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DRYING GELS
VIII. Revision and review

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In Part I of this series, a method was presented for analysis of the stresses that develop during drying of a porous body, such as a gel. That formulation did not take proper account of the effect of local variations in network shrinkage on the pressure in the liquid. In this paper, an improved analysis is presented. The form of the original equations is generally preserved, except that the pressure in the liquid is shown to depend on both the shear and bulk moduli (or viscosities), rather than simply on the bulk modulus (or viscosity). The present modification is most important for the case of a warping plate or a film on a rigid substrate. The connection of this model with those of Biot and others is discussed.

1. Introduction

The earlier parts of this series of papers were based on an analysis [1] (hereafter called Part I) that relates the pressure in the liquid phase of a porous body to the permeability and viscoelastic properties of the solid phase. The drying stresses were shown to result from pressure gradients in the liquid that produce differential strain in the solid. The purpose of this paper is to correct an error in the original analysis of the pressure distribution. In most cases, the correction has a small effect on the final expressions for the stresses. This paper considers gels that are drying by evaporation at a constant rate; gels undergoing syneresis without evaporation [2], and those in which the transport of liquid involves both diffusion and flow [3], are treated separately.

The next section examines the constitutive equation on which the stress calculations are based, and notes its connection to models used by other workers. Section 3 contains the revised analysis and the new results for the pressure and stress in a viscous gel in the form of a plate, cylinder, sphere, and film on a rigid substrate. Sections 4 and 5 present the revised analyses for elastic and viscoelastic gels, respectively. The results are summarized in sect. 6.

2. Constitutive equation for gel

In a classic series of papers, Biot developed a theory for the deformation of saturated and unsaturated porous media, assuming the solid skeleton to be homogeneous and elastic [4], or homogeneous but anisotropic and viscoelastic [5,6], or heterogeneous, anisotropic, and viscoelastic [7]. The model was tailored to describe the propagation of acoustic waves through soil [8], although it could be applied to consolidation and drying of soil. It allows for compressibility of the solid and liquid phases, and for dissipation of energy within both phases, as well as by their relative movement. A number of other workers (e.g., refs. [9–11]) have developed related models, but Johnson and Chandler [12,13] have shown that the correct ones are special cases of, or approximations * to, Biot's. The model discussed in Part I is also a special case, but is particularly adapted to the case of

* For example, the "friction factor", f, in the model of Tanaka et al. [10] appears in place of D/η_L, but it has been shown [12] that it is actually equal to $(1-\rho)^2\eta_L/D$. Therefore, that model is an approximation that is valid when the volume fraction occupied by the solid phase is small (as it was, in fact, in the gels studied by Tanaka et al.).

drying of gels in that it allows for syneresis and for simple viscoelastic behavior. A considerable simplification of Biot's results is obtained by assuming that the solid and liquid phases (but not the network) are incompressible. We now show how the constitutive equation is obtained in this case.

Consider a cube of porous material with a relative density ρ and a volume fraction of porosity $1-\rho$. The area of each face is $A = A_S + A_L$, where $A_S = \rho A$ is the fraction of that area occupied by the solid phase and $A_L = (1-\rho)A$ is the fraction occupied by the liquid. We are interested in the constitutive equation for this material, which is to say, the relationship between the stresses applied and the strains that result. For the moment we assume that the liquid has been drained away, and consider the behavior of the solid phase alone. If the solid phase is elastic, the strains in the x, y, and z directions are given by [14]

$$\epsilon_x = \frac{1}{E_p}\left[\tilde{\sigma}_x - \nu_P(\tilde{\sigma}_y + \tilde{\sigma}_z)\right],$$
$$\epsilon_y = \frac{1}{E_p}\left[\tilde{\sigma}_y - \nu_P(\tilde{\sigma}_x + \tilde{\sigma}_z)\right], \tag{1a, b, c}$$
$$\epsilon_z = \frac{1}{E_p}\left[\tilde{\sigma}_z - \nu_P(\tilde{\sigma}_x + \tilde{\sigma}_y)\right],$$

where E_p is Young's modulus for the porous network and ν_P is Poisson's ratio. The stress, $\tilde{\sigma}_x$, $\tilde{\sigma}_y$, $\tilde{\sigma}_z$, are equal to the forces on the x-, y-, and z-faces of the cube divided by the area, A, of the face; that is, they represent the average stress on the face, not the stress concentrated on the solid phase. The volumetric strain is found by summing eqs. (1a–c):

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z = \tilde{\sigma}/3K_p, \tag{2}$$

where

$$\tilde{\sigma} = \tilde{\sigma}_x + \tilde{\sigma}_y + \tilde{\sigma}_z \tag{3}$$

is the hydrostatic stress and K_p is the bulk modulus of the porous network, defined by

$$K_p = \frac{E_P}{3(1-2\nu_P)} \tag{4}$$

Two more features are needed to complete the constitutive equation for a gel: allowance for the syneresis strain rate (which occurs in the absence of applied stress) and for the presence of the liquid phase. When a force F_x is applied to the face of the cube, a portion F_{xS} of that force is borne by the solid phase and a portion F_{xL} is borne by the liquid (and $F_x = F_{xS} + F_{xL}$). The pressure in the liquid phase, P_L, is equal to the force on the liquid divided by the area of the liquid, $P_L = -F_{xL}/A_L$. The negative sign is present because the pressure in the liquid is defined as positive when compressive (so a negative pressure means a tensile stress in the liquid), whereas a stress is defined as being negative when it is compressive. It is convenient to define a *stress* in the liquid, $P = F_{xL}/A_L$, which obeys the same sign convention as a stress in the solid phase. The total stress on the face of the cube is defined as $\sigma_x = (F_{xS} + F_{xL})/A$. Thus,

$$\sigma_k = \tilde{\sigma}_k + (1-\rho)P = \tilde{\sigma}_k - (1-\rho)P_L, \quad (k = x, y, z). \tag{5}$$

Suppose we use impermeable pistons (so the liquid cannot escape) to apply stresses σ_x, σ_y, σ_z (or forces F_x, F_y, F_z) to the faces of the sample cube. To find the resulting strains, we must adapt eq. (1) to allow for the presence of the liquid. Since the liquid has no rigidity, it can exert only hydrostatic stress; that is, it exerts the same force on each face of the cube, so it must affect each component of strain equally. Therefore we can write

$$\epsilon_x = \frac{1}{E_p}\left[\tilde{\sigma}_x - \nu_P(\tilde{\sigma}_y + \tilde{\sigma}_z)\right] + cP,$$
$$\epsilon_y = \frac{1}{E_p}\left[\tilde{\sigma}_y - \nu_P(\tilde{\sigma}_x + \tilde{\sigma}_z)\right] + cP, \tag{6a, b, c}$$
$$\epsilon_z = \frac{1}{E_p}\left[\tilde{\sigma}_z - \nu_P(\tilde{\sigma}_x + \tilde{\sigma}_y)\right] + cP,$$

where c is a constant to be determined. Since the pistons are impermeable and the components of the gel are incompressible, the volumetric strain must be zero, so eqs. (2) and (6) lead to

$$\epsilon = \tilde{\sigma}/3K_p + 3cP = 0. \tag{7}$$

From eqs. (3) and (5),

$$\tilde{\sigma} = \sigma - 3(1-\rho)P = -9K_p cP, \tag{8}$$

where the second equality follows from eq. (7) and the total hydrostatic stress is

$$\sigma = \sigma_x + \sigma_y + \sigma_z. \tag{9}$$

The average force on the liquid on each face of the cube is $F_L = (1-\rho)(F_x + F_y + F_z)/3$, and the stress in the liquid is $P = F_L/(1-\rho)A$, so $\sigma = (F_x + F_y + F_x)/A = 3P$, and eq. (8) leads to

$$cP = -\rho P/3K_p, \tag{10}$$

so eq. (6) becomes

$$\begin{aligned}
\epsilon_x &= \frac{1}{E_p}\left[\sigma_x - \nu_P(\sigma_y + \sigma_z)\right] - \frac{P}{3K_p},\\
\epsilon_y &= \frac{1}{E_p}\left[\sigma_y - \nu_P(\sigma_x + \sigma_z)\right] - \frac{P}{3K_p},\\
\epsilon_z &= \frac{1}{E_p}\left[\sigma_z - \nu_P(\sigma_x + \sigma_y)\right] - \frac{P}{3K_p}.
\end{aligned} \tag{11a, b, c}$$

From eq. (8) we see that $\tilde{\sigma} = 3\ \rho P = \rho\sigma$, so the total force on the solid phase is $\rho(F_x + F_y + F_z)$; that is, the load is borne by the solid phase in proportion to the volume fraction that it occupies. Equations (11) are equivalent to those obtained by Biot [4] and Geertsma [9], for the case of incompressibility of the solid and liquid components of the gel.

For a viscous network, the constitutive equations are obtained by application of the viscous analogy [15]: the strains on the left side of eq. (11) are replaced with strain rates, and E_p, ν_P, and K_p are replaced with F, N, and K_G, respectively; F is the uniaxial viscosity (which would be measured if the drained network were subjected to uniaxial stress), and N and K_G are the Poisson's ratio and bulk viscosity of the drained network, respectively. The bulk viscosity is defined by

$$K_G = F/[3(1-2N)]. \tag{12}$$

Finally, we identify the linear syneresis strain rate as $\dot{\epsilon}_s$ and modify the constitutive equation by adding that quantity to the right side of each line in eq. (11), and applying the viscous analogy. That is, we assume that the stress-induced strain rate and the inherent syneresis strain rate are linearly additive. Thus the constitutive equations for an isotropic viscous gel are

$$\begin{aligned}
\dot{\epsilon}_x &= \dot{\epsilon}_f + \frac{1}{F}\left[\sigma_x - N(\sigma_y + \sigma_z)\right],\\
\dot{\epsilon}_y &= \dot{\epsilon}_f + \frac{1}{F}\left[\sigma_y - N(\sigma_x + \sigma_z)\right],\\
\dot{\epsilon}_z &= \dot{\epsilon}_f + \frac{1}{F}\left[\sigma_z - N(\sigma_x + \sigma_y)\right],
\end{aligned} \tag{13a, b, c}$$

where $\dot{\epsilon}_f$ is called the free strain rate and is defined by

$$\dot{\epsilon}_f = \dot{\epsilon}_s - P/3K_G = \dot{\epsilon}_s + P_L/3K_G, \tag{14}$$

and the volumetric strain is

$$\dot{\epsilon} = \dot{\epsilon}_x + \dot{\epsilon}_y + \dot{\epsilon}_z = 3\dot{\epsilon}_f + \sigma/3K_G. \tag{15}$$

The superscript dot indicates the derivative with respect to time throughout this paper. These are the constitutive equations used in Part I. Biot [6] noted that viscoelastic (or viscous) behavior could be introduced by applying the viscoelastic analogy to eq. (11), which means that the stresses, strains, and constitutive parameters are interpreted as Laplace transforms of the viscoelastic functions. However, he did not carry the analysis through, nor did he consider syneresis.

To understand the meaning of the free strain rate, consider a small cube of gel in isolation. If there is stress P in the liquid, then the force on the liquid on the x-face of the cube is $F_{xL} = PA_L$, and Newton's first law requires that it be balanced by an equal and opposite force on the solid phase, $F_{xS} = \tilde{\sigma}_x A = -F_{xL}$. If there is tension in the liquid ($P > 0$), then there is a corresponding compression on the network $[\tilde{\sigma}_x = -(1-\rho)P]$, and eqs. (5) and (9) indicate that $\sigma = 0$. In that case, according to eq. (15), the volumetric contraction rate of the gel is given by the free strain rate. That is, $\dot{\epsilon}_f$ is the linear contraction rate of the network when the forces are locally in balance. In general, however, the cube of gel is not free, but is incorporated in a larger body in which the stress in the liquid varies from place to place; each cube of gel tries to shrink at its own free strain rate (corresponding to the pressure in its pores), but they must all accommodate one another and shrink at some average rate (corresponding to force balance across the whole body). Therefore, each cube is subjected to an additional stress imposed by neighboring regions that have different free strain rates, and the local strain rate differs from $\dot{\epsilon}_f$ because of this constraint.

In the form of eq. (13) the constitutive equations take account of the pressure in the liquid, as well as the stress on the solid phase. Moreover, they are in the familiar form used in analysis of thermal stresses, where the free strain is equal to $\epsilon_f = X\Delta T$, X is the linear thermal expansion coefficient, and ΔT is the change in temperature. The analogy between drying stresses and thermal stresses, which has been noted by several authors [9,16–18], is as follows. Suppose we blow cold air on the surface of a hot plate, so that the surface cools by ΔT. The surface tries to contract by $\epsilon_f = X\Delta T$ as it cools, but its shrinkage is inhibited by the hot interior region to which it is attached. The difference between the free strain (i.e., the amount the surface would contract if it were not connected to the rest of the body) and the actual strain gives rise to a tensile stress in the surface. Similarly, when a body dries by evaporation from the surface, capillary pressure (negative pressure, tensile stress) develops in the liquid, and the suction makes the solid network contract. As in the case of the cooling plate, the surface is not free to shrink (in response to the tension in the liquid), so stresses develop in the network and cracking may result.

3. Revised analysis for viscous gel

3.1. Free strain rate versus local strain rate

The theory presented here applies to stress development during evaporation of liquid from the pores of a viscoelastic material, such as a gel. The solid phase is exposed as liquid evaporates from the exterior surface, so liquid spreads from the interior to replace the solid/vapor interface with a less energetic solid/liquid interface. As the liquid stretches forward, it goes into tension. The liquid flows according to Darcy's law, which states that the flux is proportional to the pressure gradient in the liquid; it flows toward the surface, to relieve the tension in the liquid there. The tension in the liquid is supported by the solid phase, and the resulting compressive stress in the solid causes it to contract. The deformation of the solid network affects the pressure distribution by changing the volume of the pores in which flow occurs. The purpose of the theory is to understand how the interplay of flow and deformation affect the pressure in the liquid and the stress in the solid phase. In Part I of this series [1] it was shown that the pressure (P) in the liquid phase of the porous body is related to the volumetric strain rate ($\dot{\epsilon}$) by

$$\frac{D}{\eta_L}\nabla^2 P = -\dot{\epsilon}, \tag{16}$$

where D is the permeability, η_L is the viscosity of the liquid, and ∇^2 is the Laplacian operator. Equation (16) expresses the idea that the rate of accumulation of liquid in a region equals the rate of change of pore volume there (e.g., the network contracts locally when there is a net flux of liquid out of that region). To solve eq. (16) it is necessary to express the strain rate in terms of the pressure in the liquid. Various authors have done this by using empirical (nonlinear elastic) equations [19,20], or by assuming elastic behavior with the solid and liquid phases compressible [4,9] or incompressible [10,21], or allowing the network to be purely viscous [1] or viscoelastic [5–7,22,23]. When the network is assumed to be elastic, eq. (16) has the mathematical form of the diffusion equation. Philip [19] discusses at length the methods for solving the nonlinear version of that equation that results when the permeability and elastic properties vary with the porosity (and therefore with position in the body). In this section, we use the viscous constitutive equation developed in section 2; elastic and viscoelastic behavior are considered in sections 4 and 5, respectively.

The error in the original analysis [1] was that $3\dot{\epsilon}_f$ was substituted for $\dot{\epsilon}$ in eq. (16). This is incorrect, because the *local* strain rate ($\dot{\epsilon}$) does not depend simply on the *local* pressure (P), as explained above. We now proceed to derive a proper expression for σ in terms of P to use in eq. (16).

3.2. Flat plate

For a viscoelastic plate (including one that is purely viscous or elastic), the stress in the solid phase in the plane of the plate is given by [23]

$$\sigma_x = \sigma_y = C_N(P - \langle P \rangle), \quad (17)$$

where

$$C_N \equiv (1 - 2N)/(1 - N), \quad (18)$$

and $\langle P \rangle$ is the average pressure in the liquid. Since the surface of the plate is unconstrained, $\sigma_z = 0$ and eqs. (9) and (17) lead to

$$\sigma = 3(1 - \beta)(P - \langle P \rangle). \quad (19)$$

We have introduced the parameter

$$\beta = \frac{1 + N}{3(1 - N)} = \frac{K_G}{K_G + \frac{4}{3}G_G}, \quad (20)$$

where G_G is the shear viscosity of the porous body (drained of liquid), defined by

$$G_G = F/[2(1 + N)]. \quad (21)$$

Note that $C_N = 3(1 - \beta)/2$. We expect N to be small (since a gel network would be highly compressible with the liquid removed), so β will probably lie within $\frac{1}{3} \leqslant \beta \leqslant \frac{1}{2}$. It is convenient to identify the denominator of the last term in eq. (20) by

$$H_G \equiv K_G + \tfrac{4}{3}G_G = K_G/\beta. \quad (22)$$

As $N \to 0$, $H_G \to F$; thus H_G will be similar in magnitude to the uniaxial viscosity in a gel. Combining eqs. (14), (15), and (19) we find that the volumetric strain rate is

$$\dot{\epsilon} = 3\dot{\epsilon}_s - [(1 - \beta)\langle P \rangle + \beta P]/K_G. \quad (23)$$

This indicates that *the local strain rate depends on the average pressure, as well as the local pressure*, and this is the point that was neglected in Part I. The dependence on $\langle P \rangle$ arises because the regions of high and low pressure are connected, and cannot contract freely at their natural rate ($\dot{\epsilon}_f$). Now we need to obtain an expression for $\langle P \rangle$.

Consider a gel from which liquid is evaporating at the rate $\dot{V}_E$ [volume/(area × time)]. We are interested in the period during which the gel is so compliant that the solid phase retracts into the liquid as fast as it evaporates, so that the liquid/vapor meniscus remains at the exterior surface of the body. In clay technology, this is known as the constant rate period (because $\dot{V}_E$ is constant); it ends at the leatherhard point, when the solid phase stops shrinking and the meniscus enters the body. That is the point at which the stress reaches a peak and fracture is most likely [24]. During the constant rate period, the average contraction rate of the network must equal the rate of volume loss by evaporation, so we can write the following boundary condition:

$$-A\dot{V}_E = \int \dot{\epsilon}\, dV = \int 3\dot{\epsilon}_f\, dV, \quad (24)$$

where A is the area of the exterior surface of the body (over which evaporation occurs) and the integral is taken over the volume of the body. The second equality follows from eq. (15), assuming that K_G is constant and recognizing that force balance requires the average hydrostatic stress to be zero [25]:

$$\int \sigma\, dV = 0. \quad (25)$$

From eqs. (14) and (24), the average pressure, $\langle P \rangle$, is found to be

$$\langle P \rangle \equiv V^{-1} \int P\, dV = 3K_G\dot{\epsilon}_s + K_G\dot{V}_E A/V, \quad (26)$$

where V is the volume of the body. Equations (16), (23), and (26) lead to

$$\delta^2\nabla^2 P - \kappa^2 P = \kappa^2\left[(1 - \beta)H_G\left(\frac{\dot{V}_E}{V/A}\right) - P_s\right], \quad (27)$$

where δ is a characteristic dimension of the body and the parameter κ is defined by

$$\kappa(\delta) = \sqrt{\frac{\delta^2\eta_L}{DH_G}}. \quad (28)$$

This is related to the parameter α used in Part I, except that K_G is replaced by the quantity H_G, defined in eq. (22). That substitution turns out to be the principal difference between the original and the revised analyses of the pressure distribution. The parameter

$$P_s \equiv 3K_G\dot{\epsilon}_s \quad (29)$$

is the pressure that would have to exist in the liquid to prevent contraction by syneresis (i.e., eq. (23) shows that $\dot{\epsilon} = 0$ if $P = P_s$).

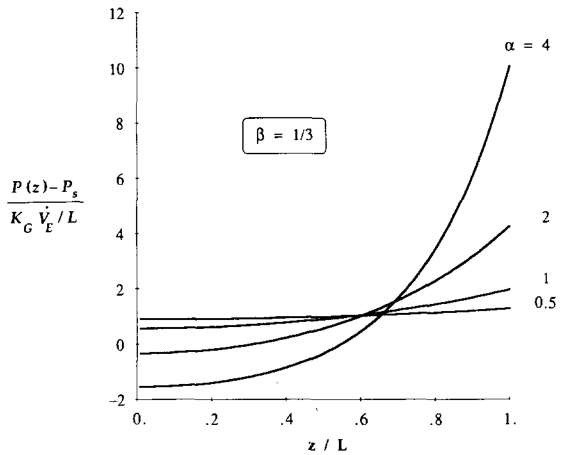

Fig. 1. Normalized pressure, $(P-P_s)/(H_G\dot{V}_E/L)$, in the liquid phase of a drying plate for several values of α, calculated from eq. (31) assuming $\beta=\frac{1}{3}$.

For a plate of thickness $2L$ with evaporation from both faces, $\delta=L$ and $A/V=1/L$, so eq. (27) reduces to

$$\frac{d^2P}{du^2}-\alpha^2P=\alpha^2\left[(1-\beta)H_G\left(\frac{\dot{V}_E}{L}\right)-P_s\right], \quad (30)$$

where $\alpha\equiv\kappa(L)$ and $u\equiv z/L$. The solution is

$$P=P_s-H_G\left(\frac{\dot{V}_E}{L}\right)\left[1-\beta-\frac{\alpha\cosh(\alpha u)}{\sinh(\alpha)}\right]. \quad (31)$$

The solution given in Part I did not include the term in $1-\beta$, and had K_G in place of H_G. (If β is set equal to 1, eq. (23) reverts to the form used in Part I; therefore, the original solution can always be obtained from the revised solution by substituting $\beta=1$.) Figure 1 illustrates the pressure distribution predicted by eq. (31) for several values of α. Neglecting syneresis, the stress in the liquid at the midline of the plate ($u=0$) is

$$P(0)=H_G\left(\frac{\dot{V}_E}{L}\right)\left[\frac{\alpha}{\sinh(\alpha)}-(1-\beta)\right]$$

$$\approx\begin{cases}K_G\left(\frac{\dot{V}_E}{L}\right), & \alpha\to0,\\ -K_G\left(\frac{\dot{V}_E}{L}\right)\left(\frac{1-\beta}{\beta}\right), & \alpha\to\infty\end{cases} \quad (32a, b)$$

which indicates that the stress becomes negative (i.e., the liquid is compressed) when α is large. (In the original solution, the stress at the midplane approached zero when α became large.) This occurs when low permeability prevents the liquid from flowing from the interior of the body; then the tensile stress in the liquid at the surface becomes high and causes contraction of the body that squeezes the liquid in the interior. Figure 1 shows that the pressure distribution approaches the high-α limit [eq. (32b)] when $\alpha\sim4$, and the low-α limit (eq. (32a)) when $\alpha\sim0.5$.

According to eqs. (17), (26), and (31), the stress in the plate is

$$\sigma_x=C_NH_G\left(\frac{\dot{V}_E}{L}\right)\left[\frac{\alpha\cosh(\alpha u)}{\sinh(\alpha)}-1\right], \quad (33)$$

which differs from the original solution [1,18] only in that H_G replaces K_G (both outside the bracket and in the definition of α). Note that $C_NH_G=2G_G$, so it is the shear viscosity of the network that appears outside the bracket. When α is small, eq. (33) reduces to

$$\sigma_x(u)\approx C_N\left(\frac{L\eta_L\dot{V}_E}{2D}\right)\left(u^2-\tfrac{1}{3}\right), \quad (34)$$

so the stress at the surface of the plate ($u=1$) is

$$\sigma_x(1)\approx C_N\left(\frac{L\eta_L\dot{V}_E}{3D}\right). \quad (35)$$

This is identical to the original solution, because the local pressure approaches the average pressure as $\alpha\to0$, and eq. (23) approaches $\dot{\epsilon}=3\dot{\epsilon}_f$.

3.3. Warping plate

If evaporation occurs from only one side of a plate (as is generally true in practice), the stress in the liquid rise monotonically from the "wet" side to the "drying" side. Consequently, the plate contracts faster on the drying side and warps, becoming concave toward the drying side [26]. In this case, the volumetric strain rate depends on the first moment of the pressure distribution, as well as on the average pressure, so the analysis is more complicated than for the flat plate. For a plate in the x–y plane with evaporation occurring from the face at $z = L$, but not from the face at $z = -L$, the strain rate in the plane of the plate can be written as [26]

$$\dot{\epsilon}_x = [P_s - \langle P\rangle - 3\langle Pu\rangle u]/3K_G, \tag{36}$$

where the average pressure is

$$\langle P\rangle = \tfrac{1}{2}\int_{-1}^{1} P(u)\,\mathrm{d}u, \tag{37}$$

and the first moment of the pressure distribution is

$$\langle Pu\rangle = \tfrac{1}{2}\int_{-1}^{1} P(u)u\,\mathrm{d}u, \tag{38}$$

and $u = z/L$. The strain rate normal to the plate is [26]

$$\dot{\epsilon}_z = 3\beta\dot{\epsilon}_f - 2N\dot{\epsilon}_x/(1-N). \tag{39}$$

The volumetric strain rate is found by substituting eqs. (36) and (39) into eq. (15); applying the boundary condition, eq. (26) with $A/L = \frac{1}{2}L$, the result is

$$\dot{\epsilon} = 3\beta\dot{\epsilon}_s - \frac{\beta P}{K_G} - (1-\beta)\left(\frac{\dot{V}_E}{2L}\right) - 3(1-\beta)\left(\frac{\langle Pu\rangle u}{K_G}\right). \tag{40}$$

The solution of eqs. (16) and (40) is discussed in Appendix 1. The rate of change of the radius of curvature, r, of the plate (normalized by the half-thickness, L) is given by [26]

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{L}{r}\right) = \tfrac{3}{2}\int_{-1}^{1}\dot{\epsilon}_f u\,\mathrm{d}u. \tag{41}$$

With eq. (A1.3) this becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{L}{r}\right) = -\left(\frac{\dot{V}_E}{2L}\right)\left\{\frac{\alpha^2[1-\tanh(\alpha)/\alpha]}{\alpha^2 - 3(1-\beta)[1-\tanh(\alpha)/\alpha]}\right\}, \tag{42}$$

where $\alpha \equiv \kappa(L)$. This result is plotted in fig. 2 together with the original solution [26] (in which the quantity in braces in eq. (42) was replaced by the quantity $[1-\tanh(\alpha)/\alpha]$). The revised solution is quite different from the original in this case. The magnitude of the curvature increases with α, because the greater pressure gradient causes more differential strain, and that produces more warping.

3.4. Cylinder

For a cylinder of radius r_0 with evaporation from the lateral surface (not from the ends), $\delta = r_0$

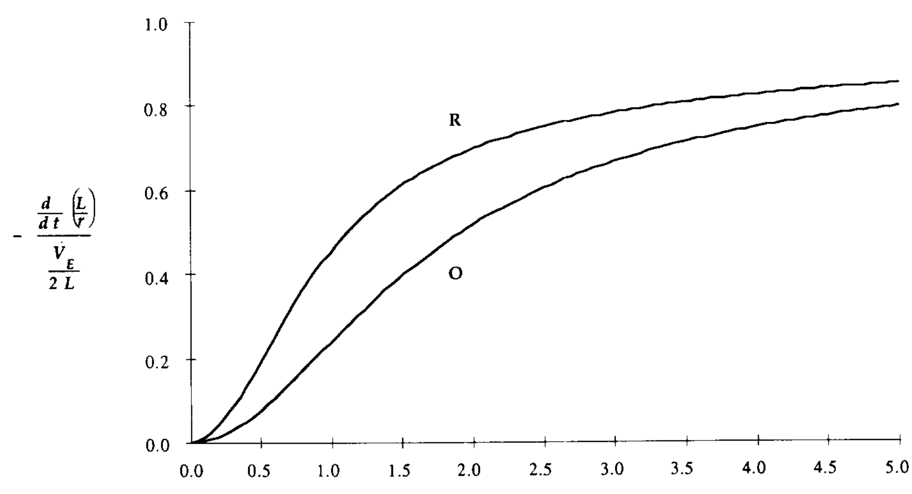

Fig. 2. Comparison of predictions of normalized curvature of warping plate calculated using revised solution (R), eq. (42) with $\beta = \frac{1}{3}$, and original solution (O) given in eq. (51) of ref. [26].

and $A/V = 2/r_0$, so eq. (27) reduces to

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}s}\left(s\frac{\mathrm{d}P}{\mathrm{d}s}\right) - \alpha_r^2 P = \alpha_r^2\left[(1-\beta)H_\mathrm{G}\left(\frac{2\dot{V}_\mathrm{E}}{r_0}\right) - P_\mathrm{s}\right] \tag{43}$$

where $s = r/r_0$ and $\alpha_\mathrm{r} \equiv \kappa(r_0)$. The solution is

$$P = P_\mathrm{s} - H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{r_0}\right)\left[2(1-\beta) - \frac{\alpha_r I_0(\alpha_r s)}{I_1(\alpha_r)}\right] \tag{44}$$

where I_0 and I_1 are modified Bessel functions of the first kind of order 0 and 1, respectively. The axial stress in the cylinder can be written as [27]

$$\sigma_z = C_N(P - \langle P\rangle), \tag{45}$$

so usings eqs. (26) and (44) we find

$$\sigma_z = C_N H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{r_0}\right)\left[\frac{\alpha_r I_0(\alpha_r s)}{I_1(\alpha_r)} - 2\right]. \tag{46}$$

As for the plate, this differs from the original solution [27] only in that H_G replaces K_G outside the bracket and in the definition of α_r.

3.5. Sphere

For a sphere of radius r_0 with evaporation from the surface, $\delta = r_0$ and $A/V = 3/r_0$, so eq. (27) reduces to

$$\frac{1}{s^2}\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2\frac{\mathrm{d}P}{\mathrm{d}s}\right) - \alpha_r^2 P = \alpha_r^2\left[(1-\beta)H_\mathrm{G}\left(\frac{3\dot{V}_\mathrm{E}}{r_0}\right) - P_\mathrm{s}\right], \tag{47}$$

where $s = r/r_0$ and $\alpha_r \equiv \kappa(r_0)$. The solution is

$$P = P_\mathrm{s} - H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{r_0}\right) \times\left[3(1-\beta) - \frac{\alpha_r^2 \sinh(\alpha_r s)}{s[\alpha_r\cosh(\alpha_r) - \sinh(\alpha_r)]}\right]. \tag{48}$$

The circumferential stress in the sphere can be written as [27]

$$\sigma_\theta = C_N(P - \langle P\rangle), \tag{49}$$

so using eqs. (26) and (48) we find that the stress at the surface of the sphere is

$$\sigma_\theta(r_0) = C_N H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{r_0}\right)\left[\frac{\alpha_r^2}{\alpha_r\coth(\alpha_r) - 1} - 3\right]. \tag{50}$$

Again, this differs from the original solution [27] only in that H_G replaces K_G outside the bracket and in the definition of α_r.

3.6. Film on rigid substrate

A film deposited on a rigid substrate cannot contract parallel to the plane (x–y) of the substrate, so $\dot{\epsilon}_x = \dot{\epsilon}_y = 0$. The stress in the plane of the film is [18]

$$\sigma_x = \sigma_y = -F\dot{\epsilon}_\mathrm{f}/(1-N) = -C_N(3K_\mathrm{G}\dot{\epsilon}_\mathrm{f}). \tag{51}$$

The volumetric strain comes entirely from contraction in the direction (z) normal to the substrate [18]:

$$\dot{\epsilon} = \dot{\epsilon}_z = 3\beta\dot{\epsilon}_\mathrm{f} = 3\beta(\dot{\epsilon}_\mathrm{s} - P/3K_\mathrm{G}). \tag{52}$$

In this case, the volumetric strain does not depend on the average pressure, but it does include a factor β that was neglected in the original solution [18]. Equations (16) and (52) lead to

$$\frac{\mathrm{d}^2P}{\mathrm{d}u^2} - \alpha^2 P = -\alpha^2 P_\mathrm{s}, \tag{53}$$

where $\alpha \equiv \kappa(L)$ and $u \equiv z/L$. This is the same as the original equation except for the definition of α. The solution of eq. (53) subject to the boundary condition

$$\frac{D}{\eta_\mathrm{L}}\frac{\mathrm{d}P}{\mathrm{d}z}\bigg|_{z=L} = \dot{V}_\mathrm{E} \tag{54}$$

(which indicates that the rate of the evaporation is matched by the flux to the surface obeying Darcy's law [1]) is

$$P = P_\mathrm{s} + H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{L}\right)\left[\frac{\alpha\cosh(\alpha u)}{\sinh(\alpha)}\right]. \tag{55}$$

Equations (14), (51), and (55) lead to

$$\sigma_x = C_N H_\mathrm{G}\left(\frac{\dot{V}_\mathrm{E}}{L}\right)\left[\frac{\alpha\cosh(\alpha u)}{\sinh(\alpha)}\right]. \tag{56}$$

Again, this differs from the original solution [18] in that H_G replaces K_G outside the bracket and in the definition of α. The difference is particularly significant in this case, because the flux defined in eq. (54) must equal the volumetric strain rate given by eqs. (24) and (52), and in the original solution it did not do so. The average strain rate of the film is

$$\frac{\dot{L}}{L} = \frac{1}{L}\int_0^L \dot{\epsilon}_z \, \mathrm{d}z = \beta\left(3\dot{\epsilon}_s - \frac{\langle P \rangle}{K_G}\right) = -\frac{\dot{V}_E}{L}, \quad (57)$$

where the second and third equalities follow from eqs. (52) and (55), respectively.

4. Elastic plate

The free strain in an elastic plate, neglecting syneresis, is given by

$$\epsilon_f = -P/3K_p, \quad (58)$$

where K_p is the elastic bulk modulus of the drained network, so the strain rate is

$$\dot{\epsilon}_f = -P/3K_p. \quad (59)$$

The volumetric strain is

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z = 2\epsilon_x + \epsilon_z. \quad (60)$$

By steps analogous to those leading to eq. (23) we find that

$$\epsilon = -\left[(1-\beta)\langle P \rangle + \beta P\right]/K_p, \quad (61)$$

so the boundary condition becomes

$$\langle \dot{\epsilon} \rangle = -\langle \dot{P} \rangle / K_p = -\dot{V}_E/L. \quad (62)$$

From eqs. (61) and (62) the volumetric strain rate is found to be

$$\dot{\epsilon} = -(1-\beta)\dot{V}_E/L - \beta\dot{P}/K_p. \quad (63)$$

Substituting this result into eq. (16) and rearranging leads to

$$\frac{\partial^2 P}{\partial u^2} - \frac{\partial P}{\partial \theta} = (1-\beta_E)\left(\frac{L^2\eta_L}{D}\right)\left(\frac{\dot{V}_E}{L}\right), \quad (64)$$

where $u = z/L$, the dimensionless time is defined as $\theta = t/\tau$, and

$$\tau \equiv \beta_E \eta_L L^2 / D K_p. \quad (65)$$

In the elastic case, β_E is given by

$$\beta_E = \frac{1+\nu_P}{3(1-\nu_P)} = \frac{K_p}{K_p + \frac{4}{3}G_p}. \quad (66)$$

Since both N and ν_p are expected to be small in a gel, $\beta \approx \beta_E \approx \frac{1}{3}$. In the original solution [21] the right-hand side of eq. (64) was zero.

The solution of eq. (64) is

$$\frac{P}{P_R} = \mu\left[\beta_E\theta + \frac{1}{2}\left(\frac{z^2}{L^2} - \frac{1}{3}\right) - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\cos\left(\frac{n\pi z}{L}\right)\mathrm{e}^{-n^2\pi^2\theta}\right], \quad (67)$$

where

$$\mu = \left(\frac{L^2\eta_L}{DP_R}\right)\frac{\dot{V}_E}{L}. \quad (68)$$

The average pressure is found from eq. (67) to be

$$\langle P \rangle = \mu\beta_E\theta P_R = K_p\dot{V}_E t/L, \quad (69)$$

and the stress is given by eq. (17) (with ν_P replacing N in the definition of C_N). As explained in ref. [28], the maximum stress occurs at the time (θ_R) when $P = P_R$ at the surface ($z = L$). The relationship between the evaporation rate (μ) and θ_R is found by setting the left-hand side of eq. (67) equal to 1:

$$\frac{1}{\mu} = \beta_E\theta_R + \frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2\theta_R\right). \quad (70)$$

The only difference between the revised and original solutions is the presence of β_E in the definition of θ.

5. Viscoelastic plate

Assuming that the stress relaxation behavior of the network can be represented by a Maxwell model [23] (the simplest possible case), the free strain rate in a viscoelastic plate is

$$\dot{\epsilon}_f = \dot{\epsilon}_s - \dot{P}/3K_p - P/3K_G, \quad (71)$$

and the volumetric strain rate is

$$\dot{\epsilon} = 3\dot{\epsilon}_f + \dot{\sigma}/3K_p + \sigma/3K_G. \quad (72)$$

The hydrostatic stress is related to the pressure by eq. (19) for a viscoelastic gel [23], so eq. (72) can be written as

$$\dot{\epsilon} = 3\dot{\epsilon}_s - \left[(1-\beta)\langle \dot{P}\rangle + \beta\dot{P}\right]/K_p - \left[(1-\beta)\langle P\rangle + \beta P\right]/K_G. \quad (73)$$

The boundary condition is

$$-\frac{\dot{V}_E}{L} = \frac{1}{L}\int_0^L \dot{\epsilon}\, dz = 3\dot{\epsilon}_s - \left(\frac{\langle \dot{P}\rangle}{K_p} + \frac{\langle P\rangle}{K_G}\right). \quad (74)$$

With eqs. (73) and (74), eq. (16) becomes

$$\frac{\partial^2 P}{\partial u^2} - \alpha^2(P - P_s) - \alpha^2(1-\beta)H_G\left(\frac{\dot{V}_E}{L}\right) = \frac{\partial P}{\partial \theta}, \quad (75)$$

where $\alpha \equiv \kappa(L)$, $u \equiv z/L$, and θ is the reduced time defined in sect. 4. The solution of eq. (75) (assuming that K_G and K_p are constant during drying) is [3]

$$\frac{P}{P_R} = \frac{\langle P\rangle}{P_R} - 2\mu\, e^{-\phi}\sum_{n=1}^{\infty}\left[\frac{(-1)^n \cos(n\pi u)}{\alpha^2 + n^2\pi^2}\right] \times e^{-n^2\pi^2\theta} + \mu\left[\frac{\cosh(\alpha u)}{\alpha \sinh(\alpha)} - \frac{1}{\alpha^2}\right], \quad (76)$$

where ϕ is another reduced time defined by $\phi = K_p t/K_G$ and μ is defined in eq. (68). This solution is obtained in Appendix B of ref. [3] (eq. (B.7), with $\mathscr{D} = 0$). The average pressure, which can be found from eqs. (74) and (76), is

$$\langle P\rangle = K_G\left(3\dot{\epsilon}_s + \dot{V}_E/L\right)\left(1 - e^{-\phi}\right). \quad (77)$$

When $K_G \to \infty$ (in which case α and $\phi \to 0$) the response of the network is purely elastic, and eq. (76) reduces to eq. (67); when the transient viscoelastic response is over ($\phi \to \infty$), eq. (76) reduces to the purely viscous solution, eq. (31). From eqs. (17), (76), and (77), the stress in a viscoelastic plate is found to be

$$\sigma_x = C_\nu H_G\left(\frac{\dot{V}_E}{L}\right)\left\{\frac{\alpha\cosh(\alpha u)}{\sinh(\alpha)} - 1 - 2\alpha^2 \times e^{-\phi}\sum_{n=1}^{\infty}\left[\frac{(-1)^n\cos(n\pi u)}{\alpha^2 + n^2\pi^2}\right] e^{-n^2\pi^2\theta}\right\}, \quad (78)$$

or, in terms of the function H defined in ref. [23],

$$\sigma_x = C_\nu H_G\left(\frac{\dot{V}_E}{L}\right)\left[\alpha\int_0^{\phi} H(z, \phi')\, d\phi' - \left(1 - e^{-\phi}\right)\right], \quad (79)$$

where C_ν is given by eq. (18) with N replaced by ν_P. Again, this differs from the original solution [23] in that H_G replaces K_G outside the bracket and in the definition of α.

6. Conclusions

The tensile stress, P, in the liquid in the pores of a drying body causes contraction of the solid phase, and the pressure distribution is influenced by that contraction. In earlier parts of this series, the pressure distribution was calculated by assuming that there was local force balance between the pressure in the liquid and the stress in the network. However, that is generally not true. In this paper we taken account of the fact that the local volumetric strain rate of the network, $\dot{\epsilon}$, depends on the average pressure, as well as the local pressure. When the correct expression is used for $\dot{\epsilon}$, the final expression for the stress differs from the original solution in that the bulk modulus or viscosity is replaced by a term that involves the bulk *and* shear modulus or viscosity. In the case of a purely elastic body, the revised analysis is a special case of that developed by Biot [4]. For simplicity, the solutions for the pressure and the stress are based on the assumption that the properties of the gel are independent of time and position; if that is not acceptable, the equations must be written in a more general form (see the example in Appendix 2) and solved numerically using the known variation of the properties.

Appendix 1: Pressure distribution in warping plate

When eq. (40) is substituted into eq. (16) the differential equation has the form

$$\frac{d^2 P}{du^2} - \alpha^2 P = a + bu, \quad (A1.1)$$

where a and b are constants. This must be solved subject to the boundary conditions

$$\frac{D}{\eta_L}\frac{\mathrm{d}P}{\mathrm{d}z} = \begin{cases} \dot{V}_E, & z = L, \\ 0, & z = -L. \end{cases} \tag{A1.2}$$

Equation (A1.1) is solved by elementary methods, leading to an expression for P involving the quantity $\langle Pu \rangle$. Multiplying the solution by u and integrating, it is possible to solve for $\langle Pu \rangle$. Then the pressure can be written as

$$P = P_s - (1-\beta)\left(\frac{H_G \dot{V}_E}{2L}\right)(1 + c_0 u) + c_1\,\mathrm{e}^{\alpha(1+u)} + c_2\,\mathrm{e}^{-\alpha(1+u)}, \tag{A1.3}$$

where the constants are given by

$$c = 1 - \tanh(\alpha)/\alpha,$$

$$c_0 = c/[1 - 3(1-\beta)c/\alpha^2],$$

$$c_1 = \left(\frac{H_G \dot{V}_E}{2L}\right)\left(\frac{\alpha}{2}\right) \times \left[\coth(\alpha) - 1 + \frac{1 - \tanh(\alpha)}{1 - 3(1-\beta)c/\alpha^2}\right],$$

$$c_2 = \left(\frac{H_G \dot{V}_E}{2L}\right)\left(\frac{\alpha}{2}\right) \times \left[\coth(\alpha) + 1 - \frac{1 + \tanh(\alpha)}{1 - 3(1-\beta)c/\alpha^2}\right]. \tag{A1.4}$$

The linear term in u did not appear in the original solution [26], because the effect of bending on the volumetric strain was ignored. The original solution is recovered by setting $\beta = 1$ in eqs. (A1.3) and (A1.4), in which case $c_1 = c_2$ and the linear term is eliminated.

Appendix 2: Viscous plate with spatially varying properties

If the properties of the body vary with position, eq. (16) becomes

$$\nabla \cdot \left(\frac{D}{\eta_L}\nabla P\right) = -\dot{\epsilon}. \tag{A3.1}$$

For a plate with F and N varying with z, the stress is [18]

$$\sigma = 2\sigma_x = \left(\frac{2F}{1-N}\right)(\dot{\epsilon}_x - \dot{\epsilon}_f), \tag{A3.2}$$

where

$$\dot{\epsilon}_x = \frac{\int_0^L [F\dot{\epsilon}_f/(1-N)]\,\mathrm{d}z}{\int_0^L [F/(1-N)]\,\mathrm{d}z}. \tag{A3.3}$$

Using eqs. (14) and (A3.2) in eq. (A3.3), eq. (15) becomes

$$\dot{\epsilon} = \beta\left(\frac{P_s - P}{K_G}\right) + (1-\beta)\left[\frac{\int_0^L (1-\beta)(P_s - P)\,\mathrm{d}z}{\int_0^L (1-\beta)K_G\,\mathrm{d}z}\right]. \tag{A3.4}$$

Eq. (A3.1) must be solved numerically using eq. (A3.4).

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