IV CHAPTER : APPENDIX

IV.1 ELASTICITY OF AN ISOTROPIC MEDIUM

The strains u_{ij} induced by stresses σ_{ij} in a homogeneous isotropic solid characterised by the Young modulus E and the Poisson ratio ν are linearly related to the σ_{ij} as follows,

$$
\begin{aligned}
u_{xx} &= \frac{1}{E}\left[\sigma_{xx} - \nu\left(\sigma_{yy} + \sigma_{zz}\right)\right]\\
u_{yy} &= \frac{1}{E}\left[\sigma_{yy} - \nu\left(\sigma_{xx} + \sigma_{zz}\right)\right]\\
u_{zz} &= \frac{1}{E}\left[\sigma_{zz} - \nu\left(\sigma_{xx} + \sigma_{yy}\right)\right]\\
u_{zy} &= \frac{(1+\nu)}{E}\sigma_{zy}\\
u_{zx} &= \frac{(1+\nu)}{E}\sigma_{zx}\\
u_{xy} &= \frac{(1+\nu)}{E}\sigma_{xy}
\end{aligned}
\qquad \text{(A. IV.1}
$$

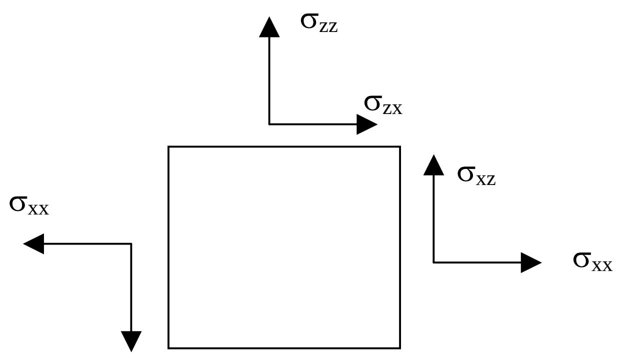

Fig.A. IV.1: Definition of stresses

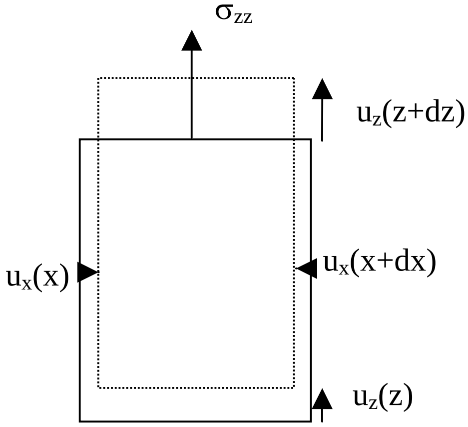

Fig.A. IV.2: Deformation of a volume element of a body subjected to a uniaxial stress along the z-axis

The deformation of a volume element subjected to a uniaxial stress along the z-axis is indicated in Fig.A. IV.2. The strain along the z-axis is defined as the relative elongation of the volume element, i.e.

$$u_{zz} = \frac{\partial u_z}{\partial z} \qquad \text{(A. IV.2}$$

and similarly the strain along the x-axis (and symmetrically along the y-axis) is defined as the relative elongation of the volume element in the x-direction, i.e.

$$u_{xx} = \frac{\partial u_x}{\partial x} \qquad \text{(A. IV.3}$$

From the equations A.IV.1 we find that

$$\begin{aligned} &u_{xx} = \frac{-\nu\sigma_{zz}}{E} \qquad u_{yy} = \frac{-\nu\sigma_{zz}}{E} \qquad u_{zz} = \frac{1}{E}\sigma_{zz} \\ &u_{zy} = 0 \qquad u_{zx} = 0 \qquad \text{and} \qquad u_{xy} = 0 \end{aligned} \qquad \text{(A. IV.4}$$

This indicates that the Young modulus controls the elongation of the body while the Poisson ratio tells us about the fractional shrinking of the body. We see indeed that

$$\nu = \frac{-u_{yy}}{u_{zz}} = \frac{-u_{xx}}{u_{zz}} \qquad \text{(A. IV.5}$$

Since the relation between stresses and strains are linear one can also express the stresses in terms of the strains. One obtains then

$$\begin{aligned} \sigma_{xx} &= \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{xx} + \nu\left(u_{yy} + u_{zz}\right)\right] \\ \sigma_{yy} &= \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{yy} + \nu\left(u_{xx} + u_{zz}\right)\right] \\ \sigma_{zz} &= \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{zz} + \nu\left(u_{xx} + u_{yy}\right)\right] \\ \sigma_{zy} &= \frac{E}{(1+\nu)}u_{zy} \\ \sigma_{zx} &= \frac{E}{(1+\nu)}u_{zx} \\ \sigma_{xy} &= \frac{E}{(1+\nu)}u_{xy} \end{aligned} \qquad \text{(A. IV.6}$$

IV.2 MODELLING OF THE INFLUENCE OF A DILATION CENTRE

We have seen that hydrogen induces long range lattice expansion of the host lattice. In order to decide about the range of the interaction we need to know how the strain field set-up by one atom varies inside a sample. We consider here the simplest (yet physically transparent) model. We assume that the sample is a sphere of radius R_2 and place a dilation centre at its centre. This dilation centre consists of a little hole of radius R_1 containing a gas under pressure p. The external pressure around the spherical sample is zero.

We consider a volume element as indicated in

Fig.A. **IV.3**. The four stresses must lead to a vanishing total force

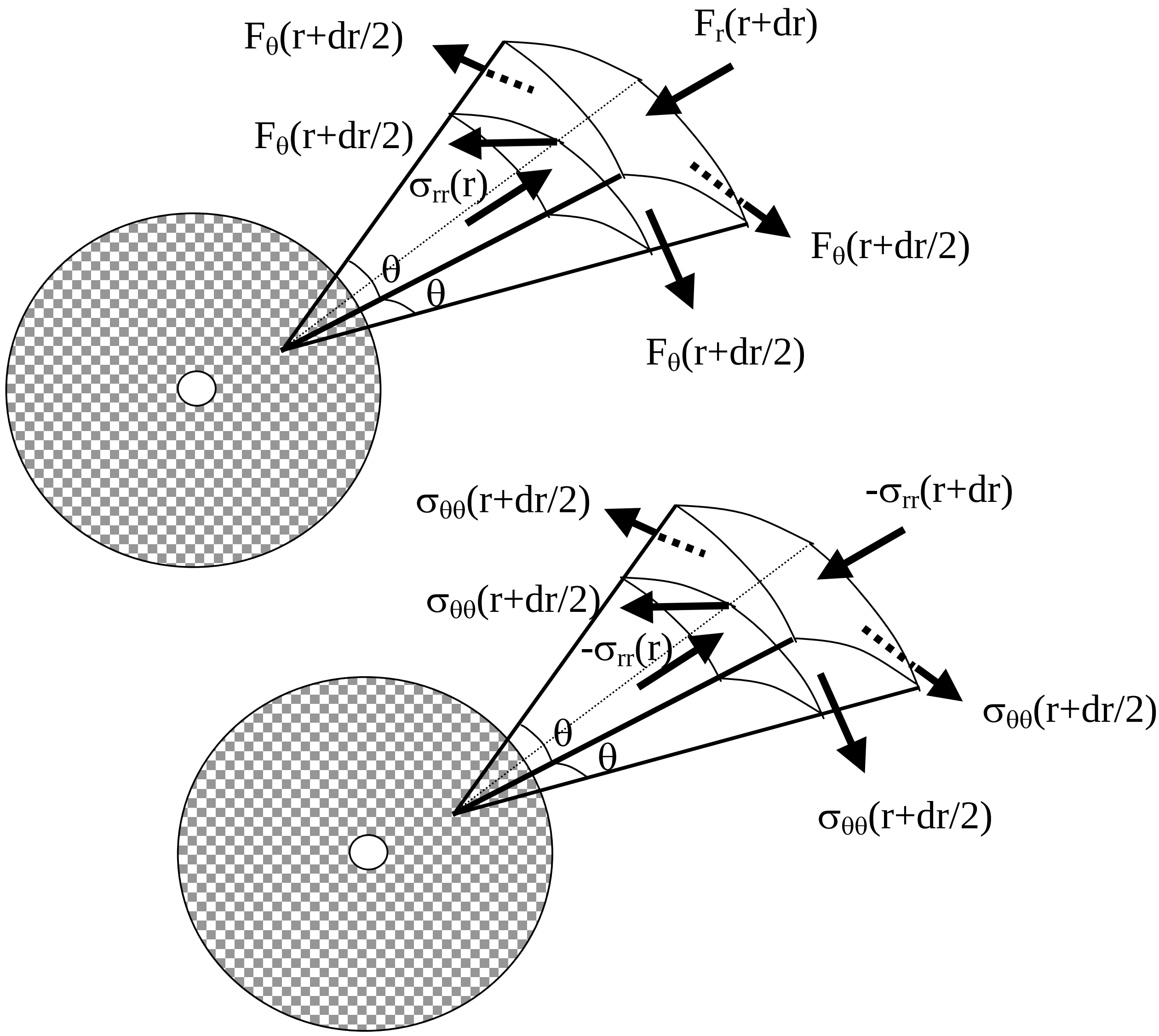

Fig.A. IV.3: A spherical sample with a central hole at pressure p. The net force on each volume element must be zero (top panel). The bottom panel shows the corresponding stresses. The negative signs are due to the choice of positive stresses in Fig.A. IV.2. This determines a differential equation for the stresses (see Eq.A.IV.7).

The net force is

$$-\sigma_{rr}\left[r+dr\right]\times\theta^{2}\left(r+dr\right)^{2}+4\sigma_{\theta\theta}\left[r+{dr}/{2}\right]\times\theta\times r\times\frac{\theta}{2}dr+\sigma_{rr}\left[r\right]\times\theta^{2}\times r^{2}=0 \qquad \text{(A. IV.7}$$

Keeping only first order terms we obtain the following equation,

$$r^{2}\frac{d\sigma_{rr}}{dr}+2r\sigma_{rr}-2r\sigma_{\theta\theta}=0 \qquad \text{(A. IV.8}$$

In spherical coordinates Hooke's law leads to

$$\begin{aligned} u_{rr} &= \frac{1}{E}\left[\sigma_{rr}-\nu\left(\sigma_{\theta\theta}+\sigma_{\theta\theta}\right)\right] \\ u_{\theta\theta} &= \frac{1}{E}\left[\sigma_{\theta\theta}-\nu\left(\sigma_{rr}+\sigma_{\theta\theta}\right)\right] \end{aligned} \qquad \text{(A. IV.9}$$

or

$$\begin{aligned} \sigma_{rr} &= \frac{E}{\left(1+\nu\right)\left(1-2\nu\right)}\left[\left(1-\nu\right)u_{rr}+\nu\left(u_{\theta\theta}+u_{\theta\theta}\right)\right] \\ \sigma_{\theta\theta} &= \frac{E}{\left(1+\nu\right)\left(1-2\nu\right)}\left[\left(1-\nu\right)u_{\theta\theta}+\nu\left(u_{rr}+u_{\theta\theta}\right)\right] \end{aligned} \qquad \text{(A. IV.10}$$

Furthermore we have

$$\begin{aligned} u_{rr} &= \frac{du}{dr} \\ u_{\theta\theta} &= \frac{u}{r} \end{aligned} \qquad \text{(A. IV.11}$$

The expression for $u_{\theta\theta}$ follows directly from the fact that a radial displacement by u(r) leads to an elongation $2\pi u$ of the spherical shell of radius r (and perimeter $2\pi r$). The angular strain is thus the ration of the shell elongation divided by the shell perimeter. Using Eqs.A.IV.10 and 11 we obtain the following differential equation for the **displacement** field (not the strain!),

$$r^{2}\frac{d^{2}u}{dr^{2}}+2r\frac{du}{dr}-2u=0 \qquad \text{(A. IV.12}$$

The solution is of the form,

$$u(r) = ar + \frac{b}{r^2} \tag{A. IV.13}$$

The two constants a and b are determined by the boundary conditions at $\sigma(r=R_1)=p$, and $\sigma(r=R_2)=0$ in Eq.A.IV.10. For this we need the strains

$$\begin{aligned} u_{rr} &= \frac{du}{dr} = a - \frac{2b}{r^3} \\ u_{\theta\theta} &= \frac{u}{r} = a + \frac{b}{r^3} \end{aligned} \tag{A. IV.14}$$

We obtain the two conditions

$$\begin{aligned} p &= \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)\left(a - \frac{2b}{R_1{}^3}\right) + 2\nu\left(a + \frac{b}{R_1{}^3}\right)\right] \\ 0 &= \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)\left(a - \frac{2b}{R_2{}^3}\right) + 2\nu\left(a + \frac{b}{R_2{}^3}\right)\right] \end{aligned} \tag{A. IV.15}$$

from which we find

$$a = \frac{pR_1^3}{R_2^3 - R_1^3}\left(\frac{1-2\nu}{E}\right) \quad \text{and} \quad b = \frac{pR_1^3 R_2^3}{R_2^3 - R_1^3}\left(\frac{1+\nu}{2E}\right) \tag{A. IV.16}$$

Since R_1 is much smaller than R_2 the Eqs.IV.A16 can be written as

$$a = \frac{pR_1^3}{R_2^3}\left(\frac{1-2\nu}{E}\right) \quad \text{and} \quad b = pR_1^3\left(\frac{1+\nu}{2E}\right) \tag{A. IV.17}$$

To model a dilation centre we need, however, to keep the product $p \times R_1^3$ finite. It is therefore meaningful to define a quantity P so that the total relative volume change of the spherical sample is simply given by

$$\frac{\Delta V_{total}}{V} = \kappa \times P \tag{A. IV.18}$$

where K is the compressibility of the material. K is related to the Young modulus and the Poisson ratio as follows

$$\kappa = \frac{3(1-2\nu)}{E} \qquad \text{(A. IV.19}$$

This is easily seen by introducing $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -p$ in Eq.A.IV.1 and by noting that

$$\frac{\Delta V_{total}}{V} = u_{xx} + u_{yy} + u_{zz} = \kappa \times (-p) \qquad \text{(A. IV.20}$$

From Eqs.A.IV15, 17 and 19 we obtain

$$P \equiv \frac{3pR_1^3}{2R_2^3}\left(\frac{1-\nu}{1-2\nu}\right) \qquad \text{(A. IV.21}$$

since for our problem of the sphere

$$\frac{\Delta V_{total}}{V} = 3\frac{u(R_2)}{R_2} \qquad \text{(A. IV.22}$$

With this definition of P we can express the **local** relative volume changes **inside** the material of the sphere (the so-called matrix) as

$$\left.\frac{\Delta V}{V}\right|_{matrixl} = u_{rr} + 2u_{\theta\theta} = 3a = P\,\frac{2(1-2\nu)^2}{E(1-\nu)} \qquad \text{(A. IV.23}$$

The remarkable implication of Eq.A.IV.23 is that the local dilation of the matrix is independent of the position inside the sphere ! This means that less dilation work is needed to insert a second dilation centre since the matrix is already expanded. This leads to an energy lowering of

$$\Delta\varepsilon_0 = -P\left.\frac{\Delta V}{V}\right|_{matrixl} = -P^2\,\frac{2(1-2\nu)^2}{E(1-\nu)} \qquad \text{(A. IV.24}$$

that corresponds to the expression

$$\Delta\varepsilon_0 = -\frac{P^2}{V}\left(\kappa - \frac{1}{C_{11}}\right) \qquad \text{(A. IV.25}$$

for a cubic crystal since

$$E = C_{11}\left(\frac{(1-2\nu)(1+\nu)}{1-\nu}\right) \qquad \text{(A. IV.26}$$

and

$$\kappa = \frac{3(1-2\nu)}{E} \qquad \text{(A. IV.27}$$

The energy lowering is independent of position of the second hydrogen; this implies that the effective H-H interaction is attractive and has an **infinite** range.
The problem considered here makes it possible to treat analytically problems with other boundary conditions. For example instead of zero pressure at the external boundary of the sphere we could impose that the displacement vanishes. This would correspond to a perfect clamping and, consequently, to a compression of the matrix. This would indeed lead then to a repulsive H-H interaction.