+	++	++	++	++
5.2	++	++	++	++	++

I.2. Mechanism of the nucleation

The phenomenon can not be attributed to the effect of shock, since it takes place even when soft high polymer is elongated quietly. It does not occur when solids are immersed in

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liquids after being injured in air. Consequently, broken pieces, roughened surface and dislocations formed by the mechanical action are not concerned in it. This indicates the necessity of the existence of some characteristic state, which is generated at the moment of fracturing and is deactivated in a very short time. Soft molecular crystals such as paraffin can not nucleate any other crystals when injured. In these cases, mechanical action only displaces molecules, but neither ruptures nor changes them. Nucleation presumably needs a more intense change, i. e. rupture of chemical bond and the like, as is obvious from the positive cases observed. In the cases of harder molecular crystals such as sulfur, nucleation takes place frequently, since mechanical rupture of molecules may be possible.

Molecules of high polymers, in contrast with paraffin etc., are ruptured on mechanical fracturing giving rise to rapid nucleation in the liquids in contact with them. No nucleation, however, is observed on fracturing soft gel of polyethylene well swelled with solvents, because each molecule is mobile in it and is not ruptured mechanically.

Nucleation of this type, in general, is entirely independent of the chemical and bond nature of both the solids and liquids, and of the property of forces acting in liquids. It seems also to be independent of the type of crystal growth, two-dimensional nucleation (water, benzene and acetic acid when ΔT is large) or screw dislocation mechanism ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$).

Free radicals (I.2.1.) and separated electric charges which give rise to a strong electric field (I.2.2.) may be presumed as the nucleating center, because these are generated at the moment of rupture of chemical bond and have short life and high energy. The following studies, however, deny the presumption.

I.2.1. Effect of free radicals: free radicals prepared chemically were added to the supersaturated solution of Na_2HPO_4 , but no nucleation took place in the following cases: Cl atom from photodecomposing AgCl, OH and HO_2 radicals from H_2O_2 decomposing on a platinum plate, and SO_4^- radical from persulfate.

Irradiation with α -rays from uranyl salt and with β -rays from ^{90}Sr salt dissolved in the liquid was also ineffective, in contrast to the formation of bubbles in superheated liquids by irradiation in a bubble chamber. The swarm of free radicals or of ions gener-

ated by irradiation thus can not give rise to nucleation of crystals.

I.2.2. Inadequacy of electrostatical explanation: the effect of electric field on nucleation of salol from the supercooled liquid (1) and of sulfur from the supersaturated CS_2 solution (2) and the like were reported. The reproducibility, however, is not high and we could not find any effect even when the field is strong. The explanation of mechanical nucleation in terms of molecular orientation under strong electric field generated momentarily does not seem to be reasonable, because non-polar benzene easily crystallizes, whereas polar salol and thymol do not. The following study on carbon tetrabromide, of which molecule is spherical and electrically isotropic, hence orientation in electric field is impossible, may give the most definite conclusion. A small quantity of the liquid was admitted in a thin glass tube of 2 mm diameter, since it can be only slightly supercooled. The temperature of self-nucleation (T_1) and that of induced nucleation (T_2) (when a piece of nickel wire immersed in the liquid was rubbed with powder of carborundum put in the tube by moving the piece magnetically) were measured in a bath by cooling very slowly (table 3).

Table 3. The effect of injuring Ni on the nucleation temperature of CBr_4 (mp = 91.3°), $T_2 - T_1$ °C

Volume of liquid (cc)	spontaneous nucleation (T_1)	induced nucleation (T_2)	effect of injuring ($T_2 - T_1$)
0.053	89.2	89.6	0.4
0.044	89.4	90.4 ~ 89.6	1.0 ~ 2.0
0.032	89.5	89.9	0.4
0.0083	89.1	89.6	0.5

The effect of injuring is always positive, though not large. Hence, electrical orientation theory must be abandoned.

I.2.3. Nucleation accompanying electrolysis: Ubbelohde (3) reported that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystallizes at a copper anode during electrolysis of the solution and it ceases when the current density is decreased. It does not occur at platinum and carbon anodes. The problem was re-examined as follows: two wire electrodes were connected to an induction coil or a neon-transformer and were introduced into the supersaturated solution of Na_2HPO_4 . Rapid nucleation took place as soon as electrolysis began at the copper anode, then, it ceased on repeated electrolysis even when new solution was used. Nucleation, however, was observed again if

another part of the anode was dipped in the solution. No nucleation took place if the anode was washed with acid, but the activity was recovered when copper turned reddish owing to oxidation in air. These facts may be explained as follows: oxide film at the copper anode is torn by violent evolution of oxygen during electrolysis under high current density, giving rise to nucleation as discussed in I, and clean copper surface as well as a platinum or carbon electrode can nucleate no more.

Accordingly, it does not seem possible to explain mechanical nucleation phenomena under simple electrostatic theory. An alternative theory will be given in III. 3.

II. Nucleation induced by mechanical shock

II.1. In supercooled liquids

Mixture of KClO_3 and red phosphorus was weighed and put in an iron test tube fixed in supercooled water (fig. 1). The powder was brought into explosion by hitting with an iron rod in the tube. If the shock of explosion is not strong enough to give rise to ice nucleation, the quantity of the powder was increased until nucleation took place.

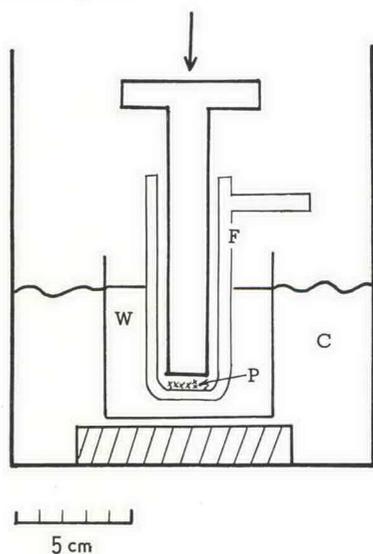


Fig. 1. An apparatus for giving mechanical shock by explosion to supercooled water to nucleate ice. C = cooling mixture, F = iron tube, fixed and immersed in W , W = supercooled water with a stirrer and a thermometer, P = powder (KClO_3 + red P)

The necessary strength of shock for nucleation decreases regularly with increasing supercooling (fig. 2). Salol and thymol did not crystallize in this way as well as in the case of fracturing of solids. The remarkable difference in the nucleation behaviour between water and these substances is discussed in III.

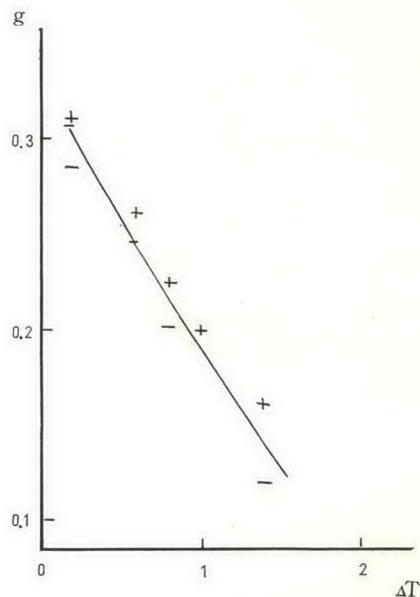


Fig. 2. The amount (g) of powder necessary to nucleate ice by the shock of explosion from supercooled water. ΔT = the degree of supercooling, + = nucleate, - = do not nucleate

II.2. Nucleation induced by shock in supersaturated solutions

Drops of supersaturated solutions of Na_2HPO_4 , Na_2SO_4 etc. were put in many pits at the surface of a thick iron plate covered with paraffin, and the effect of shock of explosion of powder in an iron cylinder welded to the plate vertically was studied statistically. The rate of nucleation was found to be approximately proportional to the amount of the powder employed (fig. 3).

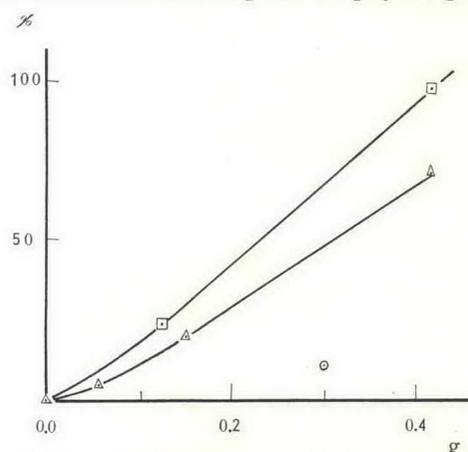


Fig. 3. The relation between nucleation rate (%) of supersaturated solutions by the shock of explosion and the amount (g) of explosive employed. \square $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ $S = 1.42$, \triangle $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ $S = 3.61$, \circ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ $S = 1.40$ (S = the degree of supersaturation)

II.3. Nucleation by spraying: nucleation of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was observed frequently when the supersaturated aqueous solution

was sprayed strongly in wet air avoiding evaporation. It can not be attributed to the effect of scratching of the wall of the sprayer with dust particles in the liquid, since it did not occur at the nozzle. It is considered to take place when the liquid is fractured.

III. Mechanism of nucleation given rise by fracturing or by shock

III.1. The state of substances when fractured or shocked

A comparatively intense change such as rupture of chemical bond is necessary for the nucleation given rise by fracturing of solids as stated in I. The formation of free radicals or unsaturated state at the surface of solids by mechanical fracturing of solids except soft molecular crystals is demonstrated by the following facts: *Kargin* et al. reported that monomers polymerize when metals or ionic crystals are crushed in the solution [naphthalene gives a negative result (4)], and *Okuyama* et al. observed growth of a solid polymer when an aluminium plate is scratched with an iron pin in a toluene solution of allyl chloride (5). Detonations of explosives are initiated by the chain reaction of free radicals generated by mechanical blow. It is certain thus that the electronic state of solids is altered remarkably and the electron cloud becomes diffuse when the solids are fractured.

According to *David* and *Hamann*, sulfur conducts metallically (6), and specific conductance of water rises to a value as high as $1 \text{ ohm}^{-1} \text{ cm}^{-1}$ (7) momentarily when shocked with explosion waves. Electron cloud of the molecules may undergo a severe deformation in this way at the moment of shock. Valence electrons are non-localized, mixing like free electrons in metals and the remaining part of the molecules are positively charged momentarily. The system may attain, as a whole, a metal-like structure conducting and cohering metallically. An analogous state will be realized two-dimensionally along the fracturing surface of solids (III. 3). Ultrasonic wave accelerates nucleation, decomposes high polymers, activates water chemically and sometimes gives rise to luminescence (8). Jet stream in liquid also decomposes high polymers (9).

These actions have been considered to be originated from an intense mechanical action accompanying cavitation. Strong spraying similarly exerts a strong local stress on liquids. These mechanical means presumably give rise to an excited state estimated above, if the strength is enough.

III.2. Relative difficulty of nucleation

The relative difficulty of nucleation may be determined by variable factors. As for the entropy factor, the molecules (or atoms or ions) may form crystal nuclei and crystals with the highest symmetry by closest packing most easily, if the form of the molecule and the field of forces acting are spherically symmetrical. These substances do not supercool much. Typical examples are carbon tetrabromide (see II. 2) and most metals which include no covalent bond. As the degree of symmetry of molecular form and of the force field decreases, that of the crystal also decreases and the probability of nucleation is diminished, because at least several tens molecules must cluster and arrange themselves with a characteristic structure to form a nucleus. If the molecule contains OH radical etc. with a directional force field, nucleation may be more difficult, especially when these radicals are localized in a large molecule. High viscosity of hydroxylic liquids also makes nucleation slower. Supercooling, therefore, increases in the following order: metals < benzene (the crystal is rhombic) < water (hexagonal, but with an open structure) < thymol and salol (rhombic, include OH radical).

Nucleation from supersaturated solutions can be discussed in an analogous way, although the problem is more complex than one component systems. For examples, easily-supersaturatable substances such as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}$, sucrose and glucose form monoclinic crystals. On the contrary, alkali halides composed of simple ions form crystals of high symmetry and do not supersaturate much, since mere clustering of ions is enough to nucleate.

In the case of nucleation from aqueous solution of ions or hydrophilic substances, it may be necessary to dehydrate a part or all of hydrated water. It is probable that this process and consequently, the energy of activation of dehydration determine the rate of nucleation and the limit of supersaturation. In these cases, strong hydration makes supersaturation easy.

III.3. Mechanism of nucleation given rise by mechanical shock or by fracturing of solids

A metal-like structure is formed of free electrons liberated from each molecule and positively charged part of it, as stated in III. 1, when substances undergo strong

mechanical forces. These are electrostricted to the closest-packed structure with higher regularity by a force analogous to metallic bond or cohesion. The cluster may become a crystal embryo or nucleus when mechanical influence disappears and the electrical neutrality of molecules is recovered, if the stricted structure is near to that of the crystal, or if it is easily convertible to the latter¹). According to *Evans* (10), ΔT of water under 2000 atm. is the same as that under 1 atm., hence it may be concluded that mechanical nucleation is not given rise by direct compression, but by the generation of a metal-like structure. If the forces are weak and ΔT is small, the embryo is smaller than the critical nucleus and the arrangement of molecules is incomplete. It is disintegrated by molecular motion as soon as the external forces pass away, without giving rise to nucleation. Nucleation in supercooled liquids given rise by fracturing of solids may be explained in an analogous way: fractured surface of solid except soft molecular crystals is momentarily covered with free radicals, and the labile electrons and positively polarized part of liquid molecules in contact with the solid surface may form a two-dimensional metallic structure and the resulting stricted layer with higher regularity may act as the nuclei, if its structure is similar to that of the crystal or if it is easily convertible to it. *Evans* (11) showed in his studies on ice-nucleation on organic crystals that a frozen mono-layer of adsorbed water can nucleate ice. It may be considered, then, that even a mono-layer of liquid is enough to nucleate if an appropriate structure is given. It is not a mere electrostatic orientation of molecules. Since the nucleation of this type is a co-operative phenomenon, mere addition of free radicals and simple electrostatic field stated in I.2 can not give rise to it. As for the solution, it is possible that mechanical forces directly supply the energy of activation necessary to dehydrate ions and hydrophilic molecules, and nucleate crystals.

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Summary

Sudden crystallization takes place frequently in supercooled liquids or in supersaturated solutions (usually of ionic compounds) when solid substances

¹) In the cases of salol and thymol, the conversion is supposed to be difficult.

immersed in the liquids are cut or fractured mechanically. Rupture of chemical bonds in the solid is essential for the nucleation and the effect disappears momentarily. Crystallization is also frequently given rise by mechanical shock in the above mentioned liquids, and may be explained as follows: electrons of the shocked molecules become labile and may behave like free electrons in metals momentarily as demonstrated experimentally. Generated free radicals and free electrons cluster into a metal-like structure and are compressed into the closest-packed structure with higher regularity by forces analogous to metallic bond. The cluster may act as the embryo and the nucleus of the crystal, if its structure resembles to that of the crystal or if it is easily convertible to the latter. Nucleation in supercooled liquids given rise by fracturing of solids is explained in an analogous way. Fractured surface of solids is momentarily covered with free radicals. The labile electrons and positively polarized part of liquid molecules in contact with the surface may form a two-dimensional metallic structure and the resulting compressed layer may act as the nucleus, if its structure is appropriate.

Zusammenfassung

Plötzliche Kristallisation geschieht oft in unterkühlten Flüssigkeiten oder in übersättigten Lösungen (gewöhnlich von Ionenverbindungen), wenn feste Substanzen, die in die Flüssigkeiten eingetaucht sind, mechanisch geschnitten oder gebrochen werden. Die Spaltung der chemischen Bindungen in den festen Substanzen scheint notwendig für die Keimbildung zu sein. Plötzliche Kristallisation wird auch durch mechanische Erschütterung in den Flüssigkeiten hervorgerufen. Diese Phänomene werden durch Einfluß delokalisierter Elektronen auf die Keimbildung erklärt.

References

- 1) *Kondoguri, W.*, Z. Physik **47**, 589 (1928).
- 2) *Buckley, H. E.*, Crystal Growth, p. 292 (London 1951).
- 3) *Ubbelohde, A. R.*, Trans. Faraday Soc., **39**, 863 (1940).
- 4) *Kargin, V. A., N. A. Plate*, Vysokomolek. soed., **1**, 330 (1959); *Plate, N. A., V. V. Prokopenko, V. A. Kargin*, *ibid.* **1**, 1713 (1959).
- 5) *Okuyama, M., H. Hirata*, Kolloid-Z. u. Z. Polymere **212** (2), 162 (1966).
- 6) *David, H. G., S. D. Hamann*, J. Chem. Phys. **28** 1006 (1958).
- 7) *idem*, Trans. Faraday Soc., **55**, 72 (1959).
- 8) *van Hook, A., F. Frula*, Ind. Eng. Chem. **44**, 1305 (1954); *Sollner, K., J. Alexander*, Colloid Chemistry V, p. 337-373 (London 1944); *Brudhomme, R. O., P. Graber*, J. chim. phys. **46** 667 (1949); *Weissler, A.*, J. acoust. Soc. Amer. **23**, 370 (1951).
- 9) *Okuyama, H., N. Sata*, Ann. Rep. Lab. Fibre Sci. **12**, 36 (1959).
- 10) *Evans, L. F.*, Nature **206**, 822 (1965).
- 11) *idem, ibid.* **213**, 384 (1967), Trans. Faraday Soc. **63**, 1 (1967).

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