Example Problem 4.1

$$\tilde{\epsilon} = \begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}$$

a. *Find the change in internal energy for an adiabatically stored solid with dielectric constant $\tilde{\epsilon}$ with the application of the generalized electric field $\vec{E}$. Assume that the solid has a linear response. Initially the a, b, and c−axes of the crystal are aligned with the x, y, z−axes of the laboratory reference frame.*

b. *The solid is rotated θ degrees about the c-axis or z-axis in laboratory frame. Now the a-axis is θ degrees from the x-axis and the b-axis is θ degrees from the y-axis. Calculate the work stored in the solid with the application of the generalized electric field $\vec{E}$.*

c. *The crystal has tetragonal symmetry which means that $\epsilon_{11}=\epsilon_{22}$. Find the rotation angle θ for which the change in internal energy from Part a is the same as that from Part b.*

Solution 4.1

a. From the first law for an adiabatic system, $dU = dW$ where dW is the work done on the system by the applied electric field.

$$\Delta U = W = V_0 \int \vec{E} \cdot d\vec{D}$$

The linear response means that $\vec{D} = \tilde{\epsilon}\vec{E}$ and $d\vec{D} = \tilde{\epsilon}d\vec{E}$. Substitution and integration give the following form for the change in internal energy.

$$\Delta U = W = \frac{V_0}{2}\vec{E}^T\tilde{\epsilon}\vec{E}$$

$$\Delta U = \frac{V_0}{2} \begin{pmatrix} E_1 & E_2 & E_3 \end{pmatrix} \begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}$$

$$\Delta U = \frac{V_0}{2} \begin{pmatrix} E_1 & E_2 & E_3 \end{pmatrix} \begin{pmatrix} \epsilon_{11}E_1 \\ \epsilon_{22}E_2 \\ \epsilon_{33}E_3 \end{pmatrix}$$

$$\Delta U = \frac{V_0}{2}\left(\epsilon_{11}E_1^2 + \epsilon_{22}E_2^2 + \epsilon_{33}E_3^2\right)$$

b. THIS PART OF THE PROBLEM IS TO SERVE AS AN ILLUSTRATION. YOU ARE NOT RESPONSIBLE FOR THIS MATERIAL IN THIS COURSE.

It is necessary to rotate the properties of the crystal to coincide with the orientation of the crystal axes with respect to the laboratory reference frame. This is done using the matrix of cosines, $\tilde{A}$. Let $\tilde{\epsilon}_L = \tilde{A}\tilde{\epsilon}$ be the dielectric constant referred to the lab reference frame.

$$\tilde{A} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

And so,

$$\tilde{\epsilon}_L = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$$

$$\tilde{\epsilon}_L = \begin{pmatrix} \epsilon_{11}\cos\theta & \epsilon_{22}\sin\theta & 0 \\ -\epsilon_{11}\sin\theta & \epsilon_{22}\cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

And the change in internal energy is given by the following.

$$\Delta U = E_1^2 \epsilon_{11}\cos\theta + E_2^2 \epsilon_{22}\cos\theta + E_3^2 \epsilon_{33} + E_1 E_2 (\epsilon_{22} - \epsilon_{11})\sin\theta$$

c. When the crystal has tetragonal symmetry the following holds.

$$\Delta U_a = \epsilon_{11}(E_1^2 + E_2^2) + \epsilon_{33}E_3^2$$
$$\Delta U_b = \epsilon_{11}(E_1^2 + E_2^2)\cos\theta + \epsilon_{33}E_3^2$$

On inspection these are equal when $\cos\theta = 1$ or $\theta = \pi/2$. We've shown that if a tetragonal crystal is rotated 90 degrees about its c-axis the crystal properties are indistinguishable from those before the rotation. This is an illustration of Neumanns Principle.

Example Problem 4.2

The equation of state for an ideal gas is $PV = nRT$. The equation of state for one mole of a van der Waals gas is below. Calculate the change in internal energy for one mole of an adiabatically contained van der Waals gas during an isothermal transformation from (P_0, V_0) to (P_1, V_1).

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Solution 4.2 From the first law: $dU = dQ + dW$ where dU is the change in internal energy, dQ is heat added to the system and dW is the work done on the system. For an adiabatic system $dQ = 0$.

$$dU = -PdV$$
$$\Delta U = -\int_{V_0}^{V_1} PdV$$

We also need $P(V)$ for one mole of gas.

$$P = \left[\frac{RT}{(V-b)} - \frac{a}{V^2}\right]$$

$$\Delta U = \int_{V_1}^{V_0} \left[\frac{RT}{(V-b)} - \frac{a}{V^2}\right] dV$$
$$\Delta U = RT \ln\left(\frac{V_0 - b}{V_1 - b}\right) + a\left(\frac{1}{V_0} - \frac{1}{V_1}\right)$$

Contrast this with the expression for an ideal gas, $\Delta U = RT \ln\left(\frac{V_0}{V_1}\right)$.

Example Problem 4.3

Find the equation of the adiabats in the P-V plane for a gas with an equation of state given by $U = AP^2V$ where A is a positive constant.

Solution 4.3

$$dU = dQ + dW$$
$$dU = -PdV$$
$$AP^2 dV + 2APV dP = -PdV$$
$$2APV dP = -(AP^2 + P)dV$$
$$\frac{dP}{AP+1} = -\frac{dV}{2AV}$$
$$\int_{P_0}^{P_1} \frac{dP}{AP+1} = -\int_{V_0}^{V_1} \frac{dV}{2AV}$$
$$\frac{1}{2A} \ln \frac{V_0}{V_1} = \frac{1}{A} \ln \frac{P_1}{P_0}$$
$$\left(\frac{V_0}{V_1}\right)^{\frac{1}{2}} = \left(\frac{P_1}{P_0}\right)$$
$$V_0^{\frac{1}{2}} P_0 = V_1^{\frac{1}{2}} P_1 = \text{constant}$$

The equation of the adiabats for this gas is $V^{\frac{1}{2}}P = \text{constant}$. Note that the equation for the adiabats of the ideal gas is similar, $PV^\gamma = \text{constant}$.