

Movement of liquid inclusions in soluble solids: An inverse Stokes' law

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The temperature distribution in an ellipsoidal liquid inclusion in a soluble solid, with a constant gradient far away from the liquid, and the movement of the liquid inclusion as a whole, which results as a consequence, are investigated. Since the solid is soluble and its concentration in solution is temperature dependent, any temperature variation in the liquid induces a concentration variation, which will transfer mass by diffusion, eroding the wall where the temperature is high and depositing solid material at the wall where the temperature is lower. This erosion or deposition will cause the liquid inclusion to move, and will, through absorption or release of latent heat, in turn affect the temperature distribution. From the result obtained for the general ellipsoid, specific results for prolate and oblate ellipsoids of revolution, the sphere, and circular and elliptic cylinders are obtained.

I. INTRODUCTION

Fluid inclusions in soluble solids are of interest not only to geologists but also to manufacturers of artificial precious stones such as emeralds. The manufacturers use a liquid called flux to dissolve at high temperatures the substance of the precious stone present in ores. When the substance cools, it will form the stone. In manufactured stones as well as in some natural precious stones, such as Columbian emerald, there are usually some fluid inclusions.

Geologists have noted the movement of fluid inclusions in soluble solids in the presence of a general temperature gradient, but no mathematical analysis has been given for it. This article provides such an analysis.

The temperature distribution in an ellipsoidal fluid inclusion and in the solid surrounding it will be found. In the analysis, latent heat absorbed when solid material is dissolved in the liquid, or released when it is deposited at the wall, is taken into account. From the result of the temperature distribution in the liquid, the speed of movement of the fluid inclusion can be deduced. By specialization, specific results for ellipsoids of revolution (prolate or oblate), the sphere, and circular and elliptic cylinders are obtained.

The velocity of the fluid inclusion is generally very small. Therefore the convective terms in the heat equation are negligible. Their effect is briefly discussed in the case of the sphere.

II. SOLUTION FOR THE GENERAL ELLIPSOID

Let the surface of the ellipsoid occupied by the liquid be given by

$$x^2/a^2 + y^2/b^2 + z^2/c^2 = 1, \quad (1)$$

where (x, y, z) are Cartesian coordinates and $a, b,$ and c the semiaxes of the ellipsoid in the coordinate directions.

For simplicity, we shall assume that the temperature in the solid far away from the liquid is

$$(T_s)_\infty = ax + T_0, \quad (2)$$

and assume, for the moment, that the fluid does not move in any direction. Then the temperature T_s in the solid and the

temperature T in the liquid satisfy

$$\nabla^2 T_s = 0, \quad \nabla^2 T = 0, \quad (3)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

At infinity, T_s must approach $(T_s)_\infty$. Inside the liquid, T must have no singularity. At the solid-liquid interface

$$T_s = T, \quad \frac{\partial T}{\partial n} = q \frac{\partial T_s}{\partial n}, \quad (4)$$

where n is the distance normal to the interface,

$$q = k_s/k, \quad (5)$$

k_s and k being the thermal conductivities of the solid and the liquid, respectively. The differential system to be solved thus consists of Eqs. (2)–(4).

Ellipsoidal coordinates (λ, μ, ν) are defined by the roots of θ in the equation

$$\frac{x^2}{a^2 + \theta} + \frac{y^2}{b^2 + \theta} + \frac{z^2}{c^2 + \theta} = 1, \quad (6)$$

considered as a cubic in θ . We let λ lie between ∞ and $-c^2$, μ between $-c^2$ and $-b^2$, and ν between $-b^2$ and $-a^2$. Thus the surfaces $\lambda = \text{const}$ are ellipsoids, $\mu = \text{const}$ are hyperboloids of one sheet, and $\nu = \text{const}$ are hyperboloids of two sheets. For $\theta = 0$, (6) becomes (1). Thus the surface conditions are applied at $\theta = 0$, or $\lambda = 0$.

Let the functions (of λ , therefore of $x, y,$ and z) $A, B,$ and C be defined by

$$A = \frac{abc}{2} \int_\lambda^\infty \frac{du}{(a^2 + u)\Delta}, \quad B = \frac{abc}{2} \int_\lambda^\infty \frac{du}{(b^2 + u)\Delta}, \quad (7)$$

$$C = \frac{abc}{2} \int_\lambda^\infty \frac{du}{(c^2 + u)\Delta},$$

where

$$\Delta = [(a^2 + u)(b^2 + u)(c^2 + u)]^{1/2}. \quad (8)$$

Then it can be shown that $Ax, By,$ and Cz all satisfy the Laplace equation. Furthermore, they tend to zero as λ ap-

proaches infinity, that is, as the distance from the origin increases indefinitely.

One assumes, then, that the temperature in the solid is

$$T_s = \alpha x + \alpha_1 A x + T_0 \quad (9)$$

and the temperature of the liquid is

$$T = \alpha' x + T_0. \quad (10)$$

The Laplace equations (3), the asymptotic condition for T_s , and the requirement of regularity for T are all satisfied, and we turn to the conditions (4), which for $\lambda = 0$ are

$$\alpha + A_0 \alpha = \alpha', \quad (11)$$

$$q[\alpha + (A_0 - 1)\alpha_1] = \alpha', \quad (12)$$

where A_0 is the value of A at $\lambda = 0$. In obtaining (12), it has been necessary to use

$$(\lambda_x, \lambda_y, \lambda_z) = \frac{2}{P} \left(\frac{x}{a^2 + \lambda}, \frac{y}{b^2 + \lambda}, \frac{z}{c^2 + \lambda} \right), \quad (13)$$

where

$$P = \frac{x^2}{(a^2 + \lambda)^2} + \frac{y^2}{(b^2 + \lambda)^2} + \frac{z^2}{(c^2 + \lambda)^2} \quad (14)$$

and

$$\frac{\partial}{\partial n} (x, y, z) = P_0^{-1/2} \left(\frac{x}{a^2}, \frac{y}{b^2}, \frac{z}{c^2} \right), \quad (15)$$

P_0 being the value of P at $\lambda = 0$.

The solution of (11) and (12) gives

$$\alpha_1 = \{(q - 1)/[q - (q - 1)A_0]\} \alpha, \quad (16)$$

$$\alpha' = \{q/[q - (q - 1)A_0]\} \alpha. \quad (17)$$

These results are already known (see Ref. 1, p. 427).

But if the solid is soluble, there will be a concentration c' (in units of mass per unit volume) in the liquid, and for the problem at hand, one can assume c' to be the saturation concentration, related to T by

$$c' = \epsilon(T - T_0) + c_0, \quad (18)$$

where c_0 is the value of c' at the origin where $T = T_0$. If the mass diffusivity of the solute in solution is κ_c , its mass is transported in the direction opposite to the temperature gradient at a rate of $\kappa_c \partial c'/\partial x$. The velocity with which the ellipsoidal boundary moves in the x direction, as a result of erosion and deposition, is then

$$u = \frac{\kappa_c}{\rho_s} \frac{\partial c'}{\partial x} = \frac{\kappa_c \epsilon \alpha'}{\rho_s}, \quad (19)$$

ρ_s being the density of the solid. The same velocity is obtained if one calculates the speed of erosion or deposition by considering the component of concentration gradient normal to the wall. The assumption of a stationary fluid is now abandoned, and replaced by the assumption that it moves with a (very small) uniform velocity.

Erosion and deposition involve latent heat, which in turn will affect the temperature distribution. The values of α , and α' given by (16) and (17) must therefore be recalculated. The normal gradient of T is $\alpha' \partial x/\partial n$, so that the solute dissolved (or deposited) per unit time per unit area is $\kappa_c \alpha' \epsilon \partial x/\partial n$. The strength of the heat sink per unit area of the boundary is then $m \alpha' \partial x/\partial n$, where

$$m = L \kappa_c \epsilon, \quad (20)$$

L being the latent heat per unit mass. Then (4) is replaced by

$$T_s = T, \quad k_s \frac{\partial T_s}{\partial n} = k \frac{\partial T}{\partial n} + m \alpha' \frac{\partial x}{\partial n}, \quad (21)$$

and (11) and (12) are replaced by

$$\alpha + A_0 \alpha_1 = \alpha', \quad (22)$$

$$k_s [\alpha + (A_0 - 1)\alpha_1] = k \alpha' + m \alpha',$$

the solution of which is

$$\alpha_1 = \{[q - (1 + mk^{-1})]/[q - (q - 1 - mk^{-1})A_0]\} \alpha, \quad (23)$$

$$\alpha' = \{q/[q - (q - 1 - mk^{-1})A_0]\} \alpha. \quad (24)$$

If the temperature gradient at infinity is in the y or z direction, the analysis is strictly similar, so that if

$$(T_s)_\infty = \alpha x + \beta y + \gamma z + T_0, \quad (25)$$

the solution is

$$T_s = \alpha x + \beta y + \gamma z + \alpha_1 A x + \beta_1 B y + \gamma_1 C z + T_0, \quad (26)$$

$$T = \alpha' x + \beta' y + \gamma' z + T_0, \quad (27)$$

where α_1 and α' are given by (23) and (24), and

$$(\beta_1, \beta') = \{ \beta/[q - (q - 1 - mk^{-1})B_0] \} \times (q - 1 - mk^{-1}, q), \quad (28)$$

$$(\gamma_1, \gamma') = \{ \gamma/[q - (q - 1 - mk^{-1})C_0] \} \times (q - 1 - mk^{-1}, q), \quad (29)$$

B_0 and C_0 being the values of B and C at $\lambda = 0$, respectively. The velocity of the fluid inclusion is

$$(u, v, w) = (\kappa_c \epsilon / \rho_s) (\alpha', \beta', \gamma'), \quad (30)$$

where u , v , and w are the velocity components in the directions of increasing x , y , and z , respectively. The speed is, in general, very small.

We now recall the assumption that the fluid moves with uniform velocity, i.e., as a solid. For this assumption not to be violated, the temperature in the fluid must be a function of height only. The cases in which this is true are:

Case 1: x -axis vertical, $\beta = 0 = \gamma$. In this case $v = 0 = w$.

Case 2: y -axis vertical, $\alpha = 0 = \gamma$. In this case $u = 0 = w$.

Case 3: z -axis vertical, $\alpha = 0 = \beta$. In this case $u = 0 = v$.

Case 4: $(\alpha', \beta', \gamma')$ are the direction numbers of the gravitational acceleration. The speed q of the fluid is, from (30),

$$(\kappa_c \epsilon / \rho_s) (\alpha'^2 + \beta'^2 + \gamma'^2)^{1/2}.$$

In all four cases the temperature gradient and the velocity of the fluid are uniform and vertical. Cases 1–3 may be considered special cases of Case 4, which is general.

We emphasize that these are all the possible cases if gravitational convection will not necessarily occur. Otherwise convection results, and the velocity of the fluid would not be uniform, and would be of much greater amplitude than that given by (30). While the problem of free convection and the problem of stability (involving double diffusion) are interesting in themselves, we exclude them from consideration in this paper.

III. EVALUATION OF A, B, AND C FOR SPECIAL FORMS OF THE ELLIPSOID

From solutions given for the general ellipsoid, solutions for its special forms can be obtained. For these forms, the functions A , B , and C can be evaluated directly, since the integrals defined by (7) are exactly integrable. From A , B , and C , one obtains A_0 , B_0 , and C_0 by putting λ equal to zero. The special cases are as follows:

Case (i). For a sphere of radius a ,

$$A = B = C = (1/3a^3)(a^2 + \lambda)^{3/2}. \quad (31)$$

This result agrees with a direct calculation by the use of a heat doublet in addition to $(T_s)_\infty$ for T_s .

Case (ii). For a prolate ellipsoid, for which $a > b = c$,

$$A = \frac{1 - e_0^2}{e_0^3} \left(\frac{1}{2} \ln \frac{1 + e'}{1 - e'} - e' \right), \quad (32)$$

$$B = C = \frac{1 - e_0^2}{2e_0^3} \left(\frac{e'}{1 - e'^2} - \frac{1}{2} \ln \frac{1 + e'}{1 - e'} \right), \quad (33)$$

where e_0 is e' for $\lambda = 0$, and

$$e' = [(a^2 - b^2)/(a^2 + \lambda)]^{1/2}. \quad (34)$$

Case (iii). For an oblate ellipsoid, for which $a = b > c$,

$$A = B = \frac{(1 - e_0^2)^{1/2}}{2e_0^3} \left(\cot^{-1} f - \frac{f}{f^2 + 1} \right), \quad (35)$$

$$C = \frac{(1 - e_0^2)^{1/2}}{e_0^3} \left(\frac{1}{f} - \cot^{-1} f \right), \quad (36)$$

where

$$f = \frac{c^2 + \lambda}{a^2 - c^2} = \frac{(1 - e'^2)^{1/2}}{e'}. \quad (37)$$

Case (iv). For a circular cylinder, with $a = \infty$, $b = c$,

$$A = 0, \quad (38)$$

$$B = C = [b^2/2(b^2 + \lambda)].$$

Case (v). For an elliptic cylinder, with $a = \infty$, $b > c$,

$$A = 0, \quad (39)$$

$$B = \frac{bc}{b^2 - c^2} \left[1 - \left(\frac{c^2 + \lambda}{b^2 + \lambda} \right)^{1/2} \right], \quad (39)$$

$$C = \frac{bc}{b^2 - c^2} \left[\left(\frac{b^2 + \lambda}{c^2 + \lambda} \right)^{1/2} - 1 \right]. \quad (40)$$

The results (32)–(36) are given in Carslaw and Jaeger (Ref. 1, p. 427), and can be obtained by direct integration.

IV. REMARKS

It can be shown that the slow movement of the fluid introduces, apart from the complications of a moving boundary, a small positive constant on the right-hand side of the second part of Eq. (3). This is tantamount to a uniform (very weak) heat sink in the liquid. In the simple case of the sphere, this results (in the next approximation) in a (secondary) temperature increasing with radial distance from the

origin. Two effects are produced. One is that the fluid is no longer in equilibrium, because of the change of its density with temperature, and a (very weak) convection will ensue. The other is that the (secondary) radial temperature field will erode the boundary through the dissolving action of the fluid, and the spherical cavity will be continually but very slowly enlarged. The liquid will continue to fill the cavity if the combined thermal expansion and expansion caused by pressure release are sufficient for it to do so without the pressure reaching the vapor pressure. When the vapor pressure is reached, evaporation will occur, and vapor will fill part of the cavity. Examination of geological specimens of salts indeed show fluid inclusions consisting of liquid as well as vapor. Migration of vapor–liquid inclusions in a solid in the presence of a temperature gradient was discussed by Anthony and Cline.²

Note that in this paper we have given a first approximation to the solution for the movement of liquid inclusions in a soluble solid, on the implicit assumption that the linear laws of thermal diffusion and mass diffusion hold. In all cases treated here the liquid inclusion moves in solid-body translation. An infinite number of possible shapes of the liquid inclusion is allowed, and the question of whether there is a unique shape of the inclusion does not arise.

Precise observations of the movement (or migration) of liquid inclusions in natural minerals are not available because the movement is extremely slow. Cline and Anthony³ observed the shape of a liquid (water) inclusion in potassium chloride in an isothermal field. To obtain the asymptotic shape (nonspherical) it was necessary to wait seven years! The shape is influenced by the structure of the mineral, which has privileged crystalline surfaces. Thus these surfaces do strongly affect this shape, and seem to impose a unique shape to the inclusion after a very long time. Cline and Anthony³ also calculated the shapes (which depend, among other things, on sizes) of liquid inclusions in the presence of a temperature gradient. But in their calculation the temperature distribution was not considered, whereas, as the calculation in this paper shows, it is very important. However, in the present calculation the effects of surface energy have been ignored. Thus the question of the asymptotic shape of a liquid inclusion, given its size, moving in a given soluble solid, including whether that shape is unique, must remain open. It seems that this rather new problem needs more attention of physicists and engineers.

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¹H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon, Oxford, 1959), pp. 425–426.

²T. R. Anthony and H. E. Cline, *Acta Metall.* 20, 247 (1972).

³H. E. Cline and T. R. Anthony, *J. Appl. Phys.* 48, 5096 (1977).