GRANULE FORMATION IN CRYOGENIC FLUIDS

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Physical phenomena taking place at the surface of a spherical granule in con-
tact with a cryogenic fluid are analyzed. A boundary condition of third kind
is obtained. Perturbation method is used to construct a solution of the Stefan
problem for bodies possessing spherical symmetry.

Solutions of order higher than the first, show a singularity at the center of
the sphere. A modified perturbation method is used to obtain an asymptotic
solution removing this singularity. The analytic solution is compared with the
experimental results and numerical solutions.

1. Model of the process of granule formation.
Formation of granules in cryogenic fluids is of great practical importance. For exam-
ple, one of the stages of the cryogenic synthesis of inorganic compounds involves rap-
id freezing of the starting solutions into spherical particles. The main purpose of
the freezing is to achieve chemical homogeneity, and rapid transition of the solution
from the liquid to the solid state prevents its constituents from separating. Although
the methods used to obtain the particles are relatively simple [1 — 3], the theoretical
problems arising in connection with the freezing process have not been studied in suf-
ficient detail.

Let us consider the mechanism of heat transfer at the boundary between a spherical
body and a cryogenic fluid. When a drop of the solution impinges on the surface of
the cryogenic fluid, the latter boils up. The vapour formed maintains the drop for
some time in a state of suspension, the drop rotating about its center and moving over
the surface of the cryogenic fluid. The behavior of the drop is due to the instability
of the flow of vapour within the gap. The thickness of the vapour layer diminishes
with time, and a moment comes when the particle becomes immersed in the fluid.
This corresponds to a change in the character of the process of boiling of the cryogenic
fluid. Heat conductivity and radiative transfer across the vapour layer separating the
drop from the cryogenic fluid provide, in this case, the heat exchange mechanism
between the drop surface and the cryogenic fluid. Analogous situation arises when a
drop reacts with a solid surface heated to a temperature exceeding the Leyden frost
point [4]. The temperature difference between the solid surface and the evaporating
drop remains constant. In the present case the temperature difference and the cor-
responding heat exchange coefficient both vary along the drop surface.

We assume that the flow of vapor in the gap is laminar and, that the vertical
component of the velocity of the vapor is small compared with the horizontal com-
ponent. Let us suppose that the thickness of the vapor layer is constant over the

whole surface of the sphere. The effective surface heat transfer coefficient α is connected with the vapor layer thickness δ by the relation $\alpha = \lambda'' / \delta$ where λ'' is the heat conductivity coefficient of the cryogenic fluid vapor.

The vapor layer thickness δ is obtained from the equation of motion of a viscous incompressible vapor (Navier — Stokes equation) and the equation of continuity, under the condition that the drop is supported on the surface of the fluid by viscous friction of the vapor evolved. Under these assumptions the equation of conservation of vapor impulses and the condition of equilibrium, have the form (equation of continuity is satisfied identically)

$$\mu'' \partial^2 u / \partial y^2 = \partial p / \partial r, \ 0 \leqslant y \leqslant \delta \qquad (1.1)$$

$$\frac{r^2 [T(t, R) - T_c] \lambda''}{L \delta \rho''} = 2 \int\limits_0^\delta r u \, dy$$

Here μ'' and ρ'' denote, respectively, the dynamic viscosity coefficient and the density of the vapor, L is the heat of the phase change of the cryogenic fluid, p and u are the pressure and horizontal component of the vapor velocity, $T(t, R)$ and T_c are the surface temperature of the drop of radius R and of the cryogenic fluid, and t is time.

Integrating the equation (1.1) under the boundary conditions $u = 0$ when $y = 0$ and $y = \delta$, gives the vapor velocity field within the gap

$$u = y (y - \delta) (2 \mu'')^{-1} (\partial p / \partial r) \qquad (1.2)$$

The pressure difference in the vapor layer is obtained from (1.2) and the second relation of (1.1), with the condition that $p(R) = p_0$, where p_0 is the vapor pressure at the drop surface, taken into account, in the form

$$p - p_0 = 3 [T(t, R) - T_c] \lambda'' \mu'' (R^2 - r^2) / (\delta^4 L \rho'')$$

The total force of pressure acting on the drop is given by

$$P = {}^3/_2 \pi R^4 [T(t, R) - T_c] \lambda'' \mu'' / (\delta^4 L \rho'')$$

Since this force is balanced by the gravity of the drop, the boundary condition at the drop surface will be

$$\mathrm{Bi} [\theta(t, 1)] = b / [1 - \theta(t, 1)]^{1/4} \qquad (1.3)$$
$$\mathrm{Bi} = \alpha R / \lambda_0, \ \theta(t, 1) = [T_0 - T(t, 1)] / (T_0 - T_c)$$
$$b^4 = 8/9 \ \lambda''^3 L \rho'' \rho_0 g R^3 / [\lambda_0^4 (T_0 - T_c) \mu'']$$

where ρ_0 is the density of the solution, g is acceleration due to gravity, T_0 is the solution temperature and Bi in the Biot number.

From (1.3) it follows that when $\theta(t, 1) \ll 1$, then the drop will be supported on the surface of the cryogenic fluid by the friction of the vapor evolved irrespective of the radius of the drop. In fact, this is not observed. When the size of the drop and the solution density reach a certain value (for water drops frozen in liquid nitrogen, $R \approx 9.5 \div 10 \ \mathrm{mm}$), the drops become immersed in the volume of the fluid almost instantly. This can apparently be explained by the fact that when the drop size or the solution density reach a certain value, then the mechanism of the vapor flow changes. The velocity of the vapor in the gap and the area of contact between the

drop and the cryogenic fluid increase with increasing radius, while (1.3) implies that the thickness of the vapor layer increases at the same time only insignificantly. The dependence of the thickness of the vapor layer on θ $(t, 1)$ is shown in Fig. 1 where the curves $1-4$ correspond to the particle radii of 0.1, 0.2, 0.3 and 0.5 mm. Under these conditions waves appear within the gap at the surface of the cryogenic fluid, and their amplitudes may be of the order of thickness of the vapor layer. A contact component of the heat flux appears, which may exceed, in the case of laminar boiling, the heat flux itself. When the fluid is in microcontact with the granule surface, the boiling is explosive and leads to an increase in the number of microcontacts as well as in the frequency of their appearance. With the process developing in this manner, the weight of the drop exceed the vertical component of the frictional forces uniformly acting from the direction of the vapor layer, and the drop becomes immersed in the bulk of the fluid.
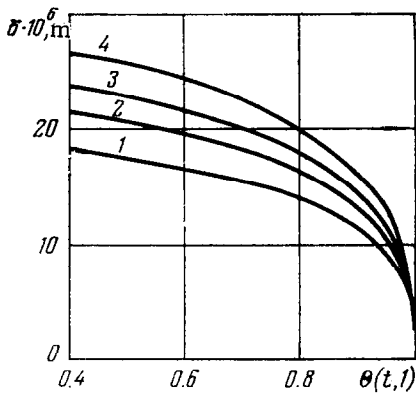

Fig. 1

Another phenomenon has come to light in the course of experiments carried out with freezing of the drops. It was found that drops of a certain, specified radius (which we shall call critical) shattered explosively some time after freezing. The critical radius could be smaller (of the order of 1 mm. for pure water [5]), or larger (for solutions of salts TsTS, TsTSL and TsTBS-1) than the radius of the drop at which it sinks.

One of the assumptions explaining the the mechanism of disintegration of the granules asserts that the freezing process is ac-companied by increase in the volume of the fluid enclosed in the frozen shell [6].

Other investigators [7] have shown that shattering of a granule is caused by a large amount of dissolved gas and large temperature gradients. In [8] and below it was shown that the disintegration of the particles is caused by the difference in the physical and rheological properties of the liquid and solid phases, and the conditions of freezing. Quantitative description of this process is outside the scope of this paper, and we shall consider here the granules of size at which no disintegration takes place.

2. F o r m u l a t i o n   o f   t h e   p r o b l e m   a n d   i t s   s o l u t i o n. Assuming that the thermophysical properties of the solid phase are independent of temperature and, that the temperature of the liquid phase is equal to the phase transition temperature, we can write the energy equation and boundary conditions in the form

$$\varepsilon w \partial v \,/\, \partial S = \partial^2 v \,/\, \partial X^2 \quad (\tau^\circ > 0, \; 0 \leqslant X \leqslant h) \tag{2.1}$$
$$\tau^\circ = 0, \; v = b \,/\, h; \; \tau^\circ > 0, \; X = h, \; \partial v \,/\, \partial X = v$$
$$\tau^\circ > 0, \; X = S, \; v = b \,/\, h$$
$$X = S, \; w = -\, h S^{-1} (\partial v \,/\, \partial X)_{X=S} \tag{2.2}$$
$$\varepsilon = c_2 (T_0 - T_c) \,/\, L_0, \; v = \theta \eta + b \,/\, h, \; w = dS \,/\, d\tau^\circ, \; h = 1 - 3/4\, b$$
$$\tau^\circ = \varepsilon h^2 \tau, \; \tau = a_0 t \,/\, R^2, \; X = h\eta, \; S = h\eta_1, \; \eta = r \,/\, R, \; \eta_1 = \xi (\tau) \,/\, R$$

Here r denotes the running radius, $\xi(\tau)$ is the radial position of the freezing front, c_2 is the heat capacity of the solid phase , L_0 is the heat of phase transition of the initial solution, a_0 is the heat conductivity coefficient of the solution, and the second boundary condition is obtained by expanding $(1 - \theta)^{3/4}$ into a binomial series with $\theta \ll 1$. The condition (2.2) represents the Stefan condition at the moving boundary.

We solve the problems of this type using the method of perturbing the regular parameter, first used in solving the first Stefan boundary problem in [9]. The method is used in [10] to fix the moving boundary with the help of the Landau transformation. The applicability of the solutions obtained by this method is limited by the existence of a singularity. The singularity which appears when the phase transition front approaches the center of the sphere, is removed in [9] with help of the Euler and Shanks transformations [11] using the method of deformed coordinates. Solutions obtained by means of these transformations yield results suitable for practical applications.

We seek the solution of the problem in the form of a power series in parameter ε

$$Y = \sum_{n=0}^{\infty} \varepsilon^n Y_n; \quad Y = v, w, \tau^\circ \tag{2.3}$$

From (2.1) — (2.3) we have the following problem for the i-th term of the expansion:

$$i = 0, \ \partial^2 v_i / \partial X^2 = 0 \tag{2.4}$$

$$i \geqslant 1, \ \partial^2 v_i / \partial X^2 = \sum_{j=1}^{i} w_{j-1} \partial v_{i-j} / \partial S$$

$$i \geqslant 0, \ X = h, \ \partial v_i / \partial X = v_i; \ i = 0, \ X = S, \ v_i = b / h$$

$$i \geqslant 1, \ X = S, \ v_i = 0; \ X = S; \ w_i = - hS^{-1} (\partial v_i / \partial X)_{X=S}$$

Solutions of the system (2.4) with the accuracy of up to and including the second order terms have the form

$$v / v_0 = 1 + \varepsilon S^{-1} C_1 + \varepsilon^2 S^{-3} C_2 \tag{2.5}$$

$$w / w_0 = 1 + \varepsilon S^{-1} D_1 + \varepsilon^2 S^{-3} D_2$$

$$v_0 = by / (hz), \quad w_0 = - b / [z (z - 1 + h)]$$

$$C_1 = \frac{b}{3y} \left(-\frac{y}{2} + \frac{y^3 + 2}{2z^2} - \frac{y}{z^3} \right)$$

$$C_2 = \frac{- b^2 (4z + 3h - 3) (y - z)}{6yz^4} \left[\frac{z^3 + 2}{z} \left(y + z - \frac{1}{3z} \right) \frac{y}{6} - \frac{y}{20} (y + z) (y^2 + z^2) - y + \frac{21}{20z} \right]$$

$$D_1 = \frac{b}{3} \left(1 - \frac{1}{z^3} \right), \quad D_2 = - \frac{b^2}{6z^4} (4z + 3h - 3) \times \left[\frac{z^3 + 2}{z} \left(\frac{z^2}{3} - \frac{1}{18} \right) - \frac{z^4}{5} - z + \frac{21}{20z} \right]$$

The zero order approximation for the temperature distribution represents a quasistationary solution. The time of freezing is found from (2.4) in the form

$$\tau_0 = b^{-1} (1 - \eta_1) [1/2 (1 - h) (1 + \eta_1) + 1/3 h (1 + \eta_1 + \eta_1^2)]$$

$$\tau_1 = - 1/3 h^{-2} [1/2 (1 - \Phi^2) - h\Phi^{-1} (1 - \eta_1)]$$

$$\tau_2 = \int_h^0 \frac{b\Phi}{3h^2\eta_1} \left[\frac{(\Phi^3 + 2) (\Phi^2 - 1/6)}{6\Phi^5 h\eta_1} - \frac{\Phi^4}{5} - \Phi + \frac{21}{20\Phi} \right] d\eta_1$$

$$\Phi = 1 + h\eta_1 - h$$

Fig. 2 depicts the dependence of the position of the freezing front on the freezing time for $\varepsilon = 0.1$ and 0.5, and the   curves $0-2$ correspond to the zero, first and second order approximations.
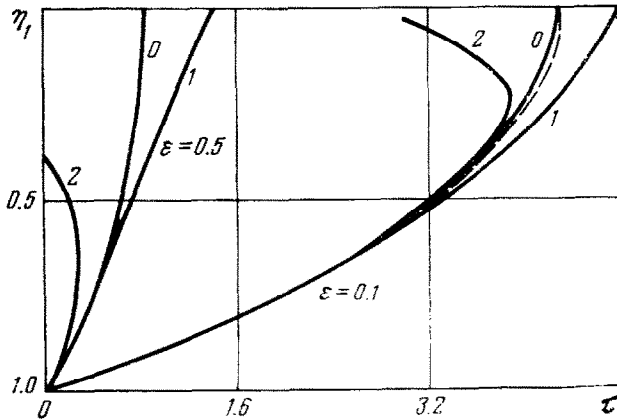

Fig. 2

Solution (2.5) obtained by the perturbation method diverges when the phase transition front approaches the center of the sphere. We remove this singularity by using, instead of the three-term expansion (2.5), a nonlinear Shanks transformation [11] which, for the time of freezing, has the form

$$\tau_* = [\tau_0 \tau_1 - \varepsilon (\tau_0 \tau_2 - \tau_1^2)] / (\tau_1 - \varepsilon \tau_2)$$

Analogous expression holds for the temperature v_* as well. Dashed line in Fig. 2 shows the dependence $\eta_1 (\tau_*)$ for $\varepsilon = 0.1$. The singularity of the solution at the sphere center is removed, but the time of complete freezing of the sphere given by the last formula is equal to the time of freezing in the zero approximation, i. e. the method yields unsatisfactory results when it comes to determining the time   of complete freezing. More accurate results are obtained by applying the Euler transformations to the series (2.5). Let us introduce the variable $\zeta = \eta / (K + \eta)$ where $\eta = 1 / S$.   We write the series (2.5) in the form of expansions in powers of ζ

$$\begin{aligned} v / v_0 &= 1 + K C_1 \varepsilon \zeta + K\varepsilon (C_1 + K C_2 \varepsilon) \zeta^2 + \\ & \quad K\varepsilon (C_1 + 2 K C_2 \varepsilon + K^2 C_2 \varepsilon^2) \zeta^3 + \cdots \\ w / w_0 &= 1 + K D_1 \varepsilon (1 + \zeta) \zeta + K\varepsilon (D_1 + K^2 D_2 \varepsilon) \zeta^3 + \cdots \end{aligned} \tag{2.6}$$

Here $K = K (\varepsilon)$ is a parameter obtained from the equation of total energy balance from the start to the completion of the freezing process

$$\int_h^0 \frac{(h \, \partial v / \partial X - v + b / h)_{X=h}}{w} \, dS - \varepsilon \int_h^0 X \left(v - \frac{b}{h} \right)_{S=0} dX = \frac{h^2}{3}$$

	H₂O		10% TsTSL			H₂O		10% TsTSL	
$R \cdot 10^3$, m	0.5	1.0	1.5	2.5	τ_2	0.2	0.69	1.02	3.82
b	0.35	0.59	0.85	1.25	$\theta°$	0.87	0.82	0.8	0.8
h	0.74	0.56	0.36	0.07	t_0, s	0.05	0.23	0.63	2.7
K_1	0.14	0.52	1.14	8.13	I	0.25	0.91	1.23	6.43
K_2	0.07	0.26	0.56	3.68	II	5.3	12.5	14.0	20.5
τ_1	0.2	0.68	1.01	3.73	III	4.83	11.76	13.24	19.4

The values of K_1 and K_2 relative to the granule radius and the values of the parameter b, are given in the above table. The sets I, II and III give the values of the theoretical (I) and experimental (II) time for which the particle floats, and (III) gives the same theoretical time for the case when $\theta = \theta'$. The Table shows that the parameter K decreases with increasing number of terms of the series, and this speaks in favor of the suitability of the expansions (2.6) in the n-th order approximation, using the approximations of the same order in ζ. For example, in the first order approximation the time of freezing is determined by the formula

$$\varepsilon \tau_1 = -\int_h^{\eta_1} \frac{\eta_1 \Phi \left(1 + K_1 h \eta_1\right) d\eta_1}{b \left[1 + K_1 h \eta_1 - \frac{1}{3} b K_1 \varepsilon \left(1 - \Phi^{-3}\right)\right]}$$

Fig. 3 depicts the dependence of the position of the freezing front on time, in the first order approximation. The curves $1-4$ correspond to the values $R = 0.3, 0.5,$ 0.8 and 1.0 mm. respectively.
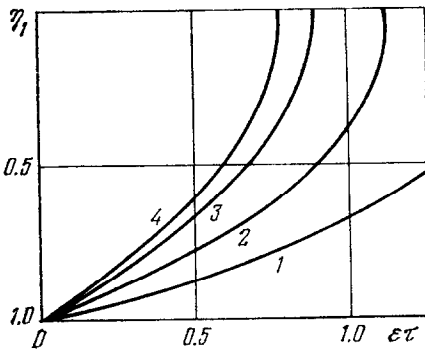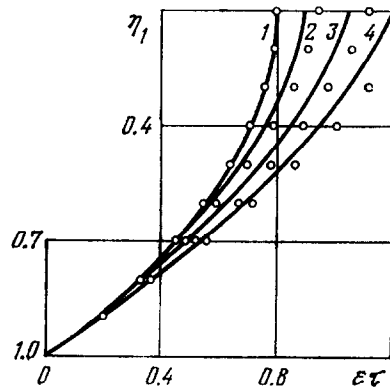

Fig. 3

Fig. 4

3. Comparison with the numerical results and experimental data. The analytic solution obtained was compared with the results of a numerical computation [12]. Fig. 4 shows the results of that comparison. The dependence of η_1 on the time of freezing is shown by solid lines $1-4$ for $\varepsilon = 0, 0.5, 1$ and 2 respectively. The empty dots correspond to the

numerical results of [12]. The numerical results diverge from the approximate solutions with the increasing value of the parameter ε. Thus the method of perturbing the regular parameter using the Euler transformation yields fully satisfactory results up to the value of $\varepsilon = 1.5$.

The results obtained were compared with the experimental data. It should be noted that since it is difficult to measure directly the time of complete freezing of the granule we measured the time for which the granule floated on the surface of the fluid. This time includes the time of complete freezing and cooling of the surface of the granule to the temperature θ°, which is the critical boiling temperature of the cryogenic fluid of second kind. The temperature difference θ° is found from the experimental data [13]. The value of θ° was also obtained from the solution of the problem of cooling the granule

$\partial\theta \, / \, \partial\tau = \partial^2\theta \, / \, \partial\eta^2 \ (\tau > 0, \ 0 \leqslant \eta \leqslant 1)$

$\tau = 0, \ \theta = -{}^{3}/_{4} \, [f(\eta) - b \, / \, h] = \Psi(\eta)$

$\tau > 0, \ \eta = 1, \ \partial\theta \, / \, \partial\eta = h\theta; \ \tau > 0, \ \eta = 0, \ \theta = 0$

$\Psi(\eta) = H \, (d + h\eta)^3 + E \, (d + h\eta) + F, \ d = 1 - h, \ H = K\varepsilon b^2 \, / \, (6 \, hd^3)$

$F = K\varepsilon b^2 \, / \, (3 \, hd^3) - b \, / \, h, \ E = b \, [1 - {}^{1}/_{3} \, K\varepsilon b \, ({}^{1}/_{2} - d^{-3})] \, / \, (hd)$

The solution of this problem has the form [14]

$$\theta = 2 \sum_{n=1}^{\infty} e^{-\beta_n{}^2\tau} \frac{(\beta_n{}^2 + h^2)}{[\beta_n{}^2 + h(1 + h)]} \sin \beta_n \int_0^1 \Psi(\eta) \sin(\beta_n\eta) \, d\eta$$

Here β_n denotes the n-th positive root of the equation $\beta \, \text{ctg} \, \beta - h = 0$. Knowing the temperature difference we can find the time of cooling. Combining the time of complete freezing and time of cooling, we compare the result with the experimental data given in Table. We see that the time of floating of the granule on the surface of liquid nitrogen determined experimentally exceeds, as a rule, substantially the time t_0 at which the boiling of second kind becomes critical.

Line (II) of the Table gives the theoretical time t of floating of the granule calculated under the assumption that the dimensionless temperature difference θ' between the surfaces of the granule and the liquid is equal to 0.01. The time is in satisfactory agreement with the experimental values.

The increase in the actual time of floating can be explained by the fact that vapor bubbles form at the surface and maintained by surface tension forces. The growth of the bubbles and their subsequent detachment from the surface is accompanied by a sharp change in the motion of the granule. Large granules $(R > 2 \text{ mm})$ execute, in this case, a shuttling motion along the height of the vessel.

Thus the results obtained and their comparison with the experimental data enable us to conclude that 1) the time of freezing is much shorter than the time spent by the granule floating on the surface of nitrogen; 2) the heat transfer coefficient remains practically constant during the time of freezing; 3) the time of floating of the granule is of the same order as the time taken to cool the granule surface to the temperature of liquid nitrogen.

REFERENCES

1. W i s s e m a, J. G., and D a v i e s, G. A. The formation of uniformly sized drops by vitrabionatomization. Can. J. Chem. Engng, Vol. 47, No. 6, 1969.

2. D a b o r a, E. K. Production of monodisperse sprays. Rev. Sci. Instrum., Vol. 38, No. 4, 1967.

3. R a j a g o p a l a n, R. C. T. and G o p a l, S. Production of monodispersed drops by vibrationsatomization. Can. J. Chem. Engng, Vol. 50, No. 3, 1972.

4. K u t a t e l a d z e, S. S. Funadamentals of the Theory of Heat Exchange. Novosibirsk, "Nauka", 1970.

5. K a u k h c h e s h v i l i, E. I., I l i u k h i n, V. V. and K a t i u k h i n, V. A. Freezing of liquid and paste-like foods in the form of granules. Kholodil'naia tekhnika, No. 5, 1972.

6. B r o w n s c o m b e, J. L. and H a l l e t t, J. Experimental and field studies of precipitation particles formed by the freezing of supercooled water. Quart. J. Roy. Meteorol. Soc., Vol. 93, No. 39B. 1967.

7. J o h n s o n, D. A. and H a l l e t t, J. Freezing and shattering of supercooled water drops. Quart. J. Roy. Meteorol. Soc., Vol. 94, No. 402, 1968.

8. K i n g, W. D. and F l e t c h e r, N. H. Pressures and stresses in freezing water drops. J. Phys. D. Appl. Phys. Vol. 6, No. 18, 1973.

9. P e d r o s o, R. I. and D o m o t o, G. A. Perturbation solutions for spherical solidification of saturated liquids. Trans. ASME, Ser. C.J. Heat Transfer Vol. 95, No. 1, 1973.

10. H u a n g C h i n g - L u n, and S h i h Y e n - R i n g. A perturbation method for spherical and cylindrical solidification. Chem. Engng Sci., Vol. 30, No. 8, 1975.

11. V a n D y k e, M. D. Perturbation Methods in Fluid Mechanics. Stanford Academic Press, New York, 1964.

12. T a o, L A. Generalized numerical solutions of freezing a saturated liquid in cylinders and spheres. AIChE Journal, Vol. 13, No. 1, 1967.

13. F a s t o v s k i i, V. G., P e t r o v s k i i, Iu. V. and R o v i n s k i i, A. E. Cryogenic Technique. Moscow, "Energiia", 1967.

14. C a r s l a w, H. S. and J a e g e r, J. C. Conduction of Heat in Solids. Oxford, Clarendon Press, 1947.

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