



## Accuracy of approximate driving force for intergranular pressure solution

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The process of intergranular pressure solution (IPS) has been described theoretically in terms of a number of distinct models, built upon a certain conceptual picture of an intergranular contact zone, in which a process of solute transfer from the solid grain to a grain boundary fluid (solvent) phase, and in it towards the rim of the contact, is kept going. In the first such model, Weyl (1959) pictured a thin film of an aqueous grain boundary fluid phase as transport avenue for the dissolved solid, and the hypothesis of an adsorbed solution-film, capable of transmitting intergranular normal and shear stresses, has subsequently been adopted by a number of authors, notably by Rutter (1976), Robin (1978), and more recently by Hickman & Evans (1995) and others. Seeking to explain IPS in thermodynamic terms, Paterson (1973) invoked Kamb's (1959) notion of a porous 'inert constraining solid' for the grain-to-grain contact zone, in which the grain boundary liquid phase could dissolve the solid phase, the latter being kept in a state of non-hydrostatic stress by the assumed 'loading frame'. A Gibbs-type equilibrium analysis applied to Weyl's model (Robin, 1978) as well as Paterson's model gave as a result the expression  $\mu = \mu_0 + f^s - f_0^s + p(1/\rho^s - 1/\rho_0^s) - (\sigma_n + p)/\rho^s$  for the mass-specific solute chemical potential equilibrating the stressed solid and the solution phase;  $f^s$  and  $\rho^s$  denote the specific Helmholtz-free energy and mass density of the pure solid,  $p$  the fluid pressure, and  $\mu_0 = f_0^s + p/\rho_0^s$  the chemical potential equilibrating solid and solution in a hydrostatic reference state at pressure  $p$ . On the basis of this equilibrium model, Rutter (1976, 1983) was able to obtain a pressure solution 'creep law', but as Lehner & Bataille (1984/85) pointed out subsequently, the underlying equilibrium assumption implied nothing else but an *a priori* assumption of grain boundary diffusion rate controlled IPS. Accordingly, if one wished to

allow for a competition between grain boundary diffusion and dissolution as potentially rate-controlling processes, Paterson's Stefan-type equilibrium assumption had to be dropped and IPS had to be described as a nonequilibrium process. In such a description, a narrow boundary layer is imagined to be cut smoothly from the immediate contact zone of two adjacent grains, allowing the use of well-defined quantities  $f^s, \rho^s, \sigma_n$  in the solid phase along the cuts. The interior of this boundary layer would comprise, both solid and grain boundary fluid phase and would contain the actual solid/liquid solution interface. Following Raj (1982), Lehner & Bataille proposed an island/channel structure for the solid phase within that boundary layer, harbouring a mobile liquid phase within the channels and possible in an adsorbed state at islands, where the solid surfaces of neighbouring grains were in contact. This corresponded to a physical realisation of the Kamb/Paterson loading frame, in which the solid phase was allowed to dissolve in the liquid phase and be transported away by grain boundary diffusion. The existence of a dynamically stable island-channel structure at grain-to-grain contacts during active IPS is suggested by experimental observations on different grain mineral species (see, e.g., Renton *et al*, 1969; Schutjens & Spiers, 1990, 1999; Cox & Paterson, 1991; De Meer & Spiers, 1999), although difficulties with the direct observation of these microstructures are considerable and their occurrence is to some extent controlled by the type of experiment (cf. the discussion in Schutjens & Spiers, 1999). In practice, i.e., in the field, the role of 'impurities' is likely to be essential. The presence of clay minerals and its effect on pore fluid chemistry is thought to be enormous and may well tip the balance decisively in favour of a dynamically roughened state of intergranular contacts (Houseknecht, 1988).

Based on this picture of a grain-to-grain contact zone, a nonequilibrium thermodynamic description of IPS could now be given (Spiers & Schutjens, 1990; Lehner, 1990), involving the entire path of a solid 'particle' from its entry into the contact zone at potential  $\mu_n^s(r) \equiv f^s - \sigma_n/\rho^s$ , at a distance  $r$  from the center of a circular grain-to-grain contact, to its exit in a dissolved state at potential  $\mu(a)$  at the rim  $r = a$  of the contact. The drop  $\mu_n^s(r) - \mu(a)$  in its chemical potential across the entire path thus constitutes the thermodynamic driving force for an element of solute mass in the process of IPS. Reintroducing the solute chemical potential  $\mu(r)$  at distance  $r$  along the contact, this driving force may then be written as the sum  $[\mu_n^s(r) - \mu(r)] + [\mu(r) - \mu(a)]$  of the forces driving the solution and grain boundary diffusion processes— the first being disregarded, if one adopts Paterson's equilibrium condition. Assuming linear relations between these driving forces and their conjugate rates of grain boundary solution and diffusion, respectively, and expressing these rates in terms of a uniform grain convergence rate  $\dot{\lambda}$ , it can be shown that (see, e.g., Lehner

& Leroy, 2004)

$$\mu_n^s(r) - \mu(r) = -(kT/\rho^s\Omega^s)\tau_S\dot{\lambda}, \quad (1)$$

$$\begin{aligned} \mu(r) - \mu(a) &\approx (kT/\rho^s\Omega^s) \ln C(r)/C(a) \\ &\approx (kT/\rho^s\Omega^s)[C(r) - C(a)]/C(a) \\ &= -8(a2/d2 - r2/d2)(kT/\rho^s\Omega^s)\tau_D\dot{\lambda} \end{aligned} \quad (2)$$

where  $\tau_S = d/K^{gb}$  and  $\tau_D = \rho^s d3/[32\rho^f C(a)\delta D_{gb}]$  are characteristic times associated with grain boundary solution and diffusion, respectively. ( $kT$  = Boltzmann factor;  $\Omega^s$  = molecular volume of solid;  $C$  = solute mass fraction,  $d$  = grain diameter;  $K^{gb}$  = phenomenological rate constant for grain boundary dissolution;  $\rho^f$  = fluid density;  $\delta$  = effective grain grain boundary width open to grain boundary diffusion;  $D_{gb}$  = grain boundary diffusivity.)

Combining (1) & (2), multiplying the result by  $\rho^s$ , subtracting the reference potential  $\rho_0^s\mu_0 = \rho_0^s f_0^s + p$ , and making use of the definition of  $\mu_n^s$ , one gets

$$\begin{aligned} \rho^s\mu_n^s(r) - \rho_0^s\mu_0 &= \psi^s - \psi_0^s - \sigma_n - p \\ &= \frac{kT}{\Omega^s} \left\{ \frac{C(a) - C_0}{C_0} - \left[ 8 \left( \frac{a2}{d2} - \frac{r2}{d2} \right) \tau_D + \tau_S \right] \dot{\lambda} \right\} \end{aligned} \quad (3)$$

where  $\psi^s = \rho^s f^s$  is the Helmholtz free energy (or strain energy) density of the pure solid phase. Averaging this over the grain-to-grain contact area  $a^2\pi$  and rearranging, we arrive at the following expression for the rate of grain convergence

$$\dot{\lambda} = \frac{-1}{4(a2/d2)\tau_D + \tau_S} \left\{ \frac{\bar{\psi}^s - \psi_0^s - \bar{\sigma}_n - p}{kT/\Omega^s} - \frac{C(a) - C_0}{C_0} \right\} \quad (4)$$

This is a nonlinear pressure solution ‘creep law’, the ratio  $a/d$  depending on  $\lambda$ . The term in parentheses constitutes the ‘driving force’ of IPS, its second, chemical part being responsible for the coupling of solute transport and deformation. It is usually assumed that the free energy term contributes little to the driving force and may be neglected against the effective stress term. This leads to the approximate result (cf. Lehner, 1995; Lehner & Leroy, 2004)

$$\dot{\lambda} \approx \frac{1}{4(a2/d2)\tau_D + \tau_S} \left\{ \frac{\bar{\sigma}_n + p}{kT/\Omega^s} + \frac{C(a) - C_0}{C_0} \right\} \quad (5)$$

In this study we examine the accuracy of this approximation. To this end, we eliminate  $\dot{\lambda}$  from Eqs. (3) and (4), to obtain

$$\sigma_n(r) = -p - \left(\frac{kT}{\Omega^s}\right) \frac{\Delta C}{C_0} + \Delta\psi^s(r) - \frac{8\left(\frac{a^2}{d^2} - \frac{r^2}{d^2}\right)\tau_D + \tau_S}{4\frac{a^2}{d^2}\tau_D + \tau_S} \left[ \Delta\bar{\psi}^s - \bar{\sigma}_n - p - \left(\frac{kT}{\Omega^s}\right) \frac{\Delta C}{C_0} \right] \quad (6)$$

Assume fixed value of  $p_1 = p + (kT/\Omega^s)(\Delta C/C_0)$  and fixed values  $[\Delta\bar{\psi}^s - \bar{\sigma}_n - p_1] = A$  and solve elastic boundary value problem for the stresses  $\sigma_{ij}|_0$ , for a given contact geometry, for boundary condition furnished by the zero order approximation

$$\sigma_n(r)|_0 = -p_1 - \frac{8\left(\frac{a^2}{d^2} - \frac{r^2}{d^2}\right)\tau_D + \tau_S}{4\frac{a^2}{d^2}\tau_D + \tau_S} \times A$$

in which  $\Delta\psi^s(r)$  is set equal to zero. Then determine  $\Delta\psi^s(r)|_0$  from  $\sigma_{ij}(r)|_0$  and compute first order approximation by solving the elastic boundary value problem for boundary condition furnished by first order approximation

$$\sigma_n(r)|_1 = \Delta\psi^s(r)|_0 - p_1 - \frac{8\left(\frac{a^2}{d^2} - \frac{r^2}{d^2}\right)\tau_D + \tau_S}{4\frac{a^2}{d^2}\tau_D + \tau_S} \times A$$

and so on, iterating until convergence is achieved. Integration of the last solution should of course confirm the equality  $\{\Delta\bar{\psi}^s - \bar{\sigma}_n - p_1\} = A$ . This integration should be run along with each step as a convergence criterium. Having obtained  $\Delta\psi^s(r)|_n$  after the  $n$ -th iteration step, we can then evaluate the error involved in its neglect.

The results of a finite element computation implementing this iterative scheme will be discussed.

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