THE VACUUM GRANULATION MECHANISM

S. M. Brazhnikov, A. Z. Volynets,
E. V. Gavrilova, and A. V. Rozhdestvenskii

UDC 536.24.037.5

A physical model is proposed for droplet dispersal during evaporative freezing under vacuum, and results are given from an experimental test. The radius at which explosive dispersal becomes possible has been determined.

Here we consider the behavior of droplets of water or aqueous solution under vacuum. When the droplets are injected into the vacuum chanber, the liquid evaporates rapidly, and if the pressure in the chamber is below the pressure corresponding to the triple point, the droplets freeze rapidly. As a rule, the freezing of such droplets is nearly always accompanied by breakup [1, 2], which takes various forms: from cracking in the granules (Fig. 1a) to vigorous explosion (Fig. 1b). It is very important to establish the relationships in this phenomenon in organizing many technological processes such as the continuous sublimation treatment of a liquid or paste materials [3], since the character of the dispersal will ultimately determine the choice of working conditions to give a product for a particular purpose as well as methods of calculating the corresponding equipment. Here we consider the granule disruption mechanism in relation to the process parameters.

Droplets may be disrupted on injection into a vacuum for two reasons: boiling under vacuum or increased pressure in the liquid core of a partially frozen drop because of the increase in volume of water on crystallization. Here we consider the second mechanism in more detail, since fairly detailed studies have been made [4] on disruption by boiling.

Of the few papers dealing with disruption produced by the increase in volume on crystalization, the fullest treatment is to be found in [1]. There the pressure increase in the liquid was deduced as a function of the position of the phase boundary, and the distributions of the radial and tangential stresses in the shell were determined for viscous and elastic models for ice. Here it was assumed that the shell in a partially frozen drop can withstand loads substantially exceeding the strength of ice without failure. As a result, it was found that the distribution of the tangential stresses differed radically from the known [5] Lamé distribution. For example, according to [1] the tangential stresses in the layer adjoining the inner surface of the shell are compressive, but as the radius increases they change sign and attain their maximum value at the outer surface (curve 1 in Fig. 2). On the other hand according to Lamé the tangential stresses are tensile ones throughout the shell and are maximal at the inner surface (curve 2 of Fig. 2).

We propose a different approach to the granulation problem. Firstly, we assume that the freezing is represented by a sequence of cycles of cracking and healing. Here the contribution from the stresses arising in the current layer of ice being formed to the stress distribution in the shell is unimportant. In other words, a Lamé distribution applies for the stresses in the shell [5]:

$$\tau_r = P\left(\frac{R^3}{r^3} - 1\right) \Big/ \left(1 - \frac{R^3}{\eta^3}\right), \quad (1)$$

$$\tau_\theta = \tau_\varphi = -P\left(\frac{R^3}{2r^3} + 1\right) \Big/ \left(1 - \frac{R^3}{\eta^3}\right). \quad (2)$$

Secondly, we assume that the behavior of the freezing drop is determined by the relation between the energy of the surface-tension forces and the potential energy of elastic deformation, which accumulates in the drop as a result of the successive cracking-healing cycles.

Then on this basis the freezing will occur as follows.

Moscow Chemical-Engineering Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 2, pp. 264-272, February, 1984. Original article submitted October 20, 1982.

 0022-0841/84/4602-0197$08.50 

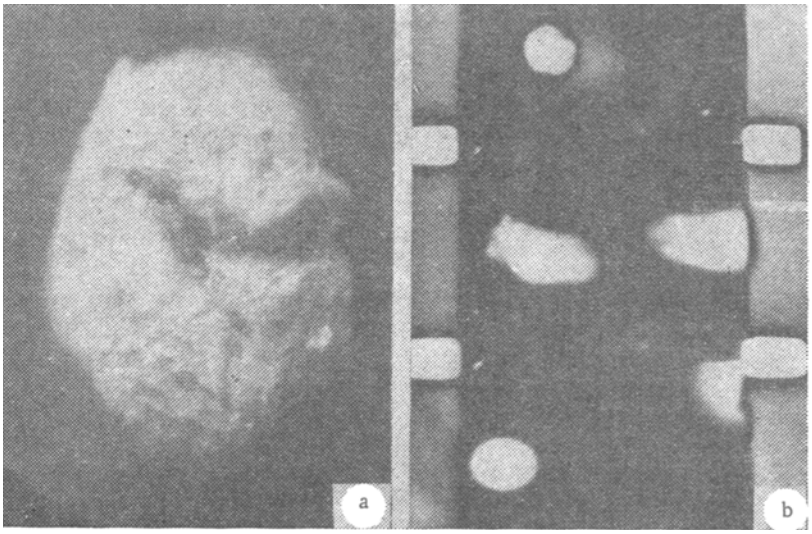

Fig. 1. Characteristic features in droplet failure: a) cracking; b) explosion.

At the start, there is vigorous evaporation, and the surface layer freezes, i.e., an ice shell is formed. The partially frozen drop then consists of a liquid core and a solid shell, with a sharp boundary (Fig. 2). The temperature at the outer surface is lower than the freezing temperature. As a result, the liquid crystallizes at the inner surface and the boundary migrates from the periphery towards the center. The specific volume of water increases on crystallization, so the liquid in the core is compressed to a certain pressure, and radial and tangential stresses arise in the shell. The pressure in the core and the stresses in the shell will be dependent on the position of the phase boundary, and therefore the same applies to the elastic energy. At a certain instant, the stresses reach the strength of ice, and the shell breaks. The further course of the process will be determined by the amount of accumulated elastic energy.

If the potential energy is approximately equal to the energy needed to break the ice shell, or somewhat larger than this, then there will be no visible disruption. In that case, the liquid flows from the core into the resulting crack, and the pressure falls to zero, so the shell is completely unloaded. The displaced liquid may flow over the shell and form a new surface as a result of the excess elastic energy. At the same time, the liquid under vacuum evaporates very rapidly. As a result, the liquid freezes rapidly and the crack in the shell is healed, and a new surface takes the form of an overlying layer. This cycle may occur repeatedly during the freezing. After the healing, a new layer of ice is formed on the inner surface, which again leads to stresses in the solid. The stresses are compressive in this layer, but the thickness of the layer is small by comparison with that of the entire shell, so the contribution from the stresses here to the general stress distribution can be neglected, i.e., we can assume that a Lamé distribution applies.

The shell thickness and the liquid pressure will increase from cycle to cycle. Consequently, the amount of accumulated eleatic energy will increase. At a certain stage in the freezing of a drop of a given size, this energy will exceed the shell disruption value. In that case, the excess potential energy will be increasing the surface of the liquid core, and following the formation of the next crack the healing is displaced by the spherical shell cracking off. The surface of the liquid is then in contact with vacuum and the liquid freezes rapidly, and the configuration of the granule is then fixed (Fig. 1a). With a given position for the phase boundary, this cracking may occur to an extent dependent on the radius of the droplet, which determines the potential energy. In the limiting case of complete disruption, all the liquid from the core is distributed as a thin layer over the inner surface of the shell. The resulting increase in surface area is maximal, and the amount of energy required for this is given by

$$W_s = 4\pi\sigma\eta^2. \quad (3)$$

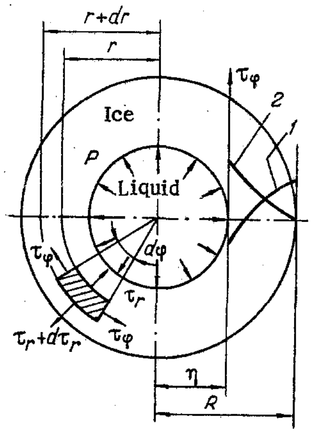


Fig. 2. Stress distribution in a shell in a partially frozen droplet: a) from [1]; 2) Lamé distribution.

Thus the potential energy of the drop is proportional to the volume, i.e., to the cube of the radius, while the energy of the surface forces is proportional to the square, so there is a critical radius beyond which the elastic energy will exceed the value defined by (3). In that case, one expects the explosive disruption, in which the excess elastic energy is transformed to kinetic energy of the fragments.

We now determine the potential energy of a partially frozen water droplet. We assume that there are only elastic strains in the ice.

It should be noted that ice is elastic only under brief loading, while under prolonged loading it acts as a viscous liquid [6]. Estimates of the viscous-stress relaxation times and the temperature pattern show that those times for an evaporative freezing under vacuum are larger by more than two orders of magnitude than the characteristic freezing time. Therefore, one is justified in using the elastic approximation.

We begin our consideration with the time at which several cracking-healing cycles have occurred and the phase boundary occupies a position with radial coordinate $\eta$, with the liquid in the core compressed to a certain pressure and with radial and tangential stresses in the shell. The elastic energy accumulated up to this time is made up of the energy of the liquid and solid phases:

$$W_p = W_l + W_i. \tag{4}$$

Each of these terms can be derived in terms of the specific elastic-strain energy and the phase volume:

$$W = \int_V u dV. \tag{5}$$

We first consider the energy acquired by the ice shell. In accordance with our hypothesis, the shell has radial compressive stresses and tangential tensile ones. The elastic energy of unit volume of the ice governed only by the stress components is then found as

$$u_i = \frac{1}{2E}(\tau_r^2 + 2(1+\mu)\tau_\varphi^2 - 4\mu\tau_r\tau_\varphi), \tag{6}$$

where $\tau_r$ and $\tau_\varphi$ are defined by (1) and (2) correspondingly.

The largest tensile stress is attained at the inner surface of the sphere:

$$\tau_{\varphi\max} = -P\left(1 + \frac{R^3}{2\eta^3}\right)\Big/(1 - R^3/\eta^3). \tag{7}$$

We equate this to the tensile strength of ice (equilibrium condition for the hemisphere) to get a relationship between the maximum pressure in the liquid core and the position of the phase boundary:

$$P = \tau_0\left(\frac{R^3}{\eta^3} - 1\right)\Big/\left(\frac{1}{2}\frac{R^3}{\eta^3} + 1\right). \tag{8}$$

We then substitute (1), (2), and (8) into (6) to get an expression for the maximum strain energy of unit volume of the shell that can be accumulated up to this instant:

$$u_i = \frac{3}{2}\frac{\tau_0^2}{E}\frac{1}{\left(1 - \frac{R^3}{\eta^3}\right)\left(1 + \frac{R^3}{2\eta^3}\right)}\left(\frac{1+\mu}{2}\frac{R^6}{r^6} - (1-2\mu)\right). \tag{9}$$

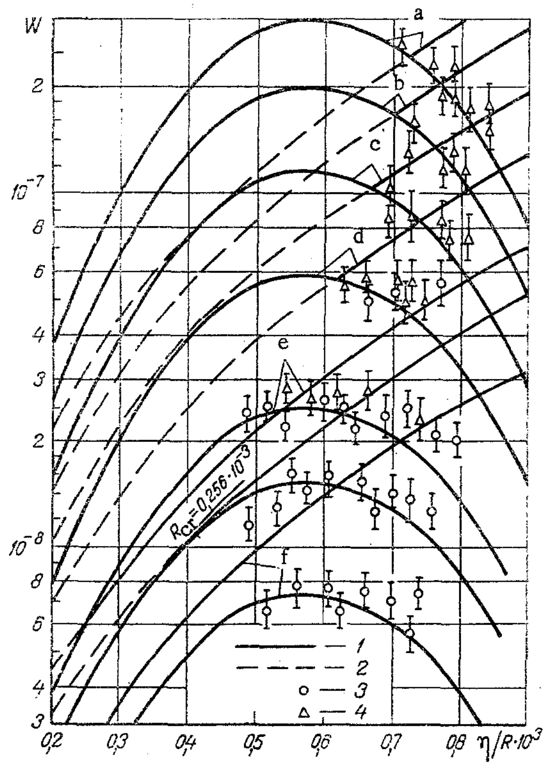


Fig. 3. Comparison of calculations on potential energy with experiment (W in J and R in m); 1) potential energy of partially frozen droplet (calculation); 2) energy of surface forces in complete cracking (calculation); 3) cracking; 4) explosion; a) R = $0.7 \cdot 10^{-3}$, b) $0.6 \cdot 10^{-3}$; c) $0.5 \cdot 10^{-3}$; d) $0.4 \cdot 10^{-3}$; e) $0.3 \cdot 10^{-3}$; f) $0.2 \cdot 10^{-3}$.

In accordance with (5), the potential energy of the entire shell is

$$W_i = 2\pi R^3 P^2 (\eta) \frac{\eta^3}{R^3} \frac{\frac{1+\mu}{2}\frac{R^3}{\eta^3} - (1-2\mu)}{E\left(\frac{R^3}{\eta^3} - 1\right)}. \tag{10}$$

We now determine the potential energy accumulated in the liquid core.

The liquid is under hydrostatic compression, so the specific elastic-strain energy will be determined only by the pressure:

$$u_l = \frac{1}{2K} P^2. \tag{11}$$

Then the following is the elastic energy of the entire volume of liquid at this stage in the freezing:

$$W_l = \frac{2}{3} \pi R^3 \frac{P^2}{K} \left(\frac{\eta}{R}\right)^3. \tag{12}$$

Finally, we have for the entire drop in accordance with (6) that

$$W_p = 2\pi R^3 P^2 \left(\frac{\eta}{R}\right)^3 \left(\frac{1}{3K} + \frac{\frac{1}{2}(1+\mu)\left(\frac{R}{\eta}\right)^3 - (1-2\mu)}{E\left(\frac{R^3}{\eta^3} - 1\right)}\right). \tag{13}$$

Figure 3 shows results obtained from (13), along with curves characterizing the energy of the surface forces during freezing for the case of complete disruption.

The results indicate some features of the behavior during freezing. The graphs show that the energy of a relatively small drop remains less than the energy needed for complete shattering at all stages. Such a drop does not shatter, and the cracks that form heal up or else there is partial shell shedding. As the radius increases, the difference between the potential energy of the drop and the complete shattering energy decreases. If the radius is larger than a certain value, the potential energy exceeds the total shattering energy. The freezing of such a drop should end in explosive shattering, with the elastic energy converted to kinetic energy of the fragments. We find that the cricial radius is $R_{cr} = 0.256 \cdot 10^{-3}$ m.

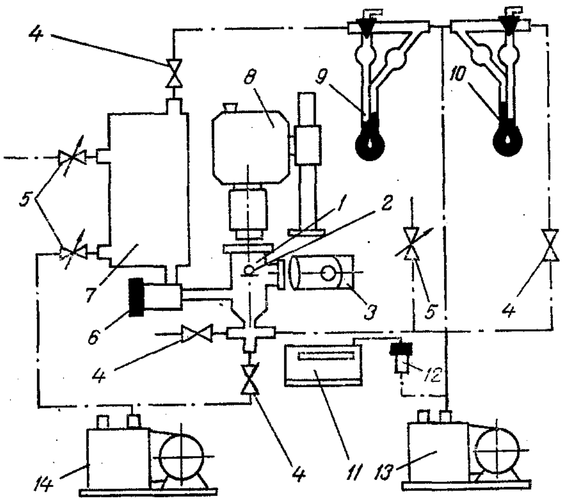

Fig. 4. Apparatus for examining droplet freezing under vacuum: 1) vacuum chamber; 2) droplet; 3) illumination system; 4) vacuum valve; 5) controlled leak; 6) electromagnetic vacuum valve; 7) balast chamber; 8) motion-picture camera; 9, 10) dibutyl phthalate vacuum gauges; 11) thermocouple vacuum gauge; 12) manometer tube; 13, 14) vacuum pumps.

An interesting point is that there is a position for the phase boundary ($R/\eta = 1.72$) such that the potential energy of the drop is maximal. This maximum occurs because in the initial period ($R/ < 1.72$), the pressure increase in the liquid predominates, while the reduction in the liquid core volume has a more marked effect at the later stages.

Two series of experiments were performed to check this model. The first series was performed with a pilot continuous-operating sublimation system with direct injection into vacuum [3]. In the experiments, a 3% solution of sodium sulfite entered the vacuum chamber as a flow of polydispersed droplets. The droplets froze during flight and struck a heated target, where the ice sublimed. This gave granules of dry salt.

The use of a weak salt solution with subsequent sublimation drying enabled one to identify the structure of the granules formed by failure. As the concentration was low, the dissolved salt was taken as having little effect on the granulation mechanism. The method enables us to avoid the difficulties associated with examining the structure of the frozen drops and to make the necessary measurements on the dry salt granules. For each granule we determined the thickness of the shell formed at the instant of disruption and the outside diameter. Knowing $\eta$, from (5) we found the corresponding value of the surface energy and compared this with the elastic strain energy calculated from (13).

The second series of experiments was performed to determine the potential energy on explosion. High-speed cinematography was used with the apparatus shown in Fig. 4. A drop of liquid 2 was placed by means of a pipette on a substrate with hydrophobic coating, which was placed in the chamber 1, where the pressure of 2500-4000 Pa was set up. The ballast chamber 7 was evacuated to a pressure at which the freezing was to be examined (this was 26.6 Pa in our experiments), after which the two chambers were connected together by the electromagnetic valve 6. The illumination system 3 and cine camera 8 were switched on synchronously. The experiments were performed with 3% $Na_2SO_3$ solution and pure water. The frame speed was 38 a second with an exposure time of 1/116 sec. The diameter range was $0.68 \cdot 10^{-3}$ -$1.194 \cdot 10^{-3}$ m. In all, 200 experiments were performed. Figure 1b shows a characteristic pattern in the explosion of a drop of distilled and outgassed water of diameter $1.1 \cdot 10^{-3}$ m. The frames enable one to determine the overall kinetic energy of the fragments from the tracks, the sizes, and the exposure times; in accordance with the model, this energy should be equal to the elastic energy accumulated in the drop.

Figure 3 compares the results with the calculations. On the whole, the experiment confirms the model.

The experiments showed that the freezing of relatively small drops with $R < 0.2 \cdot 10^{-3}$ occurs without visible disruption. However, microscopic examination of the dehydrated granules showed runs on the surface, which corresponds to repeated cracking and healing. With larger drops, there was nearly always visible bursting. Also, the tendency for the process to pass from cracking to explosion was evident. The experiments gauge the ranges in radius in which the different forms occurred. For droplets of radius $0.2 \cdot 10^{-3} \leq R \leq 0.28 \cdot 10^{-3}$ m, cracking on freezing was characteristic, whereas for ones of size $R > 0.4 \cdot 10^{-3}$ m explosion was characteristic. In the range $0.28 \cdot 10^{-3} \leq R \leq 0.4 \cdot 10^{-3}$ m, the two forms were equally probable. Therefore, the transition from cracking to explosion in fact occurs not at a single value of the radius, as the calculations imply, but over a certain range, which is quite explicable on the model. In fact, the increment in the ice layer in each cracking-healing cycle varies. Therefore, after the last healing cycle the thickness of the ice preceding visible bursting will vary. Therefore, the potential energy in a drop of a given size will also vary. The two forms of failure will occur together in the range of radii for which the deformation energy is comparable with the bursting energy. The lower end of this range, i.e., the least radius leading to explosion, is the critical radius, and experiment gives this as $R_{cr} = 0.28 \cdot 10^{-3}$ m.

The potential energy was determined from the shell thickness (in cracking) and from the fragment tracks (on explosion), and the values were in satisfactory agreement with the calculations. However, the measured potential energy and critical radius somewhat exceed the values given by the calculations, for the following reasons. Firstly, the strength of ice has been chosen inexactly, as this is dependent on the freezing conditions. Secondly, one assumes that one cannot completely ignore the viscous behavior of ice even under vacuum at high freezing rates. Therefore, the model can be refined by performing additional experiments on the behavior at different freezing rates.

## NOTATION

P, pressure; R, drop radius; D, drop diameter; $\sigma$, surface tension; $\tau_r$, radial stress; $\tau_\varphi$, $\tau_\theta$, tangential stresses; r, $\theta$, $\varphi$, spherical coordinates; $\eta$, phase transition boundary coordinate; $W_s$, work of surface tension forces; $W_p$, elastic deformation energy; $W_l$, potential energy of liquid; $W_i$, potential energy of solid; V, volume; u, elastic deformation energy of unit volume; E, Young's modulus; $\mu$, Poisson's ratio; K, bulk modulus.

## LITERATURE CITED


1. W. D. King and N. H. Fletcher, "Pressure and stresses in freezing water drops," J. Phys. D: Appl. Phys., 6, 2157 (1973).
2. D. A. Johnson and J. Hallet, "Freezing and scattering of supercooled water drops," Q. J. R. Met. Soc., 94, No. 4/5, 468 (1968).
3. A. Z. Volynets, E. V. Gavrilova, and V. M. Postnikov, "A study of continuous monodisperse granulation under vacuum," Kholod. Tekh., No. 9, 30 (1977).
4. V. I. Ivashov, "The effects of a controlled medium on heat and mass transfer in food-preparation processes," Author's Abstract of Doctoral Dissertation, Technical Sciences, Moscow (1980).
5. S. P. Timoshenko and J. Goodier, Theory of Elasticity, McGraw-Hill (1970).
6. E. Pounder, Physics of Ice [Russian translation], Mir, Moscow (1967).