

# Piezochemistry

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A material's chemical potential is the ratio of a change in free energy to a change in mass. To envisage a chemical potential one needs to have in mind a *process*, not an inert quantity of material passively occupying space. For a sample in a nonhydrostatic stress state, the process of change of mass can be associated with one set of parallel planes in the material or with another set at different orientation: chemical potential is a multi-valued, direction-dependent quantity.

Along these lines, a shear stress is a gradient of chemical potential with respect to orientation, and a shear strain rate is a flux of material down that gradient through a specific plane in space. Gibbs focussed attention on an ideal material in which both these fluxes are zero, but geological materials are not ideal in that sense. During metamorphism, grain boundaries are active sites; along with creep, diffusion and change of phase driven by non-hydrostatic stress must be common processes. The governing equations follow from a crucial postulate by Ramberg.

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## Introduction

Piezochemistry, or nonhydrostatic thermodynamics, is the study of chemical behavior of materials under nonhydrostatic stress. In this field, as in so many, Hans Ramberg's penetration opened new vistas, indicating the path by which progress could be made. The following paragraphs contain both retrospect and prospect. It is hoped thus to serve the purposes of the volume, honoring Hans by sketching developments to which his insight has led.

## Retrospect

Gibbs' discussion (1876–8) of a solid in contact with fluids at three different hydrostatic pressures is notoriously circumspect: conclusions are reached only about the chemical potential of the material of the solid in the liquid phases. The question what chemical potential could possibly be assigned to the material of the solid in the solid phase was left unanswered: there obviously is no single value that puts the solid in equilibrium simultaneously with fluid 1 at pressure  $p_1$  and with fluid 2 at pressure  $p_2$ . The resolution of this difficulty – the idea that a material's chemical potential can have several values simultaneously at the same point – is contained in the pair of papers by Ramberg eighty years later (1959, 1963).

The crucial thought is even so slightly concealed. Ramberg focuses on the PV term: "In the following discussion the term PV will, for the sake of clarity, be identified as the *potential spatial energy*" (1963, p. 242). He first gives attention specifically to processes at an interface: ". . . the quantities  $P_xV$ ,  $P_yV$  and  $P_zV$  are identical to the free-energy increments, relative to the unstressed solid, associated with disintegration or growth along the direction of the principal axes of stress" (p. 243). This thought, which can be expressed as

$$\mu_x = \mu_0 + P_xV$$

$$\mu_y = \mu_0 + P_yV$$

$$\mu_z = \mu_0 + P_zV$$

is close to that of Gibbs. But the next sentence breaks new ground: "The quantities  $P_xV$ ,  $P_yV$  and  $P_zV$  may also be regarded as the potential spatial energy of the solid in the directions of the principal axes of stress" – *three* quantities are named and they are attributes *of the solid*. Ramberg did not state "The quantities  $\mu_x$ ,  $\mu_y$  and  $\mu_z$  are the chemical potentials of the solid in the directions of the principal axes of stress" but this is a reasonably direct inference from what he did state. Thus, in one sentence, he broke out of the Gibbsian frame and provided the foundation for non-hydrostatic thermo-

dynamics – which, if we drop idealizations and grapple with the real world, is the only thermodynamics there is.

That crucial sentence was developed, as far as one can tell, in isolation from two streams of work that were flowing concurrently, but to trace developments from 1963 onward, one must put the sentence in its environment. On one hand there was work in 'thermodynamics of irreversible processes' with Prigogine as then current exemplar (Prigogine 1967), and on the other hand there was 'rational thermodynamics,' being pursued primarily by associates of Truesdell (1984). The former stream provided the concept of an *associated equilibrium state*: for any real nonequilibrium state that is of interest, one may imagine an equilibrium state that resembles it as closely as possible and use the chemical potential of the latter – (which is fully defined in Gibbsian manner) – for predicting what processes will be running in the former. The second stream provided the concept of a *chemical-potential tensor* (Bowen 1967, 1976). Bowen does not refer to Ramberg's work but the tensor he introduced is the tensor defined by  $\mu_x$ ,  $\mu_y$  and  $\mu_z$  as principal values.

Thus the three streams come together. A non-hydrostatic stress state is a nonequilibrium state for which, strictly, the chemical potential is history-dependent and not a function solely of the present state. But for the three principal stress directions, we may imagine three separate equilibrium states at hydrostatic pressures  $P_x$ ,  $P_y$  and  $P_z$ . In these imagined states we define three chemical potentials  $\mu_x$ ,  $\mu_y$  and  $\mu_z$ . At a material point inside a crystal,  $\mu_x$  is an equilibrium potential associated by an act of imagination with the direction  $x$ ,  $\mu_y$  is an equilibrium potential associated with the direction  $y$  etc. The real behavior of the sample – both its deformation and its chemical responses – can be predicted from the trio of values thus formed. Also the tensor treatment we are accustomed to for stresses can be applied, if desired, to chemical potentials: except for the base-value  $\mu_0$ , the tensor  $\underline{\mu}$  is simply  $V$  times the tensor  $\underline{\sigma}$ . (But in the view presented here, the tensor  $\underline{\mu}$  is much more artificial. The three principal stresses are actually present simultaneously in the material, whereas the three principal values,  $\mu_x$ ,  $\mu_y$  and  $\mu_z$  are created by three separate acts of the imagination and cannot possibly coexist. Thus the tensor  $\underline{\sigma}$  is in some sense real, whereas the tensor  $\underline{\mu}$  is a wholly artificial construct – but useful nonetheless.)

It remains to remark that certain aspects become more clear if we plot quantities using the orientation of a plane as a variable. The uses of this approach will now be explored and will carry us from retrospect to prospect.

### The orientation of a plane as a variable

As a first example, consider two planes whose normals make a small angle  $\delta\Theta$ , on which the normal stresses are  $\sigma$  and  $\sigma'$  (Fig. 1). Balancing forces (conservation of momentum) shows that  $2\tau = d\sigma/d\Theta$ . For a general statement we need to think of one normal as a unit vector  $\underline{n}$ , and the angle  $\delta\Theta$  as a small change  $\delta\underline{n}$  parallel to the plane, so that the second vector is a unit vector  $\underline{n} + \delta\underline{n}$ . Then the relation becomes:

$$2\tau_{\underline{n}\delta\underline{n}} = \frac{d}{|d\underline{n}|} \sigma_{\underline{n}\underline{n}} \tag{1}$$

Notation aside, the point is that a shear stress is a gradient of normal stress with respect to orientation as a variable.

For a second example, we combine equation (1) with the conclusion from the preceding section, that for any direction  $\underline{n}$  there is an associated equilibrium potential  $\mu_{\underline{n}\underline{n}}$  where

$$\mu_{\underline{n}\underline{n}} = \mu_0 + v\sigma_{\underline{n}\underline{n}} \tag{2}$$

The result is

$$\tau_{\underline{n}\delta\underline{n}} = \frac{1}{2v} \cdot \frac{d}{|d\underline{n}|} \mu_{\underline{n}\underline{n}} \tag{3}$$

with a more unfamiliar connotation: *a shear stress is a gradient of chemical potential with respect to orientation as a variable.* The idea that the normal

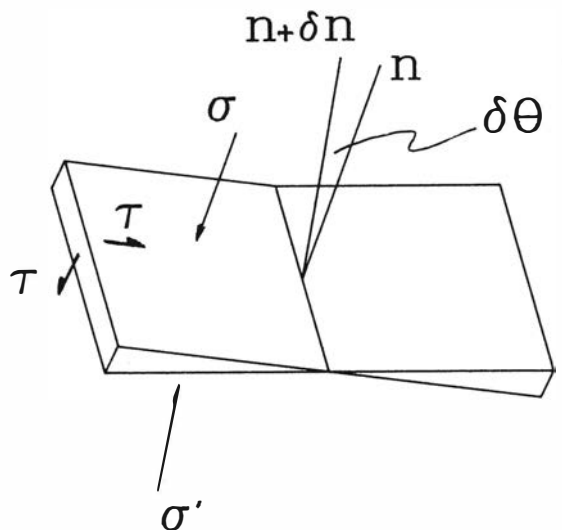


Fig. 1. Stresses on a wedge-shaped element of angular magnitude  $\delta\Theta$ .

stress exerted by, for example, a weight on a table results from a gradient of gravitational potential with position is commonplace, and we see in equation (3) a useful parallel idea.

Prospect

The key Ramberg provided gives access to a wide terrain, as yet unexplored. Here just a few salient features are indicated.

1. Equation (3) applies regardless of the rheology of the material but takes a particularly interesting form if we focus on the material's viscosity  $N$ , defined by  $\tau_{ndn} = N\dot{\gamma}_{ndn}$  or  $N \cdot d(\gamma_{ndn})/dt$  (factor of 2 optional). The result is

$$\frac{d\gamma_{ndn}}{dt} = K \cdot \frac{d}{|dn|} \mu_{nn} \tag{4}$$

where the factor  $1/2NV$  has been condensed to  $K$  to bring out most clearly the parallel with Darcy's Law, Fick's Law, etc. Shear straining is a flux of material with respect to orientation, just as percolation or diffusion is a flux of material with respect to position along some spatial direction.

2. As indicated in Fig. 2 and discussed more extensively elsewhere (Bayly 1987), the shear-strain fluxes just discussed lead to net loss of material from some orientations i.e. to shortening strains along some directions. Again in parallel with spatial-gradient equations, the linear strain  $de_{nn}$  follows

$$\frac{de_{nn}}{dt} = K \frac{d^2}{|dn|^2} \mu_{nn} \tag{5}$$

3. For flux of material driven by gradients  $d\mu/dx$  of potential with respect to position, conservation in three dimensions involves a Laplacian expression

$$\frac{dQ}{dt} = K' \left( \frac{\partial^2 \mu}{\partial x^2} + \frac{\partial^2 \mu}{\partial y^2} + \frac{\partial^2 \mu}{\partial z^2} \right) \tag{6}$$

Correspondingly, the total shortening  $de/dt$  along a given direction is a sum of terms of the type shown in equation (5)

$$\left( \frac{de_{nn}}{dt} \right)_{total} = K \left( \frac{\partial^2 \mu_{nn}}{|\partial n_\alpha|^2} + \frac{\partial^2 \mu_{nn}}{|\partial n_\beta|^2} \right) \tag{7}$$

Here  $dn_\alpha$  can be chosen arbitrarily, to lie in any plane  $\alpha$  that contains the vector  $n$ , but then  $dn_\beta$

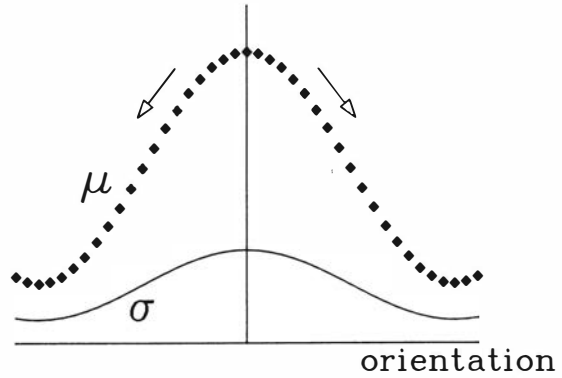


Fig. 2. Gradients and fluxes away from the plane that suffers greatest compression.

Note that for the compressive stress  $\sigma$ , all the values shown coexist simultaneously; but for the chemical potential  $\mu$ , we proceed by focussing attention on a single plane, imagining an associated hydrostatic sample and identifying a value of  $\mu$  for that sample; all values of  $\mu$  shown are possible values, but each value belongs to a sample imagined as existing in isolation. For this reason, the variation of  $\sigma$  is shown by a continuous line whereas the variation of  $\mu$  is shown by a set of isolated points.

must be taken at right angles to  $dn_\alpha$ . The sum in brackets is invariant with choice of  $\alpha$  and  $\beta$  in the same way that the Laplacian is invariant with choice of  $x$ ,  $y$  and  $z$ ; the sum in brackets also resembles another invariant, the total curvature at a point on a geometrical surface in ordinary geometrical space.

4. It is not uncommon for the stress in a material to be nonhydrostatic and to vary from point to point in the material as well. In such a case, a line-element will change length for two reasons; equations (6) and (7) both apply simultaneously. In a material of just one component, the effect that equation (6) describes is a directed self-diffusion, usually so small that it has been widely ignored (but is recognized in a geological context by Fletcher, 1982). If the effect is isotropic, the linear change  $de/dt = 1/3 dV/Vdt = 1/3 dQ/(density) \cdot dt$  per unit volume where  $dQ$  is expressed as a mass. But the effect need not be isotropic (van der Molen 1985); the effect along a line-element parallel to a direction  $n$  is controlled just by the equilibrium potential associated with planes normal to that  $n$ . In the notation of equation (5),

$$\left( \frac{de_{nn}}{dt} \right)_{total} = K^* \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{|\partial L_{n\alpha}|^2} + \frac{\partial^2}{|\partial L_{n\beta}|^2} \right] \mu_{nn}$$

The difference between  $K^*$  and  $K'$  is merely the factor just mentioned, 3 x density, but the difference between  $K^*$  and  $K$  is the factor  $L^2$ ;  $L$  is the *characteristic length*, = [(self-permeability) x (viscosity)]<sup>1/2</sup> if self-permeability is expressed in m<sup>2</sup>/Pa-sec, = [(self-diffusivity) x (viscosity) x V/RT]<sup>1/2</sup> if self-diffusivity is expressed in m<sup>2</sup>/sec.  $L$  is an index of the average distance moved through space by a material point in the micro-processes that permit change of shape, whatever they may be. If the process by which olivine creeps at 1700°K is the same as the process by which its oxygen atoms self-diffuse, then published data (Ashby and Verrall 1977, Freer 1980) suggest that for olivine at this temperature,  $L$  is of the order of 1  $\mu$ m, which is compatible with the concept of dislocation climb and published photographs of dislocation spacing (Karato et al. 1986). But this is only the most tentative of speculations.

Such a small value of  $L$  could explain why stress-driven self-diffusion has been largely unnoticed: it may be a very widespread phenomenon but occurring over such short distances, right against interfaces, as to be almost undetectable even with today's technology – except, again quoting Fletcher, for quartz in arenites where  $L$  may be closer to 1 mm and the material redistributions may be big enough to see, as quartz veins.

## Conclusion

All things flow; they flow because, in the directions of the principal axes of stress, the potential spatial energy of the solid has three separate values that may be regarded as  $P_x V$ ,  $P_y V$  and  $P_z V$ . In rearranging Ramberg's words we mark his planting of this seed.

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## Appendix

The main text presents only positive proposals and avoids the discursive. But there is an objection so obvious – that a *quantity of energy* cannot possibly vary with direction and necessarily has just a single value at any point – that attention to this difficulty is in order.

The resolution, as far as I am able to judge, lies in the point indicated in the Abstract: the chemical potential is not a quantity of energy but a ratio relating two small changes. We specify some thermodynamic system, make a small change  $\delta m_\alpha$  in its content of component  $\alpha$  by some process, and observe the change in the system's free enthalpy or Gibbs free energy  $\delta G$ . If the thermodynamic system is a sample of material in a homogeneous but non-hydrostatic stress state, the *process* of moving  $\delta m_\alpha$  across one boundary element need not be the same *process* as moving  $\delta m_\alpha$  across another boundary element. Another complication is that the ratio  $\delta G/\delta m_\alpha$  is not solely a function of the system's present state, but we minimize that difficulty by imagining a reversible process that resembles as closely as possible the process in hand. For a nonhydrostatic boundary under normal stress  $P_x$ , the closest reversible process is the introduction of mass into a hydrostatic system at pressure  $P_x$  whereas for a nonhydrostatic boundary under normal stress  $P_y$ , the closest reversible process is the introduction of mass into a hydrostatic system at pressure  $P_y$ .

Readers will see that the crucial step is the imagining of two separate associated equilibrium states. These acts of the imagination are essential. The need for them has been much obscured by use of the term "local equilibrium." Whatever value this concept may have in other contexts, for nonhydrostatically stressed materials the concept of local equilibrium cannot be used, whereas the concept of a range of associated equilibrium states has great power.

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