Legendre transforms:

\[ \tilde{U} = U - \frac{E \cdot P}{4\pi} \quad \tilde{F} = F - \frac{E \cdot P}{4\pi} \]

\[ d\tilde{F} = -\varepsilon_0 dT + \varepsilon_0 d\phi - \frac{1}{4\pi} P \cdot dE \Rightarrow \quad P = -\varepsilon_0 \left( \frac{\partial \tilde{F}}{\partial \tilde{E}} \right)_T, P \]

The relationship between thermodynamic quantities with and without the tilde is exactly that which occurs (in §5) for P: energy of electrostatic field in a vacuum.

For the integral \( \int \varepsilon_0 E \cdot dV \) can be transformed exactly. No summation to theorems at the beginning of §2, with \( \varepsilon_0 \varepsilon_0 \) and \( \text{div} P = 0 \) inside the dielectric and the boundary condition \( P_n = 4\pi \sigma_0 \) on the surface, according to

\[
\frac{1}{4\pi} \int \varepsilon_0 E \cdot dV = -\frac{1}{4\pi} \int \text{grad} \phi \cdot dV
\]

\[
\nabla \cdot (\phi \mathbf{P}) = \text{grad} \phi \cdot \mathbf{P} + \phi \mathbf{P} \cdot \nabla \phi
\]

\[
\phi = -\frac{1}{4\pi} \int \mathbf{E} \cdot dV(\nabla \cdot (\phi \mathbf{P}) - \phi \mathbf{P} \cdot \nabla \phi)
\]

\[ = \frac{1}{4\pi} \int dF \cdot \phi \mathbf{P} \quad \text{zero inside the dielectric} \]

\[ \tilde{U} = U - \frac{\varepsilon_0 E \cdot P}{4\pi} \]

\[ = U - \sum \frac{\varepsilon_0}{a} \phi_a \]

agrees with (5.5).
The variation of the free energy
For a given temperature is

$$ (\delta \mathcal{F})_T = \delta R = \sum_a \phi_a \delta e_a $$

free energy with changes on the conductors.

$$ (\delta \mathcal{F})_T = -\frac{1}{4\pi} \int dV (-E \cdot \delta D) = \frac{1}{4\pi} \int dV E \cdot \delta D = \sum_a \phi_a \delta e_a $$

$$ (\delta \mathcal{F})_T = (\delta \mathcal{F})_T - \delta \sum_a \phi_a e_a = -\sum_a \phi_a \delta e_a $$

free energy with potentials on the conductors.

*Thermodynamic potentials: minima in P, \( \mathcal{F} \), \( \mathcal{F}_T \), and (\delta \mathcal{F})_T.*

In equilibrium, \( \mathcal{F} \) and \( \mathcal{F}_T \) are minima with changes in state occurring at constant temperature and (respectively) constant charge and potentials.

*It should be remembered that these processes ARE NAND* 
(such as chemical reactions) for which the body is not at equilibrium, 
so that its state is not uniquely defined by the temp and 
(respectively) charge and potential.

In a isotropic dielectric 

$$ dU = \partial U_0 (S, p) + \frac{D \cdot dP}{4\pi e_0} $$

$$ U = U_0 (S, p) + \frac{D^2}{8\pi e_0} $$

$$ dF = dF_0 (T, p) + \frac{P \cdot dP}{4\pi e_0} $$

$$ F = F_0 (T, p) + \frac{P^2}{8\pi e_0} $$

$$ \frac{ED}{8\pi e_0} \text{ is the change in energy (for constant } S, p) \text{ or free energy (for constant } T, p) \text{ per unit volume.} $$

No dielectric medium, resulting from the presence of a field.
The expressions for the potentials $\vec{U}$ and $F$ are similarly:

$$d\vec{U} = d\vec{U}_0(s,p) - \frac{eEzE}{4\pi} \cdot \vec{U}_0(s,p) - \frac{eE^2}{8\pi} = \vec{U}(s,p)$$

$\vec{U} - \vec{U}_0$ and $U - U_0$ differ only in sign (as they did in an electric field in a vacuum.

**Inside a medium** this simple result holds good only when there is a linear relationship between $E \& D$.

Entropy density and chemical potential:

$$S = -\left(\frac{\partial F}{\partial T}\right)_\rho = S_0(T,\rho) + \frac{D^2}{8\pi e^2} \left(\frac{\partial e}{\partial T}\right)_\rho$$

If $e$ differs from zero only inside the dielectric

$$F - F_0 = \int dV (F - F_0) = \frac{1}{8\pi} \int dV E \cdot D = \frac{1}{2} \sum_e e_d \phi_a$$
The Helmholtz free energy is a minimum at equilibrium, with respect to changes in state occurring at constant temperature and changes on the conductors.

Revisit \( F = F(T, V, N) \) for an ideal gas in a cylinder.

\[
F_x(T, V) = F(T, \frac{V}{2}(1+x), \frac{N}{2}) + F(T, \frac{V}{2}(1-x), \frac{N}{2})
\]

\[
F(T, V, N) = U - TS = \frac{3}{2} NkT - TNk \ln \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{V}{N} e^{\frac{5}{2}} \right]
\]

\[
\tilde{F}(T, V; N) = -NkT \ln \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{V}{N} e^{\frac{5}{2}} \right]
\]

\[
F_x(T, V) = -\frac{N kT}{2} \ln \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{V}{N} (1+x) e^{\frac{5}{2}} \right]
\]

\[
-\frac{N kT}{2} \ln \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{V}{N} (1-x) e^{\frac{5}{2}} \right]
\]

\[
= -NkT \ln \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{V}{N} e^{\frac{5}{2}} \right] - \frac{NkTe^{\frac{5}{2}}}{2}(2-x^2)
\]

which is evidently a minimum at \( x = 0 \).
two conducting spheres connected by a wire and embedded in a dielectric.

Let the constrained charges on the two conductors be \( \frac{e}{2}(1+y) \) and \( \frac{e}{2}(1-y) \). Equilibrium should correspond to \( y = 0 \).

\[ (\delta Q_T) = \phi_1 \delta e_1 + \phi_2 \delta e_2 \]

Let's find \( \phi_i \) for a given charge state \( q_i \):

\[ \nabla \cdot D_i = 4\pi p_{ex} \]

\[ 4\pi r^2 D_i = 4\pi q_i \]

\[ D_i = \frac{q_i}{r^2} \Rightarrow E_i = \frac{q_i}{e r^2} \]

\[ (\delta Q_T) = \frac{e(1+y)}{2e\alpha} \frac{e}{2} \delta y + \frac{e(1-y)}{2e\alpha} \frac{e}{2} \delta y \]

\[ \phi_i = \frac{q_i}{e r^2} \]

which is zero for \( y = 0 \).
§11 The total free energy of a dielectric

$\mathcal{F}$ includes the energy of the electric field which polarizes the dielectric.

Total free energy LESS the energy of the field that would be present if the body were absent:

$$\mathcal{F} = \int (E^2 / 8\pi) \, dV$$

Free energy density

NEW USAGE: The difference between this new $\mathcal{F}$ and $\mathcal{F}_{\text{no field}}$ is a quantity independent of the medium, state, or properties of the dielectric.

$$\delta \mathcal{G} = \int (\delta \mathcal{F} - \mathcal{E} \cdot \delta \mathcal{E}) = \frac{1}{4\pi} \int_{\text{dV}} (E \cdot \delta P - \mathcal{E} \cdot \delta \mathcal{E})$$

$$\frac{E \cdot \delta P}{4\pi}$$

$$= \frac{1}{4\pi} \int_{\text{dV}} E \cdot \delta D + \frac{1}{4\pi} \int_{\text{dV}} (D - \mathcal{E}) \cdot \delta \mathcal{E} - \frac{1}{4\pi} \int_{\text{dV}} \frac{E \cdot \delta \mathcal{E} + (D - \mathcal{E}) \cdot \delta \mathcal{E}}{\mathcal{E}}$$

$$= \frac{1}{4\pi} \int_{\text{dV}} E \cdot (\delta P - \delta \mathcal{E}) + \frac{1}{4\pi} \int_{\text{dV}} (D - \mathcal{E}) \cdot \delta \mathcal{E} - \frac{1}{4\pi} \int_{\text{dV}} \frac{E \cdot \delta \mathcal{E} + (D - \mathcal{E}) \cdot \delta \mathcal{E}}{\mathcal{E}}$$

$$- \text{grad } \delta \mathcal{F}_0$$

$$\frac{1}{4\pi} \int_{\text{dV}} D \cdot (D - \mathcal{E}) \, \delta \mathcal{F}_0 - \frac{1}{4\pi} \int_{\text{dV}} \frac{D \cdot (D - \mathcal{E}) \, \delta \mathcal{F}_0}{\mathcal{E}}$$

$\text{const. for each conductor}$
\( \text{2nd term is also zero: } \quad E = -\nabla \phi \)

\[- \int_{\partial V} \nabla \phi \cdot (\delta E - \delta \phi) = \int_{\partial V} \phi \frac{\partial}{\partial n} (\delta E - \delta \phi) \]

\[- \int_{\partial V} (\delta E - \delta \phi) \phi \]

\[- \phi \left( \mu_0 \delta E - \mu_0 \delta \phi \right) \geq 0 \]

So that

\[\delta \mathcal{F} = -\frac{1}{4\pi} \int_{\partial V} (\delta E - \delta \phi) \cdot \delta E \, dV = -\int_{\partial V} \phi \cdot \delta E \]

\[\text{AN AMAZINGLY SIMPLE RESULT} \]

If the external electric field is uniform, then

\[\delta \mathcal{F} = -\delta E \cdot \int_{\partial V} \delta n \, dV = -\delta E \cdot \delta \phi \]

\[\delta \mathcal{F} = -\delta \alpha T - \delta \phi \cdot \partial E \]

\[\delta \phi = -\frac{\delta \alpha T}{\partial E} \]

\[\mathcal{F} = -\left( \frac{\partial \phi}{\partial E} \right)_T \]

\[\frac{\partial \mathcal{F}}{\partial \lambda} = \left( \frac{\partial \phi}{\partial \lambda} \right)_T \]

\[\text{contains a term } - \varepsilon \cdot \vec{\phi} \]
If \( P = \varepsilon E \) we can calculate, not just \( \varphi \) itself, but \( \varphi \) itself.

\[
\varphi - \varphi_0 = \int \left( \mathbf{F} - \mathbf{E}^2/8\pi \right) \cdot \mathbf{r} \, dV = \frac{1}{8\pi} \int \nabla \cdot \mathbf{E} \cdot (\mathbf{r} - \mathbf{E}^2) \\
\text{see (10.69)}
\]

\[
= \frac{1}{8\pi} \int dV \left( \varphi + \varphi_0 \right) \cdot (\mathbf{r} - \mathbf{E}) + \frac{1}{8\pi} \int dV \left( \mathbf{r} + \varphi \right) \cdot \mathbf{E}
\]

\[
\mathbf{E} + \varphi = -\nabla \varphi + \varphi_0
\]

\[
- \int dV \nabla \varphi \cdot (\mathbf{r} - \mathbf{E}) = - \int dV \cdot (\mathbf{r} - \mathbf{E}) \cdot (\mathbf{r} + \nabla \varphi) \\
+ \int dV \left( \mathbf{r} + \varphi \right) \cdot \mathbf{E}
\]

\[
\mathbf{D} \cdot \mathbf{D} = 0 \quad \text{in dielectric}
\]

\[
\mathbf{D} \cdot \mathbf{E} = 0 \quad \text{in \( \rho \) vacuum}
\]

\[
(\mathbf{r} + \varphi) \cdot \mathbf{E} = (\mathbf{r} + \varphi) (\mathbf{4\pi} \mathbf{E} - \mathbf{4\pi} \mathbf{E})
\]

\[
\therefore \quad \varphi - \varphi_0 = -\frac{1}{2} \int dV \cdot \mathbf{E} = -\frac{1}{2} \mathbf{P} \cdot \mathbf{E}
\quad \text{in a uniform field}
\]

\[
\mathbf{P} = \nabla k \varepsilon \mathbf{E}
\]

\[
\mathbf{F} = \frac{\partial \mathbf{F}}{\partial \mathbf{x}}
\]

\[
\text{now} \quad \varepsilon^2 = \frac{\text{energy}}{\text{vol}} = \frac{\text{energy}}{\text{vol}}
\]

\[
\Rightarrow \quad (\mathbf{E}) = \frac{q}{\text{vol}} \text{ coul} = \frac{\text{g cm}^2}{\text{vol}}
\]

\[
\Rightarrow \quad \mathbf{E} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul}
\]

\[
\Rightarrow \quad \text{charge} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul}
\]

\[
\Rightarrow \quad \text{charge} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul} = \frac{\text{g cm}^2}{\text{vol}} \text{ coul}
\]
\[
\frac{\partial \Phi}{\partial \varepsilon_i} = -\frac{1}{2} \mathbf{P}_i - \frac{1}{2} \varepsilon_i \varepsilon_j \frac{\partial \Phi_j}{\partial \varepsilon_i} \\
= -\frac{1}{2} \mathbf{P}_i - \frac{1}{2} \varepsilon_j V_{ij} \quad \text{\(\sum\) comes back \(\Phi\)}
\]

\[
\mathbf{P}_i = -\left( \frac{\partial \Phi_j}{\partial \varepsilon_i} \right)_r \quad \frac{\partial^2 \Phi}{\partial \varepsilon_i \partial \varepsilon_j} = -\frac{\partial \mathbf{P}_i}{\partial \varepsilon_j} = -V_{ij} \quad \text{\(\sum\) but this quantity also equals} \\
\frac{\partial^2 \Phi}{\partial \varepsilon_j \partial \varepsilon_i} = -V_{ij} \quad \Rightarrow \quad \Phi_{ij} = \Phi_{ji}
\]

back to \(\star\)

\[
\frac{\partial \Phi}{\partial \varepsilon_i} = -\frac{1}{2} \mathbf{P}_i - \frac{1}{2} \varepsilon_j V_{ij} = -\frac{1}{2} \mathbf{P}_i - \frac{1}{2} \mathbf{P}_i = \mathbf{P}_i
\]

which agrees (11, 4)

\[
\text{case when } \varepsilon \text{ is close to 1:}
\]

\[
\mathbf{D} = \varepsilon \varepsilon_0 \mathbf{E} + 4\pi \mathbf{P} \\
\varepsilon \varepsilon_0 \mathbf{E} = \varepsilon_0 \mathbf{E} + 4\pi \mathbf{P} \quad \Rightarrow \quad \mathbf{P} = \frac{\varepsilon - 1}{4\pi} \mathbf{E}
\]

Then \(\varepsilon \approx \varepsilon_0\), and

\[
\mathbf{P} \approx \frac{\varepsilon - 1}{4\pi} \mathbf{E} = \kappa \mathbf{E} \quad \Rightarrow \quad \frac{\varepsilon_0}{\varepsilon} - \mathbf{P} \approx -\frac{1}{\varepsilon_0} \kappa \int \mathbf{E} \mathbf{E}^2
\]

in a uniform field, \(\mathbf{E}^2 = \text{const} \quad \Rightarrow \quad \frac{\varepsilon_0}{\varepsilon} - \mathbf{P} \approx \frac{\varepsilon_0}{\varepsilon} - \frac{1}{\varepsilon_0} \kappa \int \mathbf{E} \mathbf{E}^2
\]

\[
\Phi - \Phi_0 = -\frac{1}{2} \kappa V \varepsilon^2
\]
In the general case of an arbitrary reln $\mathbf{A} \cdot \mathbf{E}$

Instead, we must work with

$$\sigma^2 = \int dV \left( F - \frac{E^2}{8\pi} \right) dV$$
Since I was unable to carry out the "obvious" derivation (11.12), understanding must be eluding me. I start over again w/ §10.

no field inside a conductor; any change in its thermodynamic properties amounts to an increase in the total energy. The field it produces in the surrounding space.

electric field penetrates into dielectric if affects its thermodynamic properties.

work done on uniformly insulated dielectric when internal is unchanged.

field due to external charged conductor.

change in field is due to change in the charge on these conductors.

one conductor: $E = \rho \frac{dG}{dV}$ or work done to increase its charge.

mechanical work done by the electric field on a charge $Q$ brought from $\infty$.

exacts in terms of field in the space filled by dielectric surrounding an.$$\sigma = -\frac{D_n}{\gamma r}$$

dielectric

**Comes in.**

$$\mathbf{D} = \mu_0 \mathbf{E}$$

$$\mathbf{D} \cdot \mathbf{D} = \mu_0 \mathbf{E} \cdot \mathbf{E}$$

$$\mathbf{D} = \mathbf{D}_0 \mathbf{E}$$

$$\mathbf{D} = \mathbf{E} \cdot \mathbf{E}$$

$$\mathbf{D} = \mathbf{D}_0 \mathbf{E}$$

**TOTAL CHARGE**

$$C = -\frac{1}{\gamma r} \int_{A_0} \mathbf{D} \cdot dF$$

$$R = \rho \mathbf{E} = -\frac{1}{\gamma r} \int dF \cdot \mathbf{E}$$

$$= -\frac{1}{\gamma r} \int dF \cdot (D \tau)$$

$$= -\frac{1}{\gamma r} \mathbf{F}$$
\[ d \theta A \sigma = \int dV_{\text{cyl}} \cdot D = \int dF_{\text{cyl}} = -D_n \cdot A \]

\[ \sigma = -\frac{D_n}{4\pi} \]

\[ \delta R = \phi \delta e = \int = \phi \oint \left( -\frac{\mathbf{E} \cdot d\mathbf{S}}{4\pi} \right) \]

\[ = -\oint \frac{dV \; \text{div}(\delta \mathbf{E})}{4\pi} \]

\[ \text{Integral over vol } \mathbf{E} \text{ outside conductor} \]

\[ \text{Integral is over the whole vol.} \]

\[ \text{outside the conductor} \]

\[ \delta R = \oint \frac{dV \; \mathbf{E} \cdot d\mathbf{S}}{4\pi} \]

Verifies (10.2)

\[ \text{Work done on a thermally insulated body is the change in energy at const. entropy.} \]

\[ \delta U = T \delta S + \frac{1}{4\pi} \oint dV \mathbf{E} \cdot d\mathbf{S} \]

\[ \text{TOTAL FREE ENERGY} \]

\[ \delta G = U - T S_{\text{cl}} - S_{\text{cl}} \]

\[ \delta G = \delta U - T \delta S - \delta S \]

\[ \delta S = -\delta T + \frac{1}{4\pi} \oint dV \mathbf{E} \cdot d\mathbf{S} \]
\[dU = TdS + \Sigma d\rho + \frac{E \cdot d\rho}{4\pi}\]

Energy per unit Vol. of Dielectric

\[dF = -\Sigma dT + \Sigma d\rho + \frac{E \cdot d\rho}{4\pi}\]

In particular

\[E = 4\pi \left( \frac{\partial U}{\partial D} \right)_{T, \rho} = 4\pi \left( \frac{\partial F}{\partial D} \right)_{T, \rho}\]

Remove convenient relation

Thermodynamic potentials in which components of \(E\) rather than \(D\) are the independent variables.

\[\overline{U} = U - \frac{E \cdot D}{4\pi}\]

\[\overline{F} = F - \frac{E \cdot D}{4\pi}\]

\[d\overline{U} = Td\overline{S} + \Sigma d\overline{\rho} - \frac{D \cdot dE}{4\pi}\]

Transformation from charges to potentials at the integral level:

\[\frac{1}{4\pi} \int dV E \cdot D = -\frac{1}{4\pi} \int dV \text{grad} \phi \cdot D = -\frac{1}{4\pi} \int dV \left( \nabla \phi \cdot D + \phi \nabla \cdot D \right) = 0\]

\[\frac{1}{4\pi} \int dF \text{vac. rel.} \cdot D = \frac{1}{4\pi} \int dF \text{cond.} \cdot D = \frac{1}{4\pi} \int dF \text{cond.} \cdot D \]

\[\rightarrow = \sum \frac{1}{2} \phi_{a} e_{a}\]
So we conclude that \( \tilde{U} = U - \int_V \frac{E \cdot D}{4\pi} = u - \frac{\epsilon_0 a}{2} \), in agreement with (5.5).

Infinite small change in these quantities.

In terms of the charges and potentials of the conductors.

\[
(\delta Q)_T = \delta Q = \frac{1}{4\pi} \int V (E \cdot D) dV
\]

on or inside the conductors

\[
= \frac{1}{4\pi} \int \nabla \phi \cdot D dV = \frac{1}{4\pi} \int (\nabla \phi \cdot \nabla \phi \cdot D dV) = \phi \cdot D dV
\]

outside the conductors

\[
(\delta Q)_T = \int \phi_1 \delta \phi_1 dV = \sum a \delta a
\]

variation in free energy at constant temperature

\[
E_n = \frac{e}{2\pi r^2}
\]

\[
\phi = \frac{e}{en} \Rightarrow \phi_1 = \frac{e_1}{en} \text{ at a radius in space of } e \int dF \cdot E
\]

\[
(\delta Q)_T = \frac{1}{4\pi} \left( \frac{\epsilon_0 + \delta - \frac{\epsilon_0 + \delta}{2} \delta} {2} \right) = \epsilon \int 2\pi r \phi_1 d\phi = \epsilon \frac{e}{4\pi}
\]

\[
\delta \phi_1 = \frac{\epsilon - 2}{\epsilon \frac{e}{4\pi}} \text{ which vanishes when } \delta = 0, \text{ i.e. when change is equals.}
\]
The previously derived equations are valid whether dependence of \( D \) on \( E \)

In a homogeneous isotropic dielectric \( D = \varepsilon E \)

\[
dU = T dS + S d\rho + \frac{E \cdot dD}{4\pi} = T dS + S d\rho + \frac{D \cdot dD}{\varepsilon 4\pi}
\]

\[
U = U_0(S, \rho) + \frac{D^2}{8\pi \varepsilon}
\]

\( \frac{\text{field-free value}}{\text{charge or internal energy density due to the presence of } \varepsilon \text{-field}} = \frac{\varepsilon E^2}{8\pi} = \frac{\varepsilon D^2}{8\pi} \)

**Total free energy:** Integrate over all space

\[
F = F_0(T, \rho) + \frac{D^2}{8\pi \varepsilon}
\]

\[
\frac{\delta F}{\delta \rho} = \int dV \frac{E \cdot D}{8\pi} = \frac{1}{2} \varepsilon a^2 
\]

Field-free value

In this result can also be obtained by integrating

\[
(\delta G)_T = \Sigma \varepsilon \Delta e \Delta e_a \text{. In the present case, when } D \text{ and } E \text{ are linearly related (} D = \varepsilon \cdot E \text{ would also do !), the potential due to must be } \text{area function of } \rho \text{ or charge, so integration gives}
\]

\[
\frac{\delta F}{\delta e_a} = \Sigma \varepsilon \frac{\partial e_a}{\partial e_a} e^2 = \Sigma \frac{\partial}{\partial e_a} \frac{e_a^2}{2} = \frac{1}{2} \Sigma \varepsilon \Delta e \Delta e_a
\]
These arguments do not presuppose the dielectric to fill all space outside the conductor.

If this is the case, foreign charges on the conductor's surface will be reduced by a factor \( \varepsilon / \varepsilon_0 \). The potential at the conductor and the field energy are compared with values for a field in a vacuum.

The total free energy of a dielectric

\[ \mathcal{F}_{\text{free}} = \mathcal{F}_{\text{old}} + \oint d\mathbf{V} \frac{\varepsilon_0}{8\pi} \]  

independent of dynamic state

has no effect on fundamental differential form dynamic relations

change in free energy due to change in \( B \)-field at least keep most destroying equilibrium.

\[ SF = \varepsilon \cdot \delta\varepsilon / 4\pi \]

\[ \varepsilon + (P - E) = P + E \]

\[ \delta \mathcal{F}_{\text{new}} = \frac{1}{4\pi} \oint dV (E \cdot \delta D - \varepsilon \cdot \delta \varepsilon) \]

\[ = \frac{1}{4\pi} \int dV E \cdot (\delta \varepsilon - \delta \varepsilon) - (E - P) \cdot \delta \varepsilon - (P - E) \cdot \delta \varepsilon \]

\[ \delta \mathcal{F}_{\text{new}} = \frac{1}{4\pi} \int dV E \cdot (\delta \varepsilon - \delta \varepsilon) - \frac{1}{4\pi} \int dV (E - P) \cdot \delta \varepsilon - \int dV P \cdot \delta \varepsilon \]
\[ \delta E = - \nabla \delta \phi. \]

\[ - \frac{1}{4\pi} \int dV \, (E - D) \cdot \delta E = \frac{1}{4\pi} \int dV \, (E - D) \cdot \nabla \delta \phi. \]

\[ = \frac{1}{4\pi} \int dV \, \nabla \cdot (\delta \phi \, (E - D)) - \delta \phi \, D \cdot (E - D). \]

\[ = \frac{1}{4\pi} \int dV \, \nabla \cdot (E - D) \delta \phi. \]

\[ = \frac{1}{4\pi} \sum_{a} \phi_{a} \int dV_{a} \cdot (E - D) \]

\[ = \frac{1}{4\pi} \sum_{a} \phi_{a} \left\{ -4\pi n_{a} + 4\pi n_{a} \right\} = 0 \]

Similarly \[ E = - \nabla \phi. \]

\[ \frac{1}{4\pi} \int dV \, E \cdot (\delta D - \delta E) = - \frac{1}{4\pi} \int dV \, \nabla \phi \cdot (\delta D - \delta E). \]

\[ = - \frac{1}{4\pi} \int dV \left\{ \nabla \cdot (\phi \, (\delta D - \delta E)) - (\nabla \cdot (\delta D - \delta E)) \phi \right\} \]

\[ = - \frac{1}{4\pi} \sum_{a} \phi_{a} \left\{ \delta F \cdot (\delta D - \delta E) \right\} \]

\[ = - \frac{1}{4\pi} \sum_{a} \phi_{a} \left\{ \delta F \cdot (\delta D - \delta E) \right\} \]

\[ = \frac{1}{4\pi} \sum_{a} \phi_{a} \left\{ 4\pi (e_{a} - c_{a}) \right\} = 0 \]

\[ \delta \text{ charge} = - \int dV \, D \cdot \delta E \]

\[ \text{at constant temperature}. \]
\(- P \cdot \delta E \) cannot be interpreted with free energy density. 

The change in free energy density must exist outside the body, but \(- P \cdot \delta E \) does not.

\[
E^2 - E^2 \rightarrow (E + \delta E)^2 - (E + \delta E)^2 \\
= 2E \cdot \delta E - 2 \delta E \cdot \delta E \quad \text{not equal to zero in general.}
\]

The energy density at any point in the body can only depend on the field actually present there, and not on the field which would be present if the body were removed.

\[\delta Q^F = - \delta E \cdot \oint dV P = - \delta E \cdot \Phi \]

Thermodynamic identity in this case

\[\delta Q^F = \delta dT - P \cdot dE \Rightarrow \Phi = - \left( \frac{\partial Q^F}{\partial E} \right)_T \]

This formula also follows directly from

\[\left\langle \frac{\partial A^H}{\partial E} \right\rangle_{eq} = \left( \frac{\partial \delta E}{\partial \lambda} \right)_S = \left( \frac{\partial \delta Q^F}{\partial E} \right)_T \quad \text{Hamitonian}
\]

The body in a uniform field \( E \) has a force \(- \Phi \cdot E \), so

\[\frac{\partial A^H}{\partial E} = - \Phi \]

and

\[\Phi = \left\langle \frac{\partial \delta \Phi}{\partial \delta E} \right\rangle_{eq} = \left( \frac{\partial \delta Q^F}{\partial E} \right)_T \]
off $D$ and $E$ are connected by $D = e E$, we can calculate
$G$ itself. By (10.19)

$$G = G_0 + \frac{1}{8\pi} \int_{\Omega} \left( E \cdot D - E^2 \right) \, dV$$

free energy of the
dielectric in the absence of $D$ field.

This can be identically transformed into

$$G = G_0 + \frac{1}{8\pi} \int_{\Omega} \left( E + \vec{\varepsilon} \right) \cdot (D - \vec{\varepsilon}) - \frac{1}{8\pi} \int_{\Omega} (D \cdot \vec{\varepsilon} - E \cdot \vec{\varepsilon})$$

The first terms zero: $E + \vec{\varepsilon} = -\text{grad} \phi - \text{grad} \Phi_0$

$$\left( E + \vec{\varepsilon} \right) \cdot (D - \vec{\varepsilon}) = -\left[ \nabla (\phi + \Phi_0) \right] \cdot (D - \vec{\varepsilon}) = -\nabla \cdot \left[ (D - \vec{\varepsilon})(\phi + \Phi_0) \right]$$

$$+ (\phi + \Phi_0) \nabla \cdot (D - \vec{\varepsilon})$$

$$\frac{1}{8\pi} \int_{\Omega} \left( E + \vec{\varepsilon} \right) \cdot (D - \vec{\varepsilon}) = -\frac{1}{8\pi} \int_{\Omega} \left[ \nabla \cdot \left( D - \vec{\varepsilon} \right)(\phi + \Phi_0) \right] + \frac{1}{8\pi} \int_{\Omega} \left( D \cdot \vec{\varepsilon} - E \cdot \vec{\varepsilon} \right)$$

$$= -\frac{1}{8\pi} \oint_{\text{dial}} \cdot (D - \vec{\varepsilon})(\phi + \Phi_0) \quad \text{vac}$$

$$+ \frac{1}{8\pi} \oint_{\text{cond}} \cdot (D - \vec{\varepsilon})(\phi + \Phi_0)$$

$$= \frac{1}{8\pi} \sum_{\alpha} (\phi_\alpha + \Phi_0) \, 4\pi \left( \varepsilon_\alpha - \varepsilon_0 \right) = 0$$
Hence

\[ \mathcal{F} = \mathcal{F}_0 - \frac{1}{8\pi} \int_{\Omega} (D - E) \cdot \mathbf{E} = \mathcal{F}_0 - \frac{1}{2\pi} \int_{\Omega} P \cdot \mathbf{E} \]

\[ \mathcal{F} = \mathcal{F}_0 - \frac{1}{4\pi} \int_{\Omega} P \cdot \mathbf{E} \]

\[ \uparrow \text{ Free energy of dielectric in absence of an external field} \]

\[ \text{Helmholtz free energy of a collection of macroscopic chunks of dielectric (or vacuum) each of which is homogeneous and isotropic. Less the energy of the external field that would be present in the absence of the dielectric(s).} \]

In a uniform external field,

\[ \mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \mathbf{E} \cdot \mathbf{S} \]

which can also be obtained from direct integration of

\[ \delta \mathcal{F} = -\int P \delta \mathbf{E} d\Omega \text{, for when} \]

\[ P = \mathbf{E}, \text{ the electric moment} \]

\[ \mathbf{S} \text{ must be a linear function of} \mathbf{E}. \]

\[ \text{Per polarizability depends not only on the shape (as for conductors) but also on the dielectric.} \]

From (11.16),

\[ \Theta_i = -\left( \frac{\partial \mathcal{F}}{\partial E_i} \right)^T \]

\[ \frac{\partial \Theta_i}{\partial E_k} = \nabla \Theta_i = -\left( \frac{\partial^2 \mathcal{F}}{\partial E_i \partial E_k} \right)^T \]

\[ = -\left( \frac{\partial^2 \mathcal{F}}{\partial E_i \partial E_k} \right)^T = \Theta_{ki} \]
Electrostatics of Dielectrics

This can be identically transformed into

\[ \nabla - \nabla_0 = \oint (E + \mathcal{E}) \cdot (D - \mathcal{E}) dV / 8\pi - \oint \mathcal{E} \cdot (D - E) dV / 8\pi. \]

The first term on the right is zero, as we see by putting

\[ E + \mathcal{E} = - \operatorname{grad} (\phi + \phi_0) \]

and again using the same transformation. Hence we have

\[ \nabla - \nabla_0(V, T) = - \frac{1}{2} \oint \mathcal{E} \cdot \mathcal{P} dV. \]  \hspace{1cm} (11.7)

In particular, in a uniform external field

\[ \nabla - \nabla_0(V, T) = - \frac{1}{2} \mathcal{E} \cdot \mathcal{P}. \]  \hspace{1cm} (11.8)

This last equation can also be obtained by direct integration of the relation (11.3) if we notice that, since all the field equations are linear when \( D = \varepsilon E \), the electric moment \( \mathcal{P} \) must be a linear function of \( \mathcal{E} \).

The linear relation between the components of \( \mathcal{P} \) and \( \mathcal{E} \) can be written

\[ \mathcal{P}_i = \varepsilon \varepsilon_0 \mathcal{E}_i, \]  \hspace{1cm} (11.9)

as for conductors (§2). For a dielectric, however, the polarizability depends not only on the shape but also on the permittivity. The symmetry of the tensor \( d_{ik} \), mentioned in §2, follows at once from the relation (11.6); it is sufficient to notice that the second derivative \( \partial^2 \nabla / \partial \mathcal{E}_i \partial \mathcal{E}_k = - \partial \mathcal{P} / \partial \mathcal{E}_k = - \varepsilon \varepsilon_0 \) is independent of the order of differentiation.

Formula (11.7) becomes still simpler in the important case where \( \varepsilon \) is close to 1, i.e. the dielectric susceptibility \( \kappa = (\varepsilon - 1) / 4\pi \) is small. In this case, in calculating the energy, we can neglect the modification of the field due to the presence of the body, putting \( \mathcal{P} = \kappa E \approx \kappa E \). Then

\[ \nabla - \nabla_0 = - \frac{1}{2} \kappa \oint \mathcal{E}^2 dV, \]  \hspace{1cm} (11.10)

the integral being taken over the volume of the body. In a uniform field, the dipole moment \( \mathcal{P} = \kappa \mathcal{E} \), and the free energy is

\[ \nabla - \nabla_0 = - \frac{1}{2} \kappa V \mathcal{E}^2. \]  \hspace{1cm} (11.11)

In the general case of an arbitrary relation between \( D \) and \( E \), the simple formulae (11.7) and (11.8) do not hold. Here the formula

\[ \nabla = \oint \left( F - \frac{\mathcal{E}^2}{2\pi} \right) dV = \oint \left[ F - \frac{E \cdot D}{8\pi} - \frac{1}{2} P \cdot \mathcal{E} \right] dV \]  \hspace{1cm} (11.12)

may be useful in calculating \( \nabla \); its derivation is obvious after the above discussion. The two integrands differ by

\[ - \frac{E \cdot D}{8\pi} - \frac{1}{2} P \cdot \mathcal{E} + \frac{\mathcal{E}^2}{8\pi} = - \frac{1}{8\pi} (D - \mathcal{E}) \cdot (E + \mathcal{E}); \]

after substitution of \( E = - \operatorname{grad} \phi, \mathcal{E} = - \operatorname{grad} \phi_0 \) and integration over all space, the result is zero. In (11.12), as in (11.7), the second integrand is zero outside the body, where \( P = 0 \) and \( F = E^2 / 8\pi \), so that the integration is taken only over the volume of the body.
When \( \varepsilon \) is close to 1, we can neglect \( D \) modification.

The field due to dielectric:

\[
P = \frac{1}{4\pi} \left( D - \varepsilon E \right) = \frac{1}{4\pi} (\varepsilon - 1) E
\]

\[
\Rightarrow \varepsilon E
\]

\( \varepsilon \) is the small dielectric susceptibility.

For a uniform field:

\[
\Phi = \Phi_0 - \frac{1}{2} \varepsilon E^2
\]

Over the entire body.

In the case of an arbitrary relation between \( D \) and \( E \), the simple formula

\[
\Phi = \Phi_0 + \frac{1}{2} \int dV \varepsilon \cdot P
\]

does not hold.

\[
\Phi = \int (F - \frac{\varepsilon E^2}{8\pi}) dV = \int dV \left( F - \frac{E \cdot P}{8\pi} + \left[ \frac{E \cdot P}{8\pi} - \frac{\varepsilon E^2}{8\pi} \right] \right)
\]

\[
\Rightarrow -\frac{1}{2} E \cdot P
\]

for a linear homogeneous isotropic dielectric.

Zero outside dielectric as before.

\[
= \int dV \left( F - \frac{E \cdot P}{8\pi} - \frac{1}{2} E \cdot P \right)
\]

for a linear isotropic homogeneous dielectric. These two terms combine to give \( \Phi_0, P_0 \) free energy density in the absence of \( D \) field.
AN ASIDE

Adiabatic processes L''L, SM 1, 511

- A thermally isolated system is not in general a closed system, and its energy may vary with time.
- A thermally insulated system differs from a closed system because its Hamiltonian depends explicitly on time, because the time-dependent external field \( E = E(p, q, t) \).
- The Heisenberg increase of entropy applies not only for a closed body, but also for a thermally insulated body (the entropy-free source of the time-dependent external field can be incorporated as part of the system).

- If the rate of change of the external field is sufficiently slow (ADIABATIC), the entropy of the body remains unchanged, so the process is REVERSIBLE.

**Proof:** If the field corresponds to a parameter \( \lambda \), \( \frac{dS}{dt} \) depends on \( \frac{d\lambda}{dt} \). Recall that small, so we make a Taylor series:

\[
\frac{dS}{dt} = A_0 + A_1 \left( \frac{d\lambda}{dt} \right) + A_2 \left( \frac{d\lambda}{dt} \right)^2 + \ldots
\]

- \( A_0 = 0 \) because \( \frac{dS}{dt} \) under constant external conditions.
- \( A_1 = 0 \) since the first-order term changes sign with \( \frac{d\lambda}{dt} \), whereas \( \frac{dS}{dt} \) must always be positive.

\[
\frac{dS}{dt} = A \left( \frac{d\lambda}{dt} \right)^2 \Rightarrow \frac{dS}{d\lambda} = A \left( \frac{d\lambda}{dt} \right)
\]

\[
\Rightarrow \frac{dS}{d\lambda} \text{ tends to zero when} \frac{d\lambda}{dt} \text{ approaches zero.}
\]
A purely thermodynamic method for calculating various mean values.

Body undergoes an adiabatic process. What is $\frac{dE}{dt}$?

$$E = \text{Tr} \left( \rho \hat{H} \right)$$; specifically, $$E(t) = \text{Tr} \left( \rho(t) \hat{H}(\rho, g, \lambda(t)) \right)$$

$$\frac{dE}{dt} = \text{Tr} \left( \frac{d\rho(t)}{dt} \hat{H}(t) \right) + \text{Tr} \left( \rho(t) \frac{d\hat{H}}{dt} \right)$$

$$= \frac{1}{i} \text{Tr} \left( \left[ \hat{H}(t), \frac{d\rho(t)}{dt} \right] \hat{H}(t) \right) + \text{Tr} \left( \rho(t) \frac{\partial \hat{H}}{\partial \lambda} \frac{d\lambda}{dt} \right)$$

$$\text{Tr} \left( \hat{H} \rho \frac{d\lambda}{dt} - \rho \hat{H} \frac{d\lambda}{dt} \right)$$

$$\frac{dE}{dt} = \langle \frac{\partial \hat{H}}{\partial \lambda} \rangle \frac{d\lambda}{dt}$$

Since the process is ADIABATIC ($\lambda$ changes slowly on the timescale of equilibration) $$\langle \frac{\partial \hat{H}}{\partial \lambda} \rangle = \text{Tr} \left( \rho(t) \frac{\partial \hat{H}}{\partial \lambda} \right)$$

$$= \text{Tr} \left( \rho(t) (\lambda(t)) \frac{\partial \hat{H}}{\partial \lambda} \right)$$; the average $\frac{\partial \hat{H}}{\partial \lambda}$ can be evaluated with the statistical distribution corresponding to equilibrium for a given value $\lambda$.

In a thermodynamic formulation $dE = TdS + \left( \frac{\partial E}{\partial \lambda} \right) d\lambda$, so

$$\frac{dE}{dt} = \left( \frac{\partial E}{\partial \lambda} \right) \frac{d\lambda}{dt}$$

EQUATING THERMODYNAMIC AND STATISTICAL AVERAGES, WE SEE THAT $$\langle \frac{\partial \hat{H}}{\partial \lambda} \rangle = \left( \frac{\partial E}{\partial \lambda} \right)$$

density function \( \rho(x, y, z) \)

\( \rho \, d\mathbf{V} \) is the prob that an individual particle is in vec element \( d\mathbf{V} \).

some coord transformations (translations, rotations, reflections) leave \( \rho \) invariant.

set of all such: symmetry group.

isotropic bodies have highest symmetry. (gases liquids amorphous solids)

\( \rho \) = constant

anisotropic: \( \rho \) is triply periodic.

equivalent lattice points

can be mapped to coincide by a symmetry transformation

axes of symmetry

rotary reflection axes.

crystal lattice

can possess symmetry elements consisting undistinguishable translations with no axes of symmetry

\[
\begin{align*}
\delta x \times t & = dl \\
\delta \theta & \leq d\theta
\end{align*}
\]

\[
R \left( \begin{array}{c} x \\ y \\ z \end{array} \right) + R^{-1} \left( \begin{array}{c} dx \\ dy \\ dz \end{array} \right) = \]

\[
R \left\{ \left( \begin{array}{c} x \\ y \\ z \end{array} \right) + R^{-1} \left( \begin{array}{c} dx \\ dy \\ dz \end{array} \right) \right\}
\]
"Rotation thru a certain angle followed by translation perpendicular to the axis is equivalent to rotation thru the same angle about an axis parallel to the first."

Rotation by $\phi$ about $\alpha$ followed by translation $\pm s$ is equivalent to rotation by $\phi$ about $\pm s$, a point $s$ above the mid point of $\pm s$, where $\frac{s}{\tan \phi} = \tan \frac{\phi}{2}$.

Screw axis $\frac{2\pi}{n} + t$ translation along axis.

After $n$ rotations + translation = net translation.

Periodicity not exceeding $nk$.

$d = np/n$ (p = 1, 2, ..., n-1)

Smallest period of lattice along axis.

Screw axis order 2: $d = a/2$

Order 3: $d = a/3$ or $2a/3$

Translations + Plane of Symmetry

If in a plane + translation 1 + plane equiv to reflection in a plane 11' to first.
The Bravais lattice.

Three basic lattice vectors:

\[ a = n_1 a_1 + n_2 a_2 + n_3 a_3 \]

\[ a_i' = \sum \frac{dik a_k}{b} \]

\[ a_i \text{ must be expressible as } a_i = \sum \frac{bik a_k}{b} \text{ again integer} \]

\[ \left| \frac{bik}{dik} \right| = \left| \frac{1}{dik} \right| \]

\[ \text{Determinants are reciprocal} \]

\[ \text{for } a_i \text{ to be basic lattice vector.} \]

Unit cell:

parallellepped formed by three lattice vectors from a lattice point.

whole lattice: a regular assembly
set of all equivalent rectagles is a Bravais lattice
which can be brought into equivalence by translation.
The Bravais lattice does not include any of the point lattices.

Crystal lattices in general consist of several interpenetrating Bravais lattices.

Each contains one point Bravais lattice.

The unit cells in general are not unique
resulting in various shapes, equal volumes.

Each contains one point Bravais lattice.

Unit cells in equivalent. always equal. number atoms of particular type per unit cell.

Possible crystal symmetries: Bravais lattices
which axes of symmetry cannot hold.

\[ a + 2a \sin(\phi - \pi/2) = a + 2a (\sin \phi \cos \frac{\pi}{2} + \cos \phi \sin \frac{\pi}{2}) \]
\[ = a + 2a \cos \phi = pa \]
\[ = a - 2a \cos \phi = pa \]

\[ \cos \phi = \frac{1 - \frac{p}{2}}{} \]
\[ \cos \phi = 0, \frac{1}{2}, 0, -\frac{1}{2} \]
\[ p = 0, 1, 2 \pi, -1 \]
\[ \phi = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{2} \]
\[ n = 0, 1, 2, 3, 2 \]
crystal systems: type of symmetry of a Bravais lattice: odd reflections as a point group.

Every point of a Bravais lattice is a center of symmetry. Proof:

every point of a Bravais lattice is a center of symmetry. Proof:

to each atom in a Bravais lattice, there corresponds another atom cellwise with that atom and with the lattice pt. considered.

If the center symmetry is the only symmetry element of the Bravais lattice (apart from translations) we have:

\[ a + 2a \sin (\phi - \pi/2) = a + 2a \cos \phi \sin (-\pi/2) \]
\[ \Rightarrow a - 2a \cos \phi = \rho a \]

\[ \cos \phi = \frac{\frac{1}{2} - \rho}{2} \]

\[ 1 - 2|\cos \phi| \geq 0 \]

\[ \rho = -1, 0, 1, 2, 3 \]

\[ \cos \phi = 1, \frac{3}{4}, 0, -\frac{1}{2}, -1 \]

\[ \phi = 0, \frac{\pi}{3}, \frac{2\pi}{3}, \frac{\pi}{2} \]

\[ \phi = \frac{2\pi}{n}, n = 1, 6, 4, 3, 2 \]

axes of order 2, 3, 4, and 6 are permissible.
Types of symmetry of the Bravais lattice: rotations and reflections.

Crystal systems: certain axes; planes of symmetry (a point group).

Every point in a Bravais lattice is a center of symmetry. Therefore:

If the center of symmetry is the only symmetry element of a Bravais lattice (apart from translations) we have:

1. A triclinic system — pt. group $C_1$

   - Points of a triclinic Bravais lattice lie at various equal parallelepipeds with edges of arbitrary lengths and arbitrary angles between the edges.

2. Monoclinic system: 2nd order axis, plane symmetry.

   - Plane $\Gamma m$.

   - Right parallelepiped $C_{2h}$.

   - Base-centered monoclinic.

   - Base-centered parallelogram.

   - Reflection plane.

   - Lattice points at centers of opposite rectangular faces.
orthorhombic system $\text{D}_{2h}$
rectangular parallelepiped with edges of any length.

- base-centered $\Gamma_0^b$
- body-centered $\Gamma_0^v$
- face-centered $\Gamma_0^f$

tetragonal system

right square prism

- vertex
- vertex and center

trigonal or rhombohedral

$\text{D}_{3d}$ (symmetry of rhombohedron, a solid formed by a cube by stretching or compressing it along a spatial diagonal).

#at a points at vertices

hexagonal system

$\text{D}_{6h}$

points directly from regular hexagonal prism superimposed in successive such planes.

cubic system $\Gamma+\Gamma+\Gamma \in \text{Oh}$ $\Gamma_0^e \Gamma_0^v \Gamma_0^f$

triclinic monoclinic or orthorhombic tetragonal
each contains 12 symmetry elements which appear in $\Gamma$ precedences.

- $\Gamma_t$
- $\Gamma_m$
- $\Gamma_h$
- $\Gamma_0$
- $\Gamma_r$
- $\Gamma_c$

2 types of highest symmetry
Bravais lattices are three-dimensional periodic structures, where each translation vector is a unit cell. The Bravais lattices are:

1. Simple cubic (Pc)
2. Face-centered cubic (Fcc)
3. Body-centered cubic (Bcc)
4. Tetragonal (P4)
5. Hexagonal (P6)
6. Trigonal (R3)

The unit cells of Pc and Pd are rhombohedral, and they do not form their own Bravais lattices. Instead, they form the hexagonal Bravais lattice.

Crystal systems are classified into seven categories based on the symmetry of the unit cell:

1. Triclinic (C1)
2. Monoclinic (C2)
3. Orthorhombic (Cm)
4. Tetragonal (P4)
5. Cubic (Pm3)
6. Hexagonal (P6)
7. Triclinic (C1)

Each crystal system contains a specific number of symmetry elements. For example, the cubic system contains all five symmetry elements, while the triclinic system contains only one.

The set of symmetry elements forming the class is different from the system.

Crystal classes equal to four elements system.

All classes belonging to a given system:

1. All point groups that contain the same symmetry elements.
2. All Bravais lattices have a common symmetry. Ci present in all systems.
3. Each class must be assigned to the system of lowest symmetry among those which contain it.

Ci is present in all triclinic.
a hexagonal $\rightarrow$ rhombohedral

all the classes of the rhombohedral system can be obtained with a rhombohedr or a rhombohedral Bravais lattice.

set all symmetry elements: space group.
Dielectric properties of crystals

\[ D_i = D_{0i} + \varepsilon_{ik} E_k \]

\[ \varepsilon_{ik} = \varepsilon_{ki} \]

\[ D_i = -\frac{\partial F}{\partial E_i} \]

\[ \varepsilon_{ik} = \frac{\partial D_i}{\partial E_k} = -\frac{\partial^2 F}{\partial E_k \partial E_i} \]

\[ E_i \times E_k \]

When \( D_i = \varepsilon_{ik} E_k \)

\[ d\tilde{F} = -SdT + \Psi d\rho - \mathbf{D} \cdot d\mathbf{E} / 4\pi \]

\[ = -SdT + \Psi d\rho - \varepsilon_{ik} E_i dE_k / 4\pi \]

arbitrary path from \((\rho_0, T_0)\) to \((\rho, T)\) in the density-temperature plane.

\[ \int d\tilde{F} = F_0(\rho, T) \]

\[ \int d\tilde{F} = -\varepsilon_{ik} E_i E_k / 8\pi \]

\[ \tilde{F}(T, \rho, E) = \int d\tilde{F} + \int d\tilde{F} = F_0(T, \rho) - \varepsilon_{ik} E_i E_k / 8\pi \]
\[ F = \frac{\vec{F} + E \cdot D}{4\pi} \quad (10.8) \]

\[
F(T, \rho, E) = \overline{F_0(T, \rho)} - \frac{E \cdot D}{8\pi} + \frac{E \cdot D}{4\pi} = F_0 + \frac{E \cdot D}{8\pi}
\]

same as

\[ F_0(T, \rho) \]

we want to express \( E \) in terms of \( D \):

\[ E = \varepsilon^{-1} \cdot D \]

\[ E_i = \varepsilon_i^{\text{-}1} \cdot D_k \]

\[
F(T, \rho, D) = F_0(T, \rho) + \frac{1}{8\pi} \varepsilon_{ij} \varepsilon_j^\text{-1} \cdot D_k \cdot D_i
\]

\[ = F_0(T, \rho) + \frac{1}{8\pi} \varepsilon_0^{\text{-}1} \cdot D_j \cdot D_k \quad (13.5) \]

\( \varepsilon \) can be brought into diagonal form by a suitable choice of co-ordinate axes. Principal values \( \varepsilon^{(1)}, \varepsilon^{(2)}, \varepsilon^{(3)} \).

All of these are necessarily greater than unity \((\delta/4)\).

The principal values of \( \varepsilon \) may be less than 3 for certain symmetries of the crystal.

Every symmetric second rank tensor \( T \) corresponds to a tensor ellipsoid. The length of whose semi-axes are proportional to the principal values of the tensor. The symmetry of the ellipsoid corresponds to that of the \( T \) field.
triclinic monochine rhombic

\[
\text{X: biaxial}
\]

symm. tensor rank two: tensor ellipsoid

triclinic: diagonal lattice, all 3 principal values are different.

rhombic system: 3 axes at right angles.

tetragonal Pyq, sp. prism

hexagonal

2 indep quantities: UNIAXIAL, monoclinic

diagonal: max 3 principal axes can be chosen arbitrarily.

tensor ellipsoid is a spheroid.

as regards physical properties, a crystal that is determined
by a symmetrical tensor of rank 2, the presence of an axis of symmetry
of 2nd order is equivalent to complete isotropy. No plane perpendicular to
this axis.

cubic system, all 3 principal axes same; directions arbitrary.

6 faces: in regard to dielectric properties, crystal of cubic system need not be
isotropic bodies.

Do spontaneous polarization, even in absence of an electric field.

pyroelectric: polarizability small compared to molecular fields.

\( \sigma \) ensures constancy of expansion \( \frac{\partial V}{\partial P} \).
Permeodynamic relations for a pyroelectric body.

\[ D_i = -\frac{1}{4\pi} \left( \frac{\partial \bar{F}}{\partial E_i} \right)_{T,\rho} = D_{0i} + \varepsilon_{i\lambda} E_{\lambda} \]

\[ \bar{F}(T, \rho, E) = F_0(T, \rho) - \frac{1}{4\pi} D_{0i} E_i - \frac{1}{8\pi} \varepsilon_{i\lambda} E_{\lambda} E_i \]

Free energy is

\[ F = \bar{F} + \frac{E_i D_i}{4\pi} = F_0 + \frac{1}{4\pi} \left( D_{i} - D_{0i} \right) E_i - \frac{1}{8\pi} \varepsilon_{i\lambda} E_{\lambda} E_i \]

\[ F = F_0 + \frac{1}{8\pi} \varepsilon_{i\lambda} E_i E_{\lambda} \]

The term \( F \) linear in \( E_i \) does not appear in \( F \).

Piezoelectric : in kind stresses

The total free energy of a pyroelectric

\[ \mathcal{G} = \int \left[ F - \frac{E_i D_i}{8\pi} - \frac{1}{2} P \cdot E \right] dV \]

\[ (\text{I.12}) \]

\[ \mathcal{G} = \int \left[ F - \frac{E_i D_i}{8\pi} \right] dV = \int \left[ F_0 + \varepsilon_{i\lambda} E_i E_{\lambda} \right] \frac{1}{8\pi} \left( D_{0i} + \varepsilon_{i\lambda} E_{\lambda} \right) dV \]

for \( E = 0 \)

\[ = \int \left[ F_0 - \frac{E_i D_{0i}}{8\pi} \right] dV \]
Pyroelectricity not possible for every crystal symmetry. Must be a direction which remains the same (end is not reversed). Symmetry groups w/ single axis + plane of symmetry which pass through that axis. (stabilized center of symmetry cannot be pyroelectric)

- Triclinic $C_1$
- Monoclinic $C_2$, $C_2'$
- Rhombic $C_{2v}$
- Tetragonal $C_4$, $C_{4v}$
- Cubic $C_3$, $C_{3v}$
- Hexagonal $C_6$, $C_{6v}$

No pyroelectric cubic $C_{6v}$

Under ordinary conditions, pyroelectric $C_{6v}$ have ZERO total electric dipole moment. Nonzero $E$ inside a spontaneously polarized dielectric, $P$ not zero

Small conductivity non-zero

Same effect w/ ions deposited on the surface from the air. Pyroelectric properties are also sensed when a $C_{6v}$ heated and its pole is altered.
Problem 2 5 13  L = L E C M

Determine the field of a point charge in a homogeneous anisotropic medium.

\[ \text{div} \, D = 4 \pi \varepsilon \delta^{(3)}(\vec{r}) \quad \text{(charge at the origin)} \]

\[ D_i = \varepsilon_{ik} \vec{E}_k = -\varepsilon_{ik} \frac{\partial \phi}{\partial x_k} \]

Taking the coordinate axes \( x, y, z \) along the principal axes of the tensor \( \varepsilon_{ik} \)

\[ \varepsilon_{ik} = \varepsilon^{(i)} \delta_{ik} \quad i, k = x, y, z \]

\[ \text{div} \, D = \frac{\partial}{\partial x_i} D_i = -\frac{\partial}{\partial x_i} \varepsilon^{(i)} \delta_{ik} \frac{\partial \phi}{\partial x_k} \]

\[ = -\varepsilon^{(i)} \delta_{ik} \frac{\partial^2 \phi}{\partial x_i \partial x_k} = -\varepsilon^{(i)} \frac{\partial^2 \phi}{\partial x_i^2} = 4 \pi \varepsilon \delta^{(3)}(\vec{r}) \]

Let

\[ x'_i = x_i / \sqrt{\varepsilon^{(i)}} \], so that

\[ -\frac{\partial^2 \phi}{\partial x_i'^2} = 4 \pi \varepsilon \delta(\sqrt{\varepsilon^{(x)} x'_i}) \delta(\sqrt{\varepsilon^{(y)} y'}) \delta(\sqrt{\varepsilon^{(z)} z'}) \]

\[ = \frac{4 \pi \varepsilon}{\sqrt{\varepsilon^{(x)} \varepsilon^{(y)} \varepsilon^{(z)}}} \delta^{(3)}(\vec{x}') \]

\[ \phi = \frac{e'}{r'} = \frac{e}{\sqrt{\varepsilon^{(x)} \varepsilon^{(y)} \varepsilon^{(z)}}} \left[ \frac{x^2}{e^{(x)}} + \frac{y^2}{e^{(y)}} + \frac{z^2}{e^{(z)}} \right]^{-\frac{1}{2}} \]
\[ \sqrt{\epsilon^{(x)} \epsilon^{(y)} \epsilon^{(z)}} = \sqrt{1} \] where \( 1 \) is the
determinant of \( \epsilon_i \).

\[ \frac{x^2}{\epsilon^{(x)}} + \frac{y^2}{\epsilon^{(y)}} + \frac{z^2}{\epsilon^{(z)}} = (x, y, z) \begin{pmatrix} 1/\epsilon^{(x)} & 0 & 0 \\ 0 & 1/\epsilon^{(y)} & 0 \\ 0 & 0 & 1/\epsilon^{(z)} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \]

Let \( O \left( \begin{pmatrix} x \\ y \\ z \end{pmatrix} \right) = \begin{pmatrix} \alpha & -\beta & \gamma \\ \beta & \alpha & -\gamma \\ -\gamma & \beta & \alpha \end{pmatrix} \) be a transformation to

some other coord. system, which doesn't necessarily

coincide with the principal axes of \( \epsilon_i \).

\[ (x, y, z) \begin{pmatrix} 1/\epsilon^{(x)} & 0 & 0 \\ 0 & 1/\epsilon^{(y)} & 0 \\ 0 & 0 & 1/\epsilon^{(z)} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = (\bar{x}, \bar{y}, \bar{z}) \begin{pmatrix} \epsilon^{-1} & 0 & 0 \\ 0 & \epsilon^{-1} & 0 \\ 0 & 0 & \epsilon^{-1} \end{pmatrix} \begin{pmatrix} \frac{\bar{x}}{\epsilon^{(x)}} \\ \frac{\bar{y}}{\epsilon^{(y)}} \\ \frac{\bar{z}}{\epsilon^{(z)}} \end{pmatrix}. \]

In tensor notation, we can write

\[ \Phi = \epsilon \sqrt{1} \epsilon^{-1} \epsilon \epsilon \]

as stated in problem 2.
Showing directly that a three-fold axis of symmetry (intersected by 3 reflection planes) is equivalent to complete isotropy of the dielectric response in directions perpendicular to that axis.

\[
\begin{align*}
\hat{z} & \quad \hat{x} \\
\theta & \quad \phi
\end{align*}
\]

Assume initially that the dielectric tensor
\[
\varepsilon = \varepsilon_1 \hat{1} \hat{1} + \varepsilon_2 \hat{2} \hat{2}
\]
has (possibly) different principal values \(\varepsilon_1\) and \(\varepsilon_2\), with the corresponding axes oriented arbitrarily with respect to the three reflection planes.

The electric induction is \(D = \varepsilon \cdot E\).

For the special case of \(E\) lying parallel to any of the reflection planes, we know that \(D\) must be \(\varepsilon E\), with \(\varepsilon\) the same for any of the three symmetry-related directions.

For \(E = E \hat{z}\) then
\[
D = \varepsilon E \hat{z}.
\]
Likewise, for \(E = E \left( \frac{\sqrt{3}}{2} \hat{x} - \frac{\hat{y}}{2} \right)\)
we have
\[
D = \varepsilon E \left( \frac{\sqrt{3}}{2} \hat{x} - \frac{\hat{y}}{2} \right)
\]
\[
= E \left( \varepsilon_1 \left( \frac{\sqrt{3}}{2} \sin \theta - \frac{1}{2} \cos \theta \right) \right)
+ \varepsilon_2 \left( \frac{\sqrt{3}}{2} \cos \theta + \frac{1}{2} \sin \theta \right)
\]
Because of the three-fold symmetry, the electric induction must have the same strength in each of these cases.

\[
\epsilon_1 \cos^2 \theta + \epsilon_2 \sin^2 \theta = \epsilon_1 \left( \frac{3}{4} \sin^2 \theta - \frac{\sqrt{3}}{2} \sin \theta \cos \theta + \frac{1}{4} \cos^2 \theta \right) \\
+ \epsilon_2 \left( \frac{3}{4} \cos^2 \theta + \frac{\sqrt{3}}{2} \sin \theta \cos \theta + \frac{1}{4} \sin^2 \theta \right)
\]

\[
0 = \epsilon_1 \left( \frac{3}{4} \sin^2 \theta - \frac{\sqrt{3}}{2} \sin \theta \cos \theta - \frac{3}{4} \cos^2 \theta \right) \\
+ \epsilon_2 \left( \frac{3}{4} \cos^2 \theta + \frac{\sqrt{3}}{2} \sin \theta \cos \theta - \frac{3}{4} \sin^2 \theta \right)
\]

\[
= (\epsilon_1 - \epsilon_2) \left( \frac{3}{4} \sin^2 \theta - \frac{\sqrt{3}}{2} \sin \theta \cos \theta - \frac{3}{4} \cos^2 \theta \right)
\]

\[
= (\epsilon^2 - \epsilon_1^2) \left( \frac{\sqrt{3}}{2} \cos \theta - \frac{\sqrt{3}}{2} \sin \theta \right)
\]

\[
= (\epsilon^2 - \epsilon_1^2) \left( \frac{\sqrt{3}}{2} \cos(2\theta + \frac{\pi}{6}) \right) \quad 0 \leq \theta < \frac{\pi}{6}
\]

The argument of the cosine is

less than \( \frac{3\pi}{6} = \frac{\pi}{2} \)

so we must have \( \epsilon_1 = \epsilon_2 \);

The two values are equal, so

\[
\Xi = \epsilon (ii + jj) \) is proportional to the identity tensor, and \( \theta \) becomes arbitrary.
The sign of the dielectric susceptibility,

change in the electric component of the total free energy of a body when \( \epsilon \) undergoes an infinitesimal change.

isotropic but not necessarily homogeneous

\[
\delta G = \delta G_0 = \int \frac{D^2}{8\pi\epsilon} \, dv
\]

free energy in presence of D field.

When \( \epsilon \) changes, so does \( \Phi \) the induction

\[
\delta \Phi = \int \frac{D \cdot \delta D}{4\pi\epsilon} \, dv - \int \frac{SeD^2}{8\pi\epsilon} \, dv
\]

\[
= \int \frac{E \cdot \delta D}{4\pi} \, dv - \int \frac{E^2}{8\pi} \delta \epsilon \, dv
\]

work done in

uninfinitesimal changes in source.

since we're considering constant source, this term vanishes.

\[
\delta G = -\int \frac{E^2}{8\pi} \delta \epsilon \, dv
\]

any increase in \( \epsilon \) leads to a decrease in the free energy.

free energy always decreased when uncharged conductors are brought into a dielectric medium.
we said in §7 that \((\xi - 1)/4\pi\) is positive.

The total change in the free energy of a dielectric isemiconductor placed
in an electric field is negative.

The change in the free energy of a body being regarded as a result of
perturbation of its quantum energy level by an electric field

\[
\Delta G - G_0 = \sum_n \frac{1}{2} \sum_m \frac{1}{E_n^{(0)} - E_m^{(0)}} \left| V_{nm} \right|^2 \left( w_n - w_m \right) + \frac{1}{2kT} \left( V_{nn} - \frac{\sum m}{\sum m} \right)^2
\]

\[
W_n = \exp \left( \frac{\Delta G_0 - E_n^{(0)}}{kT} \right)
\]

From StatPhys §32

\[
\hat{H} = \hat{H}_0 + \hat{V}
\]

\[
E_n = E_n^{(0)} + V_{nn} + \sum_m \frac{1}{E_n^{(0)} - E_m^{(0)}} \left| V_{nm} \right|^2
\]

\[
e^{-F/T} = \sum_n e^{-E_n/T}
\]

\[
\frac{-F}{T} = \ln \sum_n e^{-E_n/T}
\]

\[
= \ln \left\{ \sum_n \frac{e^{-E_n/T}}{\sum_n e^{-E_n/T}} \right\}
\]

\[
\frac{N}{e^{-F_0/T}} + \ln \left( \frac{\sum_n e^{-\left(E_n^{(0)} + E_n^{(1)} + E_n^{(2)}\right)/T}}{\sum_n e^{-E_n^{(0)}/T}} \right)
\]
\[ F = F_0 - T \ln \left\{ 1 - \sum_n \frac{E_n^{(2)}}{T} - \sum_n \frac{E_n^{(1)}}{T} W_n \right\} + \frac{1}{2T} \sum_n \frac{E_n^{(1)}}{T}^2 \]

\[ F = F_0 + \sum_n W_n E_n^{(1)} + \sum_n W_n E_n^{(2)} - \frac{1}{2T} \sum_n \left( \sum W_n E_n^{(1)} \right)^2 \]

\[ \ln (1 + x) = x - \frac{x^2}{2} \]

\[ 1 \text{st term: linear in field; non-zero only for pyroelectric bodies} \]

\[ \frac{d}{dx} = \frac{1}{1 + x} \]

\[ \frac{d^2}{dx^2} = -\frac{1}{(1 + x)^2} \]

\[ \sum_n W_n E_n^{(2)} = \sum_n \sum_m \frac{W_m / V_{nm}}{E_m^{(2)} - E_n^{(1)}} \]

\[ = \frac{1}{2} \sum_n \sum_m \frac{W_n / V_{nm}}{E_n^{(1)}} + \frac{1}{2} \sum_n \sum_m \frac{W_m / V_{nm}}{E_m^{(2)} - E_n^{(1)}} \]

\[ = -\frac{1}{2} \sum_n \sum_m \left( \frac{W_m - W_n}{V_{nm}} \right)^2 \frac{1}{E_n^{(1)} - E_m^{(2)}} \]

If we consider the change in free energy as \( dF \), resulting in a gradual change in dielectric constant of the body from \( E_0 \) to a given value \( E \), it follows that from (14.1) that \( F - F_0 \) is negative only if \( E > 1 \).
The total free energy is diminished, in particular, when any change is brought upon a dielectric body from infinity. (an increase in \( \varepsilon \) in a certain volume around the charge)

should prove \( F \) cannot attain a minimum for any finite distance.

directing motion of a dielectric body in an almost uniform field

\[
\delta F = -\frac{E^2}{8\pi} \int dV \delta \varepsilon
\]

\[
\delta F - \delta \varepsilon = -\frac{E^2}{8\pi} \int dV \varepsilon_i^n (r)
\]

to minimize \( F \), body moves in direction of increasing \( E \).
Reminding myself of the proof of (14.12)

For an arbitrary relation between $D$ and $E$

$$\frac{1}{8\pi} \int dV \left\{ \varepsilon^2 - E \cdot D - \frac{1}{2} P \cdot \varepsilon \right\}$$

volume over side conductors (sources)

$$= \frac{1}{8\pi} \int dV \left\{ \varepsilon^2 - E \cdot D - (D - E) \cdot \varepsilon \right\}$$

$$= \frac{1}{8\pi} \int dV \left( \varepsilon + E \right) \cdot (\varepsilon - D) = \frac{1}{8\pi} \int dV \ \text{grad} (\phi + \phi_0) \cdot (\varepsilon - D)$$

$$= \frac{1}{8\pi} \int dV \left\{ \text{div} \left[ (\phi + \phi_0)(\varepsilon - D) \right] - (\phi + \phi_0) \ \text{div} (\varepsilon - D) \right\}$$

$$= \frac{1}{8\pi} \oint d\mathbf{r} \cdot \left[ (\phi + \phi_0)(\varepsilon - D) \right] - \frac{1}{8\pi} \int dV (\phi + \phi_0) \ \text{div} (\varepsilon - D)$$

closed surface w/ area element pointing outward at infinity and from the dielectric to source conductors

$$= \frac{1}{8\pi} \oint d\mathbf{r} \cdot \left[ (\phi + \phi_0)(\varepsilon - D) \right] = -\frac{1}{8\pi} \left( \phi + \phi_0 \right) 4\pi \left( \varepsilon - \varepsilon_0 \right)$$

surface int. at zero vanishes because the fields x potentials do so.

both terms zero outside the conductor

be constant on surface of any conductor

outward from the conductor

$$= -\frac{1}{8\pi} \left( \phi + \phi_0 \right) 4\pi \left( \varepsilon - \varepsilon_0 \right)$$
"When E changes, so does the induction..."

Even though \( \nabla \cdot D = \mu \nabla \rho \), it is NOT correct to think of \( \rho \) as a source for \( D \) in the same way that \( \rho \) itself is a source for \( E \); In addition, \( \nabla \cdot E = \mu \nabla \rho \), we also have \( \nabla \times E = 0 \). But the curl of \( D \) is non-zero in general.

An example: a dielectric needle in a constant field along its axis.

\[
\begin{align*}
\frac{\epsilon}{r} & \to \\
- & \quad \quad 0 \\
E &= E \quad \text{everywhere except near the ends of the needle. Since }
D &= \epsilon E = \epsilon E \quad \text{in the interior of the needle, a change in}
\end{align*}
\]

\[
\left\{ \begin{array}{c}
\frac{\partial E}{\partial t} \\
\epsilon
\end{array} \right\} 
\]

\[
\begin{align*}
\oint \nabla \cdot D &= \epsilon \nabla \cdot D \\
abl \times \text{curl} D &= a(\epsilon E - \epsilon) = a(\epsilon - 1) \epsilon
\end{align*}
\]

\[
\text{(The apparent dependence on } b \text{ comes from the fact that } \text{curl } D \text{ diverges at the boundary.)}
\]

\[
\text{(The dielectric is } b \text{ inclusion.)}
\]
Back to our problem of the total free energy of a pyroelectric and its change under a change in \( \varepsilon \).

From (11.12)

\[
\delta G = \int (F - \frac{E^2}{8\pi}) dV = \int dV (F - \frac{E \cdot D}{8\pi} - \frac{D \cdot \varepsilon}{2})
\]

all space outside conductors, electric body only.

From (11.7) \( F = F_0 + \frac{1}{8\pi} \varepsilon_{ik} \left( D_i - D_{0i} \right) \left( D_k - D_{0k} \right) \)

Using the first equality in (11.12) (which would give the same result for \( \delta G \) without the \( E^2 \) contribution):

\[
\delta G = \frac{1}{8\pi} \int dV \varepsilon_{ik} \left( D_i - D_{0i} \right) \left( D_k - D_{0k} \right)
\]

\[+ \frac{1}{2\pi} \int dV \varepsilon_{ik} \left( D_i - D_{0i} \right) \delta D_k
\]

\[
\varepsilon_{ik} \varepsilon_{kj} = \delta_{ij} \Rightarrow \delta \varepsilon_{ik} \varepsilon_{kj} + \varepsilon_{ik} \delta \varepsilon_{kj} = 0
\]

\[
\delta \varepsilon_{ik} \varepsilon_{kj} \varepsilon_{jk} = - \varepsilon_{ik} \delta \varepsilon_{kj} \varepsilon_{jk}
\]

\[
\delta \varepsilon_{ik} = - \varepsilon_{ik} \delta \varepsilon_{kj} \varepsilon_{jk}
\]

\[
\delta \varepsilon_{ik} = - \varepsilon_{ik} \delta \varepsilon_{kj} \varepsilon_{jk}
\]
We find

$$
\delta \mathcal{F} = - \frac{1}{8\pi} \int dV \ e_{ij} \ \delta e_{ij} \ (D_i - D_i)(D_k - D_k) + \frac{1}{9\pi} \int dV \ E_k \ \delta D_k
$$

$$
= - \frac{1}{8\pi} \int dV \ E_k \ \delta e_{ij} \ E_j + \frac{1}{9\pi} \int dV \ E_k \ \delta D_k
$$

Since the volume integral is overall all space, by (10.2)
the latter term gives the work done in changing the external charge (on the conductors). There is no such change in external charge, so this term vanishes,

$$
\delta \mathcal{F} = - \frac{1}{8\pi} \int dV \ E \cdot \delta e \cdot E
$$

A result essentially ally similar to (14.1)

Now the integrand can only be nonzero in side the dielectric
Now we try the other route, relying on the second member of (11.12).

We'll need

\[
\delta(E \cdot D) = \delta \left\{ \epsilon_{ik} (D_k - D_{0k}) D_i \right\} \frac{3}{2}
\]

\[
= \delta \epsilon_{ik} (D_k - D_{0k}) D_i + \epsilon_{ik} \delta D_k D_i + \epsilon_{ik} (D_k - D_{0k}) \delta D_i
\]

\[
= -\epsilon_{ik} \delta \epsilon_{lj} \epsilon_{jk} (D_l - D_{0l}) D_i + 2 \epsilon_{ik} \delta D_k D_i - \epsilon_{ik} D_{0k} \delta D_i
\]

\[
\frac{E_j}{E_j}
\]

\[
\delta(E \cdot D) = -\epsilon_{ik} \delta \epsilon_{lj} E_j D_i + 2 \epsilon_{ik} \delta D_k D_i - \epsilon_{ik} D_{0k} \delta D_i
\]

\[
= -\epsilon_{ik} \delta \epsilon_{lj} E_j D_i + 2 \epsilon_{ik} \delta D_k (D_i - D_{0i}) + \epsilon_{ik} D_{0i} \delta D_k
\]

\[
\delta(E \cdot D) = -\epsilon_{ik} \delta \epsilon_{lj} E_j D_i + 2 \epsilon_{ik} \delta D_k D_i + \epsilon_{ik} D_{0i} \delta D_k
\]

\[
\delta(P \cdot E) = \delta \left( \frac{D - E}{4\pi} \right) \cdot \xi = \frac{1}{4\pi} \delta \left( D_i - \epsilon_{ik} (D_k - D_{0k}) \right) \xi
\]

\[
= \frac{1}{4\pi} \left( \delta D_i + \epsilon_{ik} \delta \epsilon_{lj} \epsilon_{jk} (D_l - D_{0l}) - \epsilon_{ik} \delta D_k \right) \xi
\]

\[
\frac{E_j}{E_j}
\]

\[
\delta(P \cdot E) = \frac{1}{4\pi} \left( \delta D_i + \epsilon_{ik} \delta \epsilon_{lj} E_j - \epsilon_{ik} \delta D_k \right) \xi
\]
Substitution in (11.12) yields

\[ \delta \mathcal{F} = \int d^3 \mathbf{r} \left\{ -\frac{1}{\varepsilon_0} \varepsilon_2 \delta \varepsilon_{ij} E_j \left[ \nabla \times \mathbf{E} \right]_i + \frac{1}{4\pi} \varepsilon_2 \delta \mathbf{D} \cdot \mathbf{E} \right\} \]

This term can't be omitted, since the integral is not over all space.

\[ = \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \left[ \mathbf{D} \cdot \mathbf{E} \right]_i - \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \mathbf{D} \cdot \mathbf{E} \]

Doing so:

\[ \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \mathbf{D} \cdot \mathbf{E} \]

\[ = \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \left( \mathbf{D}_i - \mathbf{D}_i \right) \delta \varepsilon_{ij} - \mathbf{D}_i \varepsilon_2 \mathbf{E}_j \cdot \mathbf{E}_i \]

\[ = \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \mathbf{D}_i - \mathbf{D}_i \varepsilon_2 \mathbf{E}_i \cdot \mathbf{E}_i \]

\[ = \frac{1}{8\pi} \varepsilon_2 \mathbf{E}_i \cdot \mathbf{D}_i - \mathbf{D}_i \varepsilon_2 \mathbf{E}_i \cdot \mathbf{E}_i \]
Examining the 3rd line

\[ - \frac{1}{8\pi} \sum \delta D_i + \varepsilon_{ik} \delta \varepsilon_{nk} E_j - \varepsilon_{ik} \sum \delta D_k \varepsilon_{n} E_i \]

\[ = - \frac{1}{8\pi} \left( \delta D_i - \delta E_i \right) \varepsilon_i \]

We find

\[ \delta \mathcal{F} = - \frac{1}{8\pi} \int_{\text{dielectric}} \left( D_0 \varepsilon E_i + \left( \delta D_i - \delta E_i \right) \varepsilon_i \right) \]

I'm unsure of agreement w/ previous expression (p. 13)
Free energy change in a pyroelectric due to a change in $\varepsilon$.

From (11.12)

$$\delta G = \int dV \left(F - \frac{E^2}{\varepsilon \pi}\right) = \int dV \left(F - \frac{E_i E_j}{\varepsilon \pi} - \frac{1}{2} P \cdot \varepsilon\right)$$

This integral vanishes in the vacuum.

For a pyroelectric, from (13.1), the free energy density is

$$F = F_0 + \varepsilon_{ik} \frac{E_i E_k}{\varepsilon \pi}$$

$$\delta G = \int dV \left\{ \varepsilon_{ik} \frac{E_i E_k}{\varepsilon \pi} + \frac{\varepsilon_{ik}}{4\pi} E_i \delta E_k \right\}$$

$$\delta E_k = \delta \left\{ \varepsilon_{il} \left(D_e - D_0\right) \right\}$$

$$\varepsilon_{ij} \varepsilon_{jk} = \delta_{ik} \Rightarrow \delta \varepsilon_{ij} \varepsilon_{jk} + \varepsilon_{ij} \delta \varepsilon_{jk} = 0$$

$$\delta E_{ij} \varepsilon_{kl} + \varepsilon_{ij} \delta E_{kl} = 0$$

$$\delta e_{ik} = - \varepsilon_{ij} \delta e_{jh}$$
\[ \delta \mathcal{F} = \int_{\text{all space}} \sum \left\{ \frac{\delta e_{ih}}{8\pi i} E_i E_h + \frac{1}{4\pi i} e_{ih} e_i \left( -e_j^{-1} \delta e_{jk} e_l \delta_{hl} (D_e - D_{de}) + e_{hl} \delta D_e \right) \right\} \]

\[ \delta \mathcal{F} = \int_{\text{all space}} \left\{ \frac{\delta e_{ih}}{8\pi i} E_i E_h - \frac{1}{4\pi i} E_j \delta e_{jk} E_h + \frac{1}{4\pi i} E_l \delta D_e \right\} \]

\[ \delta \mathcal{F} = -\frac{1}{8\pi i} \int_{\text{all space}} \delta e_{ih} E_i E_h + \frac{1}{4\pi i} \int_{\text{all space}} E_l \delta D_e \]

Integrand is only nonzero inside the dielectric. The word zero in changing the charge on external conductors.

\[ \delta \mathcal{F} = -\frac{1}{8\pi i} \int_{\text{dielectric}} E_i \delta e_{ih} E_h \]

In terms of the induction this becomes

\[ \delta \mathcal{F} = -\frac{1}{8\pi i} \int_{\text{dielectric}} e_{ij}^{-1} (D_i - D_{ij}) \delta e_{ih} e_{kl}^{-1} (D_e - D_{de}) \]

\[ \delta \mathcal{F} = \frac{1}{8\pi i} \int_{\text{dielectric}} (D_i - D_{ij}) \delta e_{ij}^{-1} (D_e - D_{de}) \]

essentially similar to (14.1)
In relying on the second member of (11.12), we need

\[-\frac{1}{\delta \pi} \delta (E \cdot D) = -\frac{1}{\delta \pi} \delta E_i D_i - \frac{1}{\delta \pi} E_i \delta D_i\]

\[E_i = \varepsilon_{ij}^{-1} (D_j - D_{oj})\]

\[\delta E_i = \delta \varepsilon_{ij}^{-1} (D_j - D_{oj}) + \varepsilon_{ij}^{-1} \delta D_j\]

\[-\frac{1}{\delta \pi} \delta (E \cdot D) = -\frac{1}{\delta \pi} \delta \varepsilon_{ij}^{-1} (D_j - D_{oj}) D_i - \frac{1}{\delta \pi} \varepsilon_{ij}^{-1} \delta D_j D_i\]

\[-\frac{1}{\delta \pi} \delta (E \cdot D) = -\frac{1}{\delta \pi} \delta \varepsilon_{ij}^{-1} (D_j - D_{oj}) D_i - \frac{1}{\delta \pi} \varepsilon_{ij}^{-1} \delta D_j D_i + \frac{1}{\delta \pi} D_{io} \varepsilon_{ij}^{-1} \delta D_j\]

\[-\frac{1}{2} \delta (P \cdot \varepsilon) = -\frac{1}{\delta \pi} \delta [(P - E) \cdot \varepsilon] = -\frac{1}{\delta \pi} (\delta D_i - \delta E_i) \varepsilon_i\]

\[-\frac{1}{2} \delta (P \cdot \varepsilon) = -\frac{1}{\delta \pi} (\delta D_i - \delta \varepsilon_{ij}^{-1} (D_j - D_{oj}) - \varepsilon_{ij}^{-1} \delta D_j) \varepsilon_i\]
Substituting these expressions in (11.12) and keeping the \( \frac{1}{4\pi} E_2 \delta D_2 \) contribution to \( \delta F \) since we're integrating just over the dielectric, we find

\[
\delta F = \frac{1}{8\pi} \int dV \left\{ \varepsilon_{ij} \nabla^2 \delta \varepsilon_{ij} (\mathbf{D}_e - \mathbf{D}_o) + 2 \varepsilon_i \delta D_i 
\right\}
\]

\[
- \varepsilon_{ij} (\mathbf{D}_j - \mathbf{D}_o) \delta D_i - 2 \varepsilon_i \delta \varepsilon_{ij} \delta D_j + \rho_i \varepsilon_{ij} \delta D_j
\]

\[
-(\delta \mathbf{D}_i - \varepsilon_{ij} (\mathbf{D}_j - \mathbf{D}_o) - \varepsilon_{ij} \delta D_j) \mathbf{E}_i
\]

Moreover, this agrees with previous \( \varepsilon \), \( \rho \) derivation.
\[ E = 0 \text{ for pyroelectric slab} \]

\[ D = \varepsilon_0 \varepsilon' E \]

\[ \nabla \int dV \left[ (D - D_0) \delta E - \varepsilon' D - \varepsilon'' D_0 \right] \]

\[ D = E + 4\pi P \]
\[ = D_0 + \Sigma E \]

Here there is no extraneous charge (and \( D \times D = 0 \) by symmetry) so we expect that \( D \cdot D = 4\pi P \text{ex} = 0 \)

\[ \Rightarrow D = 0. \text{ Is this consistent with presence of a nonzero polarization?} \]

\[ E \Rightarrow E = 0 \]

\[ D \cdot E = 4\pi P \Rightarrow -E \Delta A = 4\pi \sigma \Delta A \]
\[ E = -4\pi \sigma \]

\[ D \cdot P = -P \Rightarrow [P = \sigma] \]

\[ \therefore D = E + 4\pi P = -4\pi \sigma + 4\pi \sigma = 0 \]

\[ \text{independent of } \varepsilon. \]
\[ \delta \mathcal{F} = \frac{1}{8\pi} \int dV \, D_0 \, \delta \mathcal{E}' \]

\[ \delta \mathcal{F} = \frac{1}{8\pi} \int dV \left( D_0 \, \delta \mathcal{E}' - \mathcal{E}' \, D_0 \, \delta \mathcal{D} \right) \]

but \( D = 0 \) independently, \( \mathcal{E}' \), so \( \mathcal{E} \mathcal{D} = 0 \)!

**SLAB config' for \( \mathcal{E} \neq 0 \)**

\[ \vec{D}_0 \]

\[ \mathcal{E} \rightarrow \]

\[ \mathcal{E} = \mathcal{D}_0 + \mathcal{E} \mathcal{E} \text{ inside INDEP of } \mathcal{E}. \]

\[ \mathcal{D} = \mathcal{E} \text{ outside} \]

But the absence of extraneous charge on the surface \( \mathcal{D}_0 \)

SLAB implies \( \mathcal{D} = \mathcal{E} \) inside as well

\[ \therefore \mathcal{E} = \mathcal{D}_0 + \mathcal{E} \mathcal{E} \]

\[ \mathcal{E}' \mathcal{E} = \frac{(\mathcal{E} - \mathcal{D}_0)}{\mathcal{E}} \]

Intrinsic surface charge density is determined from \( \text{div } \mathcal{E} = 4\pi \sigma \)

\[ -A \mathcal{E} + A \mathcal{E} = 4\pi \sigma \mathcal{A} \]

\[ \mathcal{E} - \mathcal{E} = 4\pi \sigma \]
\[ \nabla \cdot \mathbf{P} = - \rho \quad \text{given} \quad - \mathbf{A} \mathbf{P} = - \mathbf{A} \mathbf{\sigma} \]
\[ \mathbf{P} = \mathbf{\sigma} \quad \text{as usual} \]

Do our vector fields obey \( \mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \)?

\[ \mathbf{E} + 4\pi \mathbf{P} = \mathbf{E} + 4\pi \mathbf{\sigma} = \mathbf{E} + 4\pi \left( \frac{\mathbf{E} - \mathbf{E}}{4\pi} \right) = \mathbf{E} \]

From p. 3
\[ \delta \mathcal{F} = \frac{1}{8\pi} \int \mathcal{d}V \ (\mathbf{E} - \mathbf{E}_0)^2 \delta \mathbf{E}^\prime \]

From p. 5
\[ \delta \mathcal{F} = \frac{1}{8\pi} \int \mathcal{d}V \left\{ - (\mathbf{E} - \mathbf{E}_0) \delta \mathbf{E}^\prime \mathbf{D}_0 + \delta \mathbf{E}^\prime (\mathbf{E} - \mathbf{E}_0) \mathbf{E} \right\} \]
\[ \delta \mathcal{F} = \frac{1}{8\pi} \int \mathcal{d}V \ (\mathbf{E} - \mathbf{E}_0)^2 \delta \mathbf{E}^\prime \]

AGREES!!
Needle shaped pyroelectric

\[ E \rightarrow \]

\[ E = \varepsilon E \Rightarrow D = E + 4\pi P \]
\[ = \varepsilon E + D_0 \]
\[ \rightarrow \]
\[ P = \frac{\varepsilon - 1}{4\pi} E + \frac{D_0}{4\pi} \]

From p.3, a change in \( E \) leads to

\[ \delta \mathcal{F} = - \frac{1}{8\pi} \int \text{d}V \frac{E^2}{\varepsilon} \delta \varepsilon = - \frac{E^2}{8\pi} \int \text{d}V \delta \varepsilon \]

\( \text{dielectric} \)

\[ \frac{\partial}{\partial \varepsilon} \left\{ -\varepsilon E \delta \varepsilon^{-1} D_0 - \varepsilon^{-1} D_0 \delta \varepsilon E \right\} \]

\[ = \frac{1}{8\pi} \int \text{d}V \delta \varepsilon \left\{ \frac{\delta \varepsilon}{E} D_0 - \frac{\delta \varepsilon}{\varepsilon} D_0 \right\} \]

\[ = \frac{1}{8\pi} \int \text{d}V \delta \varepsilon \left\{ \frac{\delta \varepsilon}{E} D_0 - \frac{\delta \varepsilon}{\varepsilon} D_0 \right\} \]

\[ = \left( \delta \varepsilon \frac{E}{E} + \delta \varepsilon \frac{D_0}{D_0} - \frac{\delta \varepsilon}{E} \right) \]

\[ \delta \mathcal{F} = - \frac{E^2}{8\pi} \int \text{d}V \delta \varepsilon \]

\( \text{dielectric} \)

AGREES
pyroelectric sphere

We repeat the arguments of §8 for \( E = 0 \) but \( D \neq 0 \).

The potential outside the sphere is

\[ \phi^{(e)} = A D_0 \cdot \frac{\mathbf{r}}{r^2} \]

Inside the sphere

\[ \phi^{(i)} = -B D_0 \cdot \mathbf{r} \]

Continuity of the potential at the surface of the sphere gives

\[ A D_0 \cdot \frac{R}{R^3} = -B D_0 \cdot R - \frac{A}{R^3} = B \]

\[ \phi^{(i)} = \frac{A}{R^3} D_0 \cdot \mathbf{r} \]

\[ E^{(i)} = -\frac{A D_0}{R^3} \]

\[ D^{(i)} = D_0 + \varepsilon E^{(i)} = D_0 \left( 1 - \frac{\varepsilon A}{R^3} \right) \]

Continuity of the normal component of \( D \) :

\[ D^{(e)} = E^{(e)} = -\nabla \phi^{(e)} = -A \nabla \left( D_0 \cdot \frac{\mathbf{r}}{r^3} \right) \]

\[ = -A \left\{ D_0 \cdot \frac{1}{r^3} - \frac{3 D_0 \cdot \mathbf{r} \cdot \mathbf{r}}{r^5} \right\} \]
At the boundary: \( D^{(e)} = -\frac{A}{R^3} \cdot D_0 \cdot \left( 1 - 3^\frac{R^2}{R^2} \right) \)

\( D^{(i)}_n = D^{(e)}_n \) given \( D_{on} \left( 1 - \epsilon^A_3 R^3 \right) = -\frac{A}{R^3} \cdot D_{on} \left( -Z \right) \)

\[ 1 = \frac{\epsilon + 2}{R^3} A \]

\[ A = \frac{R^3}{\epsilon + 2} \]

\[
\therefore \quad E^{(i)} = -\frac{D_0}{\epsilon + 2} \\
D^{(i)}_n = D_0 \left( 1 - \frac{\epsilon}{\epsilon + 2} \right) = \frac{2D_0}{\epsilon + 2} 
\]

What is the polarizability?

\[
P = \frac{1}{4\pi} \left( D^{(i)}_n - E^{(i)} \right) = \frac{1}{4\pi} \frac{D_0}{(\epsilon + 2)^2} \left( 2 - (-1)^3 \right) \\
= \frac{3}{4\pi} \frac{D_0}{\epsilon + 2} \quad \text{The larger the } \epsilon, \text{ the smaller is } P.\]
The expression on p. 3 of [13 June 03] gives

$$\delta \mathcal{F} = - \frac{1}{8\pi} D_0^2 \int dV \delta \varepsilon / (\varepsilon + 2)^2$$

dielectric

for the pyroelectric sphere ($\varepsilon = 0$)

We have

$$\delta D = - \frac{2D_0 \delta \varepsilon}{(\varepsilon + 2)^2}$$

$$D - D_0 = D_0 \left( \frac{\varepsilon}{\varepsilon + 2} - 1 \right) = D_0 \left( \frac{\varepsilon}{\varepsilon + 2} - \frac{\varepsilon + 2}{\varepsilon + 2} \right)$$

$$= - \frac{\varepsilon D_0}{\varepsilon + 2}$$

So the expression on p. 5 of [13 June 03] gives

$$\delta \mathcal{F} = \frac{1}{8\pi} D_0^2 \int dV \left\{ \frac{\varepsilon D_0}{\varepsilon + 2} \left( - \frac{\delta \varepsilon}{\varepsilon^2} \right) D_0 - \frac{1}{2} \frac{D_0}{D_0} \left( - \frac{2D_0 \delta \varepsilon}{(\varepsilon + 2)^2} \right)^2 \right\}$$

$$= \frac{1}{8\pi} D_0^2 \int dV \delta \varepsilon \left\{ - \frac{1}{(\varepsilon + 2)^2} + \frac{2}{3(\varepsilon + 2)^2} \right\}$$

$$= \frac{1}{8\pi} D_0^2 \int dV \delta \varepsilon \left\{ \frac{-(\varepsilon + 2)^2 + 2}{(\varepsilon + 2)^2 \varepsilon} \right\}$$

$$\delta \mathcal{F} = - \frac{1}{8\pi} D_0^2 \int dV \delta \varepsilon / (\varepsilon + 2)^2 \left( = - \frac{1}{8\pi} \frac{D_0^2 \delta \varepsilon}{\varepsilon + 2} \varepsilon \right)$$

AGREES! because we've tacitly assumed a uniform $\varepsilon$. 
§ 15 Electric forces in a fluid dielectric

Ponderomotive forces act on a dielectric when an arbitrary non-uniform electric field is applied.

\[ f_e dV = \text{force on a volume element } dV \]

\[ \text{force density.} \]

Conservation of momentum: the force acting on the matter in \( dV \) is the change in its momentum per unit time = amount of momentum entering its surface per unit time.

- \( \sigma_{ik} \) momentum flux tensor

\[ \int f_i dV = \text{rate of change of momentum} \]

\[ \int (- \sigma_{ik} \delta \tau_k) \]

\( \sigma_{ik} \) is called the stress tensor (minus the momentum flux tensor).

\[ \sigma_{ik} \delta f_k = \sigma_{ik} N_k df \]

\( i \)th component of the force on a surface element \( df \)

\[ \sigma_{ik} \delta f_k = \sigma_{ik} N_k df \]

\[ \int f_i dV = \int \left( \frac{\delta \sigma_{ik}}{\delta x_k} \right) dV \]

\[ \int dV \cdot V = \int dV \frac{\partial V_k}{\partial x_k} \]

Since \( \delta V_k / \delta x_k \) is arbitrary

\[ f_i = \frac{\partial \sigma_{ik}}{\partial x_k} \]

Body force in terms of stress tensor.

Now calculate stress tensor.
any small region of surface may be regarded as a plane, and the properties of the body and the electric field remain uniform. The plane parallel layer of material (of thickness \( d \)) in an electric field which is uniform, but whose direction is arbitrary.

(15.1) Plane-parallel layer material

The field may be imagined to be due to conducting planes having appropriate charge distributions, applied to the surfaces of the layer.

\[ \varepsilon \]

potential of conductor remains constant at every point

\[ \varphi_1 \]

homogeneous deformation \( \vec{D} \) is uniform.

- \( \partial \vec{D} / \partial n \) face is extended

- \( \sigma_n \) \( \vec{D} \)

decrease in \( \int F dV \)

\[ \int F dV \]

\[ \vec{F} \rightarrow - \sigma_n \vec{n} \times \vec{E} \]

The work done in an infinitesimal deformation \( d\vec{F} \) is

\[ \text{work done} = \text{increase in free energy} \]

\[ \text{used during elastic} = \text{decrease in free energy} \]

\[ \delta W = - \frac{dE}{dV} \]

\[ 0 \cdot \delta E = \delta (\varepsilon F) \]

\[ = \delta \varepsilon F + \delta \varepsilon F \]
- \sigma h N x - \text{force exerted by the layer on unit area of its surface}
- \sigma h N \delta x - \text{work done by the layer on unit area of its surface}

\sigma h N \delta x = \delta (h F) = h \delta F + h \delta \bar{F}

\Rightarrow \bar{F} = \bar{F}(T, p, E) \quad \text{pure shear do not affect the thermodynamic state}
\delta \bar{F} = \left( \frac{\partial \bar{F}}{\partial E} \right)_{T, p} \delta E + \left( \frac{\partial \bar{F}}{\partial p} \right)_{T, E} \delta p
\Rightarrow \delta p = \frac{1}{\gamma} \left[ \frac{\partial E}{\partial h} \right]_{p, T} \delta p

\text{No change in density of layer}
\Rightarrow \delta p = - p \frac{dh}{h}

\text{variation in p field is scale as follows}
\Rightarrow \text{at z appear matter which was originally at z - y}

\text{constant potential with conducting plane}
\Rightarrow \text{each particle carries its potential with it}

\text{No change in potential at a given point is}
\delta \phi = \phi(z - y) - \phi(z) = -z \cdot \nabla \phi = \frac{y}{z} E

\text{change in potential at a given point in space}
\Rightarrow \delta E = - \frac{h}{\frac{\partial E}{\partial z}}
\Rightarrow \delta E = - \frac{h}{\frac{\partial E}{\partial z}} E
\[ \delta h = \varepsilon_z = \Xi \varepsilon \]

\[ \sigma_{\text{inh}} \varepsilon_{\text{m}} \eta_\text{m} = h \delta \vec{F} + \vec{F} \, dh \]

\begin{align*}
&= h \left( \frac{P}{\rho} \delta \varepsilon + \frac{\varepsilon \cdot E}{\frac{\delta F}{\delta \rho}} \delta \rho \right) + \vec{F} \, dh \\
&= h \left( \frac{P}{\rho} \delta \varepsilon + \frac{\varepsilon \cdot E}{\frac{\delta F}{\delta \rho}} \delta \rho \right) + \vec{F} \, \Xi \, \varepsilon \, \eta_\text{m} \\
\end{align*}

\[ \sigma_{\text{inh}} \varepsilon_{\text{m}} \eta_\text{m} = \left( \frac{P}{\rho} \delta \varepsilon + \frac{\varepsilon \cdot E}{\frac{\delta F}{\delta \rho}} \delta \rho \right) + \vec{F} \, \Xi \, \varepsilon \, \eta_\text{m} \]

\[ \sigma_{\text{inh}} \varepsilon_{\text{m}} \eta_\text{m} = \left( \frac{P}{\rho} \delta \varepsilon + \frac{\varepsilon \cdot E}{\frac{\delta F}{\delta \rho}} \delta \rho \right) + \vec{F} \, \Xi \, \varepsilon \, \eta_\text{m} \]

\[ \sigma_{\text{inh}} \varepsilon_{\text{m}} \eta_\text{m} = \left( \frac{P}{\rho} \delta \varepsilon + \frac{\varepsilon \cdot E}{\frac{\delta F}{\delta \rho}} \delta \rho \right) + \vec{F} \, \Xi \, \varepsilon \, \eta_\text{m} \]

\[ \sigma_{\text{inh}} \varepsilon_{\text{m}} \eta_\text{m} = \Xi \varepsilon \left\{ \frac{D_h E_i}{\Pi} - \frac{\delta F}{\delta \rho} \rho \delta \varepsilon + \vec{F} \delta \varepsilon \right\} \]

\[ E \text{ and } D \text{ are parallel } \}

\[ \Xi \, \varepsilon \]

\[ \Xi \, D_h \Xi = E_h D_i \text{ so that } \sigma_{\text{inh}} \Xi \text{ is symmetrical.} \]
\[ p = -\frac{\partial \mathcal{G}}{\partial \mathcal{V}} = -\frac{\partial (\mathcal{V} \mathcal{F})}{\partial \mathcal{V}} = -\frac{\partial (\mathcal{V} \mathcal{F}/m)}{\partial (\mathcal{V}/m)} \]

\[ = -\frac{\partial (D/F)}{\partial (\mathcal{V}/m)} = -\frac{1}{\mathcal{F}} \frac{\partial \mathcal{F}}{\partial (\mathcal{V}/m)} - \mathcal{F} = \rho \frac{\partial \mathcal{F}}{\partial (\mathcal{V}/m)} - \mathcal{F} \]

\[ \mathcal{A}(\mathcal{V}/m) = -\frac{1}{\rho^2} \frac{\partial \rho}{\partial \mathcal{V}} \]

\[ \sigma_{ik} = \left\{ F_0 - \rho \left( \frac{\partial F_0}{\partial \rho} \right)_T \right\} \delta_{ik} + \left\{ -\frac{\mathcal{E}^2}{8\pi} + \rho \frac{\partial}{\partial \rho} \frac{\mathcal{E}^2}{8\pi} \right\} \frac{\partial}{\partial \mathcal{V}} \delta_{ik} + \frac{\varepsilon_i \varepsilon_k}{4\pi} \]

\[ \delta_{ik} = -\rho \frac{(\partial F_0}{\partial \rho} \left( \frac{\partial F_0}{\partial \rho} \right)_T \right\} \delta_{ik} - \delta_{ik} \]

In a vacuum \( \mathcal{E} = 1 \), \( \rho_0 = 0 \)

\[ \sigma_{ik} = -\frac{\mathcal{E}^2}{8\pi} \delta_{ik} + \frac{\varepsilon_i \varepsilon_k}{4\pi} = \frac{(\varepsilon_i \varepsilon_k - \frac{1}{2} \delta_{ik} \mathcal{E}^2)}{4\pi} \]

The Maxwell stress tensor

Forces on the surface of separation from two adjoining media: equal and opposite

\[ \sigma_{ik} n_k = -\sigma_{ik} n'_k \quad \mathcal{N} = -\mathcal{N}' \quad \Rightarrow \]

\[ \sigma_{ik} n_k = \sigma_{ik} n'_k \]

Equality of tangential forces:

\[ (\mathcal{F} - \rho (\partial \mathcal{F}/\partial \rho)_{E,T}) \delta_{ik} n_k + \frac{\varepsilon_i D_k}{4\pi} n_k = (\mathcal{F}' - \rho' (\partial \mathcal{F}'/\partial \rho')_{E,T'}) \delta_{ik} n_k + \frac{\varepsilon_i' D'_k}{4\pi} n_k \]

Tangential component

\[ \frac{E_i D_k}{4\pi} = \frac{E_i' D_k'}{4\pi} \]

satisfied by virtual No boundary condition on \( E_i \) and \( D_k \)
condition of equality of the normal component is a non-trivial condition on the pressure difference between the two media.

\[ -\rho_0 (\rho, T) - \frac{E^2}{\varepsilon_0} \left[ \varepsilon - \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \right] + \frac{\varepsilon E_n^2}{4\pi} = -\rho_{atm} - \frac{E_z^2}{8\pi} + \frac{E_n^2}{4\pi} \]

\[ -\rho_0 (\rho, T) + \frac{E^2}{8\pi \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T} - \frac{E}{8\pi} (E^2 - 2E_n^2) = -\rho_{atm} - \frac{1}{8\pi} (E_z^2 - E_n^2) \]

\[ E_z = E_z' \quad D_n = \varepsilon E_n = D'_n = E'_n \]

\[ p_0 - \rho_{atm} = \frac{\rho E^2}{8\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T - \frac{1}{8\pi} (\varepsilon E_z^2 - \varepsilon E_n^2 - E_z^2 + \varepsilon E_n^2) \]

\[ p_0 - \rho_{atm} = \frac{\rho E^2}{8\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T - \frac{1}{8\pi} (e-1) (E_z^2 + \varepsilon E_n^2) \]

Determines the density of the liquid near its surface from the electric field in it.

Body forces in a dielectric medium.
Body forces in a dielectric medium

\[
\mathbf{f}_i = \frac{\partial \sigma_{ik}}{\partial x_k} = \frac{2}{\varepsilon_0 c^2} \left\{ -p_0 \delta_{ik} - \frac{E_i^2}{8\pi} \left[ \varepsilon - \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \delta_{ik} + \frac{\varepsilon E_i E_k}{4\pi} \right\}
\]

\[
= -\frac{\partial p_0}{\partial x_i} + \frac{2}{\varepsilon_0 c^2} \frac{E_i^2}{8\pi} \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \frac{\partial}{\partial x_k} \varepsilon E_k + \frac{\partial}{\partial x_k} \left( \frac{\varepsilon E_i E_k}{4\pi} \right)
\]

\[
= \frac{2}{\varepsilon_0 c^2} \left[ -p_0 + \frac{E_i^2}{8\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \frac{\partial}{\partial x_i} \varepsilon + \frac{E_i E_k}{4\pi} \frac{\partial}{\partial x_k} \varepsilon
\]

\[
+ \left[ -\frac{\varepsilon}{8\pi} \frac{\partial}{\partial x_i} E_i E_k + \frac{\partial}{\partial x_k} E_i E_k \right]
\]

\[
\frac{1}{4\pi} \left[ \frac{1}{2} \frac{\partial E_i^2}{\partial x_i} + \frac{\partial}{\partial x_k} E_i D_k \right]
\]

\[
= \frac{1}{4\pi} \left[ -E_i D_k \frac{\partial E_k}{\partial x_i} + E_i \frac{\partial D_k}{\partial x_i} \right]
\]

\[
= \frac{1}{4\pi} \left[ -D_k \frac{\partial E_k}{\partial x_i} + D_k \frac{\partial E_i}{\partial x_k} \right]
\]

\[
= \frac{1}{4\pi} D_k \varepsilon_{iklm} \frac{\partial}{\partial x_l} E_m
\]

\[
\nabla \times \mathbf{E} = 0
\]

\[
\nabla \cdot \mathbf{D} = \varepsilon \nabla \cdot \mathbf{E} = \varepsilon_0 c^2 \frac{\partial \mathbf{E}}{\partial t}
\]

\[
\nabla \times \mathbf{B} = \mu_0 \frac{\partial \mathbf{E}}{\partial t} - \mu_0 \mathbf{j}
\]

\[
\nabla \cdot \mathbf{B} = 0
\]
If the dielectric contains an internal charge of density \( \rho \), the force \( \mathbf{F} \) contains a further term \( \frac{\mathbf{E}}{4\pi} \text{div} \mathbf{D} = \rho \text{ex} \mathbf{E} \).

However, it must not be supposed that this result is obvious.

In a gas \( \varepsilon = \varepsilon_0 \alpha \) density,

\[
\varepsilon - 1 = \rho \frac{\varepsilon}{\varepsilon_0}
\]

\[
\frac{\partial \varepsilon}{\partial \rho} = \frac{\varepsilon - 1}{\rho}
\]

\[
\mathbf{f} = -\text{grad} \rho + \frac{1}{8\pi} \text{grad} \left[ \varepsilon^2 (\varepsilon - 1) \right] = \frac{E^2}{8\pi} \text{grad} \varepsilon
\]

\[
\mathbf{f} = -\text{grad} \rho + \frac{1}{8\pi} \text{grad} (\varepsilon - 1) \text{grad} E^2
\]

\( \varepsilon \) is a function of \( \rho \) and \( T \).

\[
\text{grad} \varepsilon = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \text{grad} T + \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \text{grad} \rho
\]

(15, 12) become

\[
\mathbf{f} = -\text{grad} \rho_0 (\rho, T) + \frac{1}{8\pi} \text{grad} \left[ \varepsilon^2 \rho \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T \right] - \frac{E^2}{8\pi} \varepsilon \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \text{grad} T + \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \text{grad} \rho
\]

\[
\mathbf{f} = -\text{grad} \rho_0 (\rho, T) + \frac{1}{8\pi} \text{grad} \left[ \varepsilon^2 \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \right] - \frac{E^2}{8\pi} \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho \text{grad} T
\]

\( d\mathbf{U} = TdS - PdV \)

\( G = U - TS + PV \)

\( dG = dTdS - dPdV - dSdT + PdV + VdP \)

\( dS = SdT + VdP \)

\( F = U - TS \)

\( dF = -SdT - PdV + \left( \frac{\partial \varepsilon}{\partial T} \right)_\rho TdV \)
What is the differential of \( U = \alpha(V) \)?

\[
\begin{align*}
\delta U &= T \delta e - p \delta V + \left( \frac{\partial U}{\partial N} \right)_S \delta N \\
U &= N V \\
S &= N S \\
N &= V N \quad \text{\# per unit vol.} \\
p &= \frac{N}{N} \quad \text{\# mass p.}
\end{align*}
\]

\[
\begin{align*}
V dU + UdV &= T(SeU + V dS) - p dV + \left( \frac{\partial U}{\partial N} \right)_S V dN + N \left( \frac{\partial U}{\partial N} \right)_S V dN \\
V dU &= dV(-U + T S - p + N \left( \frac{\partial U}{\partial N} \right)_S V) + V T dS + \left( \frac{\partial U}{\partial N} \right)_S V dN \\
dU &= \frac{dV}{V} \left( -U + T S - p + N \left( \frac{\partial U}{\partial N} \right)_S V \right) + T dS + \left( \frac{\partial U}{\partial N} \right)_S V dN
\end{align*}
\]

\( dS = \left( \frac{\partial S}{\partial p} \right)_{s,V} = \frac{S}{p} \quad \text{(3.6)} \)

\( \delta S = \left( \frac{\partial S}{\partial p} \right)_{s,v} \delta V = \frac{\delta S}{\delta V} \)

\( dU = T dS + \delta V dP \)

\( \uparrow S = \left( \frac{\partial U}{\partial P} \right)_{s,v} \)
Since \( \varepsilon(T, \rho) = \varepsilon_0(T, \rho) - \frac{E^2}{\delta \rho} \frac{\partial \varepsilon}{\partial \rho} \),

we have

\[ \mathbf{f} = -\rho \text{ grad } \varepsilon \]

for a fluid dielectric of uniform composition and temperature in mechanical equilibrium gives

\[ 0 = \mathbf{f} = \mathbf{F} = \varepsilon_0 - \frac{E^2}{\delta \rho} \frac{\partial \varepsilon}{\partial \rho} \]

change in density \( \propto E^2 \)

on last two terms in (16.15), \( \rho = \text{const} \)

\[ \mathbf{f} = -\text{ grad } \left\{ \rho_0 + \frac{\rho E^2}{\delta \rho} \frac{\partial \varepsilon}{\partial \rho} \right\} = \frac{E^2}{\delta \rho} \frac{\partial \varepsilon}{\partial \rho} \]

at uniform \( T \),

\[ \mathbf{f} = 0 \quad \Rightarrow \quad \rho_0 - \frac{\rho E^2}{8 \pi} \frac{\partial \varepsilon}{\partial \rho} = \text{const} \]
Electric Forces in solids.

deformations (pure strains) can change the dielectric properties of a solid body.

1st: isotropic in the absence of a field. 2nd deformed body micromechanical dielectric tensor $\epsilon_{ij}$ replaces scalar dielectric permittivity.

$$\epsilon_{ij} = \epsilon_0 \delta_{ij} + \varepsilon_{ij}$$

$\varepsilon_{ij}$ is the most general tensor of rank two which can be constructed linearly from the components $\epsilon_{ij}$.

In a solid body $F$ depends on all the components of the strain tensor $\varepsilon_{ij}$.

$$\delta F = -\rho \delta E + \frac{\partial F}{\partial \rho}$$

For the virtual displacement considered

$$\nu (x, y, z) = z \frac{\delta}{\delta n}$$

$$\nu_{ij} = \frac{1}{2h} \left( \frac{\partial^2 z}{\partial x_i} + \frac{\partial^2 z}{\partial x_j} \right)$$

$$\frac{\partial z}{\partial x_i} = \frac{z(x_i + \delta x_i) - z(x_i)}{\delta x_i}$$

$$\frac{\partial z}{\partial x_i} = \frac{1}{\cos \theta}$$

$$\tan \theta = \frac{\delta z}{\delta x_n}$$
\[ R_n = \cos \theta_n \]

\[ \frac{\partial z}{\partial x_n} = \frac{z(x_n + \delta x_n) - z(x_n)}{\delta x_n} = \cos \theta_n = n_k \]

\[ \nabla \theta = \frac{1}{2h} (n_k \delta \xi + n_i \delta \xi) \]

[THIS IS NOT \( \delta \theta \), SINCE \( \xi \) IS AN INFINITESIMAL DISPLACEMENT]

\[ \delta F = -\frac{P \delta E}{4\pi} + \left( \frac{\delta \tilde{F}}{\delta \xi} \right) \left( \frac{1}{2h} \right) n_k \delta \xi + \left( \frac{\delta \tilde{F}}{\delta \eta_i} \right) \left( \frac{1}{2h} \right) n_k \delta \xi_i \]

\[ \delta F = -\frac{P \delta E}{4\pi} + \frac{1}{h} \left( \frac{\delta \tilde{F}}{\delta \xi} \right) n_k \delta \xi_i \quad (16.2) \]

\[ \text{Instead of (15.7), we find for the stress tensor (15.7) is } \sigma_{ij} = \frac{E}{E_i E_k} \delta_{ij} + \frac{E_i E_k}{4\pi} \]

\[ \text{FROM } \delta F = -\frac{P \delta E}{4\pi} + \left( \frac{\delta \tilde{F}}{\delta \xi} \right) \delta \xi + \frac{E_i E_k}{4\pi} \]

Here, again

\[ \delta_{ik} \delta_{in} = \frac{h}{4\pi} \delta \tilde{F} + \tilde{F} \delta \xi_b \]

\[ \tilde{F} = \frac{1}{h} \left( \frac{\delta \tilde{F}}{\delta \xi} \right) \left( \frac{1}{2h} \right) n_k \delta \xi_i \]

\[ E_i \delta \xi_i \]

\[ \tilde{F} \delta \xi_b \]

\[ \begin{align*}
\sigma_{ik} \delta_{in} &= h \delta_{ik} + \frac{1}{4\pi} \delta \tilde{F} + \tilde{F} \delta \xi_b \\
(16.2) \quad \tilde{F} &= \frac{h}{\delta \xi} \left( \frac{\delta \tilde{F}}{\delta \xi} \right) \\
&= \frac{1}{4\pi} \left( \frac{\delta \tilde{F}}{\delta \xi} \right) \left( \frac{1}{2h} \right) n_k \delta \xi_i + \tilde{F} \delta \xi_b \nabla \theta \end{align*} \]
\[ D_i = \varepsilon_{ik} E_k \text{ (neither pyroelectric nor piezoelectric)} \]

\[ F = F_0 - \varepsilon_{ij} E_j E_k \frac{\partial}{\partial \varepsilon_{ij}} \]

\[ \frac{\partial F}{\partial \varepsilon_{ik}} = \frac{\partial F_0}{\partial \varepsilon_{ik}} - \sum_{j,k} \frac{\varepsilon_{ij}}{\varepsilon_{ik} \varepsilon_{jk}} E_j E_k \frac{\varepsilon_{ik}}{8\pi} \]

\[ \Theta \frac{\partial E_j}{\partial \varepsilon_{ik}} = \Theta \left\{ \varepsilon_0 \frac{\partial E_j}{\partial \varepsilon_{ik}} + a_i \varepsilon_{ij} + a_k \varepsilon_{ik} \right\} \]

\[ = a_i \delta_{ijk} + a_k \delta_{ik} \delta_{jm} \delta_{jm} E_j \]

\[ \frac{\partial F}{\partial \varepsilon_{ik}} = \frac{\partial F_0}{\partial \varepsilon_{ik}} - \sum_{j,k} \frac{a_i \delta_{ijk} + a_k \delta_{ik}}{\varepsilon_{ik} \varepsilon_{jk}} \frac{E_j E_k}{8\pi} \]

\[ \frac{\partial F}{\partial \varepsilon_{ik}} = \frac{\partial F_0}{\partial \varepsilon_{ik}} - a_i \frac{E_i E_k}{8\pi} - a_k \frac{E_k E_i}{8\pi} \]

\[ \sigma_{ik} = \sum_{j,k} \left( \frac{F_0 - \varepsilon_{ij} E_j E_k}{8\pi} \frac{\delta_{ik}}{\varepsilon_{ik} \varepsilon_{jk}} + \frac{\delta_{ik}}{\varepsilon_{ik} \varepsilon_{jk}} \right) - \frac{a_i E_i E_k}{8\pi} \]

From (16.3)

\[ = \sigma_{ik}^{(0)} - \frac{a_k E_k}{8\pi} \left( a_i E_i + \varepsilon_{ij} E_j E_k \right) \]

\[ = \sigma_{ik}^{(0)} - \frac{a_k E_k}{8\pi} \left( \varepsilon_{ij} + 2 \varepsilon_{ik} \right) E_j E_k \]

\[ \text{CLOSE, BUT NO CIGAR} \]
We've derived (16.2): (4. 8)

$$\delta F = -P \cdot \delta E / 4\pi + \left( \frac{\delta i_n_k}{\ln \eta} \right) \delta F / \Omega_{ik}$$

Instead of (15.7) for the stress tensor

$$\sigma_{ik} = \left[ F - P (\delta F / \delta x) \right] \delta n_k + E_i D_{i k} / 4\pi$$

which expresses the work done by a boundary layer in an isothermal deformation at constant potential

$$\delta h = \delta x \cdot n_k = \delta x \cdot n_k \delta n_k$$

$$\delta \bar{F}$$ is given by (16.2)

$$\sigma_{ik} \delta x \cdot n_k = -h \frac{D_j \delta E_j}{4\pi} + \delta x \cdot n_k \left( \frac{\delta F}{\delta \Omega_{ik}} \right) \delta E_T + F \delta x \cdot n_k \delta n_k$$

$$\delta E_j = -n_j \frac{E_x \delta x}{h}$$

$$\sigma_{ik} \delta x \cdot n_k = D_j n_j \frac{E_x \delta x}{4\pi} + \delta x \cdot n_k \left( \frac{\delta F}{\delta \Omega_{ik}} \right) \delta E_T + F \delta x \cdot n_k \delta n_k$$

$$\sigma_{ik} = \frac{E_i D_{i k}}{4\pi} + \left( \frac{\delta F}{\delta \Omega_{ik}} \right) \delta E_T + F \delta \Omega_{ik}$$

Eq. (16.3)
For a body which is neither pyroelectric nor piezoelectric
\[ D_i = \varepsilon_i \varepsilon_0 E_k, \quad F = F_0 - \varepsilon_{ij} E_j E_k / 8\pi \]

\[ \frac{\partial F}{\partial u_{ik}} = \frac{\partial F_0}{\partial u_{ik}} - \frac{\varepsilon_{ij}}{8\pi} E_j E_k \frac{1}{8\pi} \]

\[ \varepsilon_{ij} = \varepsilon_0 \delta_{ij} + a_{ij} \delta_{ij} + a_{jij} \]

\[ \frac{\partial E_{ij}}{\partial u_{ik}} = a_{ij} \delta_{kl} + a_{jlm} \delta_{lm} \]

\[ \frac{\partial F}{\partial u_{ik}} = \frac{\partial F_0}{\partial u_{ik}} - \frac{a_{ij}}{8\pi} \delta_{ij} E_j E_k \frac{a_{jkl}}{8\pi} \delta_{kl} E_j E_k \]

\[ \begin{array}{c}
\frac{\partial F}{\partial u_{ik}} = \frac{\partial F_0}{\partial u_{ik}} - \frac{a_{ij}}{8\pi} E_i E_k - \frac{a_{jkl}}{8\pi} E_j E_k \delta_{ik} \delta_{kl} \\ \\
\end{array} \]

we then put \( \varepsilon_{ik} = \varepsilon_0 \delta_{ik} \) everywhere in (1b.3) and obtain

\[ \sigma_{ik} = \frac{E_i \varepsilon_k^{(0)}}{8\pi} E_j + \frac{\partial F_0}{\partial u_{ik}} - \frac{a_{ij}}{8\pi} E_i E_k - \frac{a_{jkl}}{8\pi} E_j E_k \delta_{ik} \]

\[ + \left( F_0 - \varepsilon_{ij} E_j E_k / 8\pi \right) \delta_{ik} \]

\[ \sigma_{ik} = \sigma_{ik}^{(0)} + \frac{1}{8\pi} \left( 2E_i \varepsilon_k^{(0)} E_j - a_{ij} E_i E_k \right) \]

\[ \sigma_{ik} = \sigma_{ik}^{(0)} + \frac{1}{8\pi} \left( 2E_i \varepsilon_k^{(0)} - a_{ij} \right) E_i E_k + \frac{1}{8\pi} \left( \varepsilon_{ik}^{(0)} E_j E_k + a_{2} E_j E_k \right) \]

\[ \sigma_{ik} = \sigma_{ik}^{(0)} + \frac{1}{8\pi} \left( 2E_i \varepsilon_k^{(0)} - a_{ij} \right) E_i E_k - \frac{1}{8\pi} \left( \varepsilon_{ik}^{(0)} + a_{2} \right) E_j E_k \]

\[ \sigma_{ik} = \sigma_{ik}^{(0)} + \frac{1}{8\pi} \left( 2E_i \varepsilon_k^{(0)} - a_{ij} \right) E_i E_k - \frac{1}{8\pi} \left( \varepsilon_{ik}^{(0)} + a_{2} \right) E_j E_k \]
\( \Delta \phi = \frac{1}{2} \text{curl}(\nabla) \) because points are displaced by \( u = \Delta \phi \times E \)

\[
(\text{curl} u)_i = \varepsilon_{ijk} \frac{\partial}{\partial j} u_k = \varepsilon_{ijk} \frac{\partial}{\partial j} \Delta \phi_k \nabla_m
\]

\[
= \varepsilon_{ikl} \varepsilon_{jlm} \delta_{p_k} \delta_{l_m} = (\delta_{km} \delta_{i_l} - \delta_{km} \delta_{i_k}) \delta_{p_k} = (3 \delta_{i_l} - \delta_{i_k}) \delta_{p_k} = 2 \delta_{i_l}
\]

Whence,

\[
\Delta \phi_i = \frac{1}{2} (\text{curl} u)_i \quad \text{as stated.}
\]

\[
y = z \frac{E}{h} \quad \Delta \phi_i = \frac{1}{2} \varepsilon_{ijk} \frac{\partial}{\partial j} z \frac{E_k}{h} = \frac{1}{2} \varepsilon_{ijk} n_j \nabla \frac{E_k}{h} = \frac{1}{2h} (n \times E)_i;
\]

\[
\Delta \phi = \frac{1}{2h} n \times E
\]

\[
\Rightarrow \quad \Delta \Phi = -n (E \cdot \nabla) - \frac{1}{2h} \frac{(n \times E) \times E}{h}
\]

The first term in (16.2) becomes

\[
- \frac{1}{4\pi} \frac{D \cdot E}{h} = - \frac{D_j \varepsilon_{ji}}{4\pi} \frac{E_i - n(E \cdot E)}{h}
\]

\[
= \frac{D_j}{8\pi h} \left( \Xi (n \cdot E) + n (\Xi \cdot E) \right)
\]

\[
= \frac{1}{8\pi h} \left[ (D \cdot \Xi)(n \cdot E) + (D \cdot n)(\Xi \cdot E) \right] = \frac{1}{4\pi h} \Xi \cdot n \left( D_j E_j + D_k E_k \right)
\]
\[
\sigma_{ik} = \frac{1}{8\pi} (E_i E_k - \frac{E^2}{2} \delta_{ik}) \quad E \text{ is the field in the fluid, } E^2 \text{ is its permeability.}
\]

\[
F = \oint \mathbf{E} \cdot d\mathbf{F} = \frac{\varepsilon}{2\pi} \int \left\{ E(E \cdot n) - \frac{E^2}{2} n^2 \right\} \, dF
\]

For a dielectric not
\[
\varepsilon_{ik} = \varepsilon_{ik}^{\text{air}} + \text{other terms}
\]

Stresses inside a solid dielectric

\[
\text{(not needed for total force } F \text{ or total torque } \mathbf{r} \text{ exerted on the body.)}
\]

Body at rest in a fluid medium

\[
F_i = \oint \sigma_{ik} n_k dF
\]

\[
\text{in the continuous, cohesive (15.4) (body) or (15.9) (fluid medium)}
\]

Condition for equilibrium: \( p_0 - \frac{E^2}{2\varepsilon} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \text{const in fluid applied to partly}

\[
\text{Pasternak tensor (15.9) is constant in uniform property}
\]

\[
\text{pressure, } \varepsilon \text{ and torque } \mathbf{r}
\]
Total force on a dielectric into which electric field is which would be present if it weren't:

Virtual translation $u$

$$
(11.3) \quad \delta Q = - \int \mathbf{P} \cdot \epsilon \, d\mathbf{v}
$$

$$
\delta \mathbf{E} = \mathbf{E}(C+u) - \mathbf{E}(C) \quad \text{curl} \, \mathbf{E} = 0; \, \mathbf{E} = \text{const}
$$

$$
(\rho \cdot \text{grad}) \mathbf{E} = (\mathbf{u} \cdot \text{grad}) \mathbf{E}
$$

$$
\left[ A \times (B \times \mathbf{E}) \right]_i = \varepsilon_{ijk} A_j \varepsilon_{klm} B_k E_m
$$

$$
= \varepsilon_{ijk} \varepsilon_{klm} A_j B_k E_m
$$

$$
= (\delta_i^l \delta_j^m - \delta_i^m \delta_j^l) A_j B_k E_m
$$

$$
= A_j B_i C_j - A_j B_j C_i
$$


If $B \times \mathbf{E} = 0$, then

$$
A_j B_i C_j = A_j B_j C_i
$$

Here,

$$
u_j \cdot \delta \mathbf{E}_i = u_j \varepsilon_{ij} \mathbf{E}_j = \varepsilon_i (u_j \mathbf{E}_j)
$$

$$
\mathbf{P} \cdot \delta \mathbf{E} = P_i u_j \varepsilon_{ij} \mathbf{E}_j = P_i \varepsilon_i u_j \mathbf{E}_j
$$

$$
\delta Q = - \mathbf{u} \cdot \int d\mathbf{V} \mathbf{P} \cdot \text{grad} \mathbf{E} = - \mathbf{u} \cdot \mathbf{F} \implies \mathbf{F} = \int d\mathbf{V} (\mathbf{P} \cdot \text{grad}) \mathbf{E}
$$
Trying again on the torque experienced by a dielectric solid in an external electric field.

Under a rotation $\delta \phi$, the displacement is $\mathbf{U} = \delta \phi \times \mathbf{E}$. The field changes by $\mathbf{E}(t+\delta t) - \mathbf{E}(t) = \mathbf{U} \cdot \nabla \mathbf{E}$ due to the translation, but also rotates by $-\delta \phi$ with respect to the crystal axes. Thus, effectively,

$$\delta \mathbf{E} = -\delta \phi \times \mathbf{E} + \mathbf{U} \cdot \nabla \mathbf{E}.$$ The free energy change is

$$\delta \mathcal{F} = -\int \mathbf{d}V \mathbf{P} \cdot \delta \mathbf{E} = \int \mathbf{d}V \mathbf{P} \cdot (\delta \phi \times \mathbf{E}) - \int \mathbf{d}V \mathbf{P} \cdot [\mathbf{U} \cdot \nabla (\mathbf{E} \cdot \mathbf{E})]$$

$$= -\delta \phi \int \mathbf{d}V \mathbf{P} \times \mathbf{E} - \int \mathbf{d}V \mathbf{P} \cdot \sum_{\mathbf{E}} \mathbf{U} \times [\mathbf{E} \times \mathbf{E}]$$

$$+ \int \mathbf{d}V \mathbf{P} \cdot \sum_{\mathbf{E}} \mathbf{U} \cdot \mathbf{E}$$

$$= -\delta \phi \int \mathbf{d}V \mathbf{P} \times \mathbf{E} - \delta \phi \int \mathbf{d}V \mathbf{P} \times \sum_{\mathbf{E}} (\mathbf{F} \cdot \mathbf{E})$$

Since $\delta \mathcal{F} = -\delta \phi \cdot \mathbf{T}$, we have the torque

$$\mathbf{T} = \int \mathbf{d}V \mathbf{P} \times \mathbf{E} + \int \mathbf{d}V \mathbf{E} \times \sum_{\mathbf{E}} (\mathbf{F} \cdot \mathbf{E}) \tag{16.11}$$

The second term, which vanishes for a uniform external field.
Piezoelectrics, take 2.

Internal stresses in piezoelectric bodies are proportional to an external electric field.

The deformation of a piezoelectric is accompanied by the appearance of a field proportional to the deformation

\((16.5)\) without quadratic term:

\[ \sigma_{ik} = \bar{F} \delta_{ik} + \left( \frac{\partial \bar{F}}{\partial u_{ik}} \right) \]

\(\bar{F}\) here is the free energy per unit vol of space

\[ F' = \frac{V'}{V} F \left( \frac{V'}{V} \right) \] is the free energy per unit vol of the undeformed crystal.

\(V\) - small element of spatial volume
\(V'\) - corresponding element of undeformed crystal

In the presence of a deformation along \(x\):

\[ x_0 \rightarrow x_1 (1 + \frac{\partial u_x}{\partial x}) = x_1 (1 + u_{xx}) \]

Same thing for \(y\) and \(z\), so

\[ V = x_1 y_1 z_1 (1 + u_{xx})(1 + u_{yy})(1 + u_{zz}) \]

\[ \frac{V}{V'} = \left( 1 + u_{zz} \right) \]
\[ F' = \tilde{F} (1 + \varepsilon \varepsilon) \]

\[ \frac{\partial \tilde{F}}{\partial u_{ik}} = \frac{\partial \tilde{F}}{\partial u_{ik}} (1 + \varepsilon \varepsilon) + \tilde{F} \frac{\partial \varepsilon \varepsilon}{\partial u_{ik}} \]

\[ \delta_{ik} \delta_{he} = \delta_{ih} \]

The stress tensor, a property of the undetermined body.

\[ \varepsilon_{ik} = \frac{\partial \tilde{F}}{\partial u_{ik}} \]

\[ d\tilde{F} = -S_{ik} T + \varepsilon_{ik} d\varepsilon_{ih} - D \cdot dE_{1 / \gamma T} \]

Instead of \( u_{ik} \) we use \( \varepsilon_{ik} \)

\[ d\tilde{F} = \tilde{F} - u_{ik} \varepsilon_{ik} \]

\[ d\tilde{F} = d\tilde{F} - u_{ik} d\varepsilon_{ik} - d\varepsilon_{ik} \varepsilon_{ik} \]

\[ d\tilde{F} = -S_{ik} T - u_{ik} \varepsilon_{ik} - D \cdot dE_{1 / \gamma T} \quad (17.4) \]

\[ D = D_0 + \varepsilon_{ik} E_k + \gamma \tau \delta_{i,k} \delta_{he} \quad (17.6) \]

Piezoelectric tensor

\[ \delta_{i,k} e = D_{i,k} \]
Thermodynamic potential of a non-piezoelectric solid in the absence of a field is:

\[ \tilde{\Phi} = \tilde{\Phi} = \tilde{\Phi}_0 - \frac{1}{2} \mu_{iklm} \sigma_{ik} \sigma_{lm} \]

\[ \Phi_{el} = \frac{1}{2} \mu_{iklm} \sigma_{ik} \sigma_{lm} \]

\[ \Phi_{el} = \Phi_{el} - \sigma_{ik} \sigma_{ik} \]

\[ \Phi_{el} = \frac{1}{2} \mu_{iklm} \sigma_{ik} \sigma_{lm} \]

\[ \Phi_{el} = \tilde{\Phi}_0 - \frac{1}{2} \mu_{iklm} \sigma_{ik} \sigma_{lm} + \text{stuff} \]

\[ \frac{\partial \Phi_{el}}{\partial \tilde{E}_{i}} = -\frac{1}{4\pi} D_{i} - \frac{1}{4\pi} \tilde{D}_{0i} - \tilde{E}_{i} \epsilon_{ik} \tilde{E}_{i} - \tilde{\gamma}_{ijkl} \tilde{\sigma}_{ik} \tilde{\sigma}_{jl} \]

\[ \text{stuff} = -\frac{1}{4\pi} \tilde{D}_{0i} \tilde{E}_{i} - \frac{1}{8\pi} \tilde{E}_{i} \epsilon_{ik} \tilde{E}_{i} - \tilde{\gamma}_{ijkl} \tilde{\sigma}_{ik} \tilde{\sigma}_{jl} \]

\[ \tilde{\Phi} = \tilde{\Phi}_0 - \frac{1}{2} \mu_{iklm} \sigma_{ik} \sigma_{lm} - \frac{1}{4\pi} \tilde{D}_{0i} \tilde{E}_{i} - \frac{1}{8\pi} \tilde{E}_{i} \epsilon_{ik} \tilde{E}_{i} - \tilde{\gamma}_{ijkl} \tilde{\sigma}_{ik} \tilde{\sigma}_{jl} \]

Whence:

\[ \Phi_{el} = -\left( \frac{\partial \tilde{\Phi}_0}{\partial \tilde{\sigma}_{ik}} \right)_{\tilde{E}_{i}} = \mu_{iklm} \sigma_{ik} \sigma_{lm} + \epsilon_{ij} \epsilon_{ik} \tilde{E}_{j} \]

(17.8)
\[ \sigma_{ik} = 0 \]

\[ \text{div } \mathbf{D} = 0 \]

\[ \text{curl } \mathbf{E} = 0 \]

\[ \text{elastic equilibrium} \]

\[ \text{equations elastic equilibrium} \]

\[ \frac{\partial \sigma_{ik}}{\partial x_n} = 0 \]

\[ \mathbf{E} = \mathbf{E}_0 \]

Field is uniform deformation homogenous \[ \Rightarrow u_{ik} = 0 \Rightarrow \sigma_{ik} = 0 \]

**bodies ellipsoidal from point surface**

**Field is uniform deformation homogenous \[ \Rightarrow u_{ik} = 0 \Rightarrow \sigma_{ik} = 0 \]**

**x-th symmetry?**

\[ 3 \times 6 = 18 \]

**no piezoelectric can have a center of symmetry.**

\[ \text{on reflection w.r.t. center co-ordinates tensor of rank 3 changes sign.} \]

**all pyroelectric are piezo electric**

\[ \text{number components} \]

\[ \sqrt{3 \times 6 = 18} \text{ indep components} \]

\[ \text{actual number of indep components is usually much lower.} \]

**components of \( \mathbf{E} \), \( \mathbf{D} \) are unaltered in symmetry transformations**

**not piezoelectric body can have a center of symmetry, in particular, isotropic**

**an inversion through a center of symmetry. the components of a tensor of rank 3 changes sign**

**pyroelectric and piezo**

\[ D_i = D_{oi} + \varepsilon_{ik} E_k + \delta_{ik} \]  

\[ D_i = \varepsilon_{ik} E_k + \delta_{ik} \]
homogeneous deformation. All
\[ u_{ik} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) = \text{const} \]

\[ u_{ik} = \mu \partial_{ik} E + \frac{\partial u_k}{\partial x_i} E \Rightarrow \sigma_{ik} = \text{const} \]

for a constant volume element, it is zero (no external mechanical force).

\[ 0 = \int \sigma_{ik} n_k df = \text{area} \ n_k \ \sigma_{ik} \Rightarrow \sigma_{ik} = 0 \]

point group \( D_2 \)

perpendicular axis, no direction charged \( \Rightarrow \) no pyroelectricity

\[ D_{oi} = 0 \]
§18 Thermodynamic Inequalities

\[ \delta F = \int F(T, P, \rho) \, dV \]

\[ \text{div } P = 0 \quad \text{inside the dielectric} \]

\[ \oint_{\partial V} \mathbf{E} \cdot d\mathbf{l} = 4\pi \rho \quad \text{on the surface of a conductor which carries a given charge} \]

\[ \text{do not require it to obey } \nabla \times \mathbf{E} = 0, \text{ where } \mathbf{E} = \left( \frac{\partial F}{\partial P} \right)_{T, \rho} \frac{4\pi}{\varepsilon_0} \]

\[ \text{or the Dirichlet condition: } \phi = \text{const on the surface of a conductor} \]

In the thermodynamic condition that \( F \) is a minimum, only states of possible values are considered.

Lagrangemethod of multipliers

\[ 0 = \int \left( \delta F + \frac{1}{4\pi} \int \nabla \phi \cdot \delta P \right) \, dV + \frac{\phi_0}{4\pi} \oint \mathbf{E} \cdot d\mathbf{l} \]

\[ \delta F = \left( \frac{\partial F}{\partial P} \right)_{T, \rho} \delta P = \frac{\mathbf{E} \cdot \delta P}{4\pi} \]

\[ \int dV \phi \cdot \nabla \phi = \int dV \nabla \cdot (\phi \mathbf{E}) - \int dV \mathbf{E} \cdot \nabla \phi \]

\[ = \int dV \phi \mathbf{E} \cdot \nabla \phi - \int dV \mathbf{E} \cdot \nabla \phi \]

\[ 0 = \frac{1}{4\pi} \int \mathbf{E} \cdot [\delta P (\phi_0 - \phi)] + \frac{1}{4\pi} \int dV \mathbf{E} \cdot \delta P + \frac{1}{4\pi} \oint dV \mathbf{E} \cdot d\mathbf{l} \]

\[ \Rightarrow \phi = \phi_0 \text{ on the surface} \]

\[ \nabla \phi = -\mathbf{E} \text{ elsewhere} \Rightarrow \mathbf{E} \times \mathbf{E} = 0 \]
\[ \delta \mathcal{F} = \int \delta V \cdot \mathbf{E}(T, \mathbf{p}, E) \]

Energy functional for \( n \) spherical shells

\[ \delta \mathcal{F} = \int \delta V \frac{\partial \mathcal{F}}{\partial \mathbf{E}} \cdot \delta \mathbf{E} = -\frac{1}{4\pi} \int \delta V \mathbf{D} \cdot \delta \mathbf{E} = +\frac{1}{4\pi} \int \delta V \mathbf{D} \cdot \nabla \phi \]

\[ \rightarrow \]

\[ = \frac{1}{4\pi} \int \delta V \nabla \cdot (\mathbf{D} \delta \phi) - \frac{1}{4\pi} \int \delta V \delta \phi \mathbf{D} \cdot \mathbf{D} \]

\[ \rightarrow \]

\[ = \frac{1}{4\pi} \int \delta V \mathbf{D} \cdot \delta \phi - \frac{1}{4\pi} \int \delta V \delta \phi \mathbf{D} \cdot \mathbf{D} \]

\[ \int \delta \phi = 0 \text{ on surface} \]

\[ \int \delta \phi \mathbf{D} \text{ in bulk} \]

\[ \frac{\delta \mathcal{F}}{\delta \mathbf{D}} = \frac{\mathbf{E}}{4\pi} = 0 \]

Calculation of the sufficient condition requires checking the second variation:

when there is a linear relationship between \( \mathbf{D} \), \( \mathbf{E} \):

\[ F = F_0 + \int \delta V \frac{\mathbf{D}^2}{8\pi\epsilon_0} \]

minimum only if \( \epsilon > 0 \) and nonnegative definite. Then \( \mathbf{D} \),
Thomson's Theorem (§2)

energy of electrostatic field of conductors

charge distribution undergoes small change (total unaffected)
charges may penetrate

\[ \delta U = - \frac{1}{4\pi} \int dV \cdot E \delta E = - \frac{1}{4\pi} \int dV \text{ grad } \phi \cdot \delta E \]

\[ = - \frac{1}{4\pi} \int dV \text{ div } (\delta \delta E) + \frac{1}{4\pi} \int dV \phi \cdot D \cdot \delta E \]

\[ = - \frac{1}{4\pi} \int \delta F \cdot (\delta \delta E) + \frac{1}{4\pi} \int dV \phi \cdot D \cdot \delta E \]

\[ \delta Q = \int dV \phi \delta \rho \]

\[ = 0 \quad \text{requires } \phi = \text{const. since } \int dV \delta \rho = 0 \]

back to § 18.

\[ \delta F = \int \delta F(T, p, D) dV \]

require

\[ \text{div } D = 0 \quad \int D \cdot \delta F = 0 \quad \text{me} \]

do not require

\[ \phi = \text{const. at surface of conductor} \]

\[ \text{curl } E = 0 \quad \text{where } E = 4\pi \frac{\delta F}{\delta D} \]

\[ \delta G = \int \delta F dV - \frac{1}{4\pi} \int dV \phi \delta D + \delta F \mid_{\text{surface of conductors}} \]

\[ \delta F = \frac{\delta F}{\delta D} \cdot \delta D = \frac{1}{4\pi} E \cdot \delta D \]

\[ \delta G = \frac{1}{4\pi} \int dV E \cdot \delta D - \frac{1}{4\pi} \int \delta D \cdot (\delta E) + \frac{1}{4\pi} \int \delta V \delta D \cdot \text{grad } \phi \]

\[ + \frac{1}{4\pi} \delta F \cdot \delta D \]

\[ = \frac{1}{4\pi} \int dV (E + \text{grad } \phi) \cdot \delta D + \frac{1}{4\pi} \int \delta F \cdot \delta D (\phi_0 - \phi) + \int dV E \cdot dD \]

\[ \Rightarrow E = - \text{grad } \phi \]

\[ \Rightarrow \phi = \phi_0 \quad \text{on surface of conductor} \]
arbitrary adh. bhm. D \neq E

second variation of (18.1) vary simultaneously \( D \neq \rho \)

sufficient conditions for (18.1) to be minimum

\[ D = D_x \hat{D} \] before variation

\[ D = \sqrt{D_x^2 + D_y^2 + D_z^2} \]

\[ \frac{\partial D}{\partial D_x} = \frac{D_x}{D} \bigg|_{D_x = 0} = 0 \]

\[ \frac{\partial^2 D}{\partial D_x} = \frac{1}{D} - \frac{D_x}{D^2} \frac{\partial D}{\partial D_x} = \frac{1}{D} - \frac{D_x^2}{D^2} \bigg|_{D_x = 0} = \frac{1}{D} \]

\[ \delta D = \frac{1}{2D} \delta D_x^2 + \frac{1}{2D} \delta D_y^2 + \delta D_x \]

second variation of \( \delta D \):

\[ (\delta D) \frac{\partial F}{\partial D} \left[ (\delta D_x)^2 + (\delta D_y)^2 \right] + \int \delta V \left\{ \frac{1}{2} \frac{\partial^2 F}{\partial D^2} (\delta D_x)^2 + \frac{\partial^2 F}{\partial \rho^2} \delta D_x \delta \rho + \frac{1}{2} \frac{\partial^2 F}{\partial \rho^2} (\delta \rho)^2 \right\} \]

positive if

\[ \frac{1}{D} \frac{\partial F}{\partial D} \]

is positive

\[ \frac{\partial F}{\partial D} = \frac{E}{4\pi} \quad \frac{1}{D} \frac{\partial F}{\partial D} = \frac{E}{4\pi D} \] positive if \( E / D \) is in same direction

second term requires

\[ \frac{\partial^2 F}{\partial \rho^2} > 0 \]

note:

\[ \frac{\partial^2 F}{\partial \rho^2} > \left( \frac{\partial^2 F}{\partial D^2} \right) \frac{1}{\delta^2 F/\delta \rho^2} \]

\[ a \chi^2 + b \chi y + c y^2 > 0 \]

\[ \chi = \frac{x y}{\text{arb. const.}} \]

\[ a \chi^2 + b \chi + c > 0 \quad \Rightarrow \quad c > 0 \]

\[ \chi = -b \pm \sqrt{b^2 - 4ac} \quad \Rightarrow \quad \frac{b^2 - 4ac}{\delta^2 F/\delta \rho^2} > 0 \]

\[ \frac{\partial^2 F}{\partial \rho^2} \left( \frac{\partial^2 F}{\partial \rho^2} \right) > 0 \]
\[ U = \frac{1}{8\pi} \int dV E^2 \] all space
change distribution on the conductor undergoes an infinitesimal change
\[ \oint \vec{D} \cdot d\vec{V} = 0 \]

\[ SU = \frac{1}{4\pi} \int dV \vec{E} \cdot \delta \vec{E} = -\frac{1}{4\pi} \int dV (\nabla \phi) \cdot \delta \vec{E} \]

\[ = -\frac{1}{4\pi} \int dV D \cdot (\delta \vec{E}) + \frac{1}{4\pi} \int dV \phi \, D \cdot \delta \vec{E} \]

\[ \text{subsidiary condition } \vec{E} = -\nabla \phi \]
field vanishes at infinity
\[ SU = \int dV \phi \, \delta \vec{p} \] vanishes if \( \phi = \text{const.} \) inside conductor.

Our initial considerations:
\[ \delta \vec{E} = \int E(\tau, \rho, \vec{E}) d\vec{V} \]

In the absence of a dielectric \( \vec{E} = \vec{U} \) and \( F = \vec{U} = E^2 / 8\pi \)

\[ U = \frac{1}{8\pi} \int dV E^2 \]

(18.2) \( \text{div} \vec{D} = 0 \) inside, \( \text{no electric charge} \)
\( \text{div} \vec{E} = 0 \) in vacuum

(19.3) \( \int \text{div} \vec{D} d\vec{V} = \) inside the conductor \( \delta \vec{p} = 0 \)

It is very much the common viewpoint in Thomson's paper; charge is moved around inside the electric field. The line integral of \( E = -\nabla \phi \)

\[ SU = \frac{1}{4\pi} \int dV E \cdot \delta \vec{E} = -\frac{1}{4\pi} \int dV \nabla \phi \cdot \delta \vec{E} = -\frac{1}{4\pi} \int dV D \cdot (\nabla \phi \delta \vec{E}) \]

\[ + \frac{1}{4\pi} \int dV \phi \, D \cdot \delta \vec{E} = \int dV \phi \, \delta \vec{p} = 0 \text{ if } \phi = \text{const.} \text{ inside conductor} \]
Since \( \frac{\partial F}{\partial \rho} = \delta \) \( \frac{\partial F}{\partial \mathcal{D}} = \mathcal{E} \mathcal{H} \pi \)

\[
\frac{\partial F}{\partial \rho} > 0 \quad \text{chemical potential increases with density}
\]

\[
\frac{1}{4\pi} \frac{\partial E}{\partial \rho} \frac{\partial E}{\partial \mathcal{D}} - \frac{\partial E}{\partial \mathcal{D}} \frac{1}{4\pi} \frac{\partial E}{\partial \rho} > 0
\]

as a Jacobian

\[
\frac{\partial (E, \mathcal{D})}{\partial (\rho, \mathcal{D})} > 0
\]

switching to \( \mathcal{D}, \mathcal{E} \)

\[
\frac{\partial (E, \mathcal{D})}{\partial (\rho, \mathcal{D})} = \frac{\partial (E, \mathcal{D})}{\partial (\mathcal{D}, \mathcal{E})} \frac{\partial (\mathcal{D}, \mathcal{E})}{\partial (\rho, \mathcal{D})}
\]

\[
\frac{\partial E}{\partial \mathcal{D}} = \left( \frac{\partial E}{\partial \mathcal{D}} - \frac{\partial \mathcal{D}}{\partial \rho} \frac{\partial E}{\partial \rho} \right) \frac{\partial \mathcal{D}}{\partial \rho}
\]

\[
\frac{\partial E}{\partial \rho} > 0 \quad \frac{\partial \mathcal{D}}{\partial \rho} > 0
\]

in the absence of a field

\[
\frac{\partial E}{\partial \mathcal{D}} > 0 \quad \frac{\partial \mathcal{D}}{\partial \rho} > 0
\]

(\ref{18.7}) may be violated while (\ref{18.7}) is not.

\[
\frac{\partial (E, \mathcal{D})}{\partial (\rho, \mathcal{D})} = 0 \quad \text{critical state}
\]

\[
\frac{\partial (E, \mathcal{D})}{\partial (\rho, \mathcal{D})} = \frac{\partial (E, \mathcal{D})}{\partial (\mathcal{D}, \mathcal{E})} \frac{\partial (\mathcal{D}, \mathcal{E})}{\partial (\rho, \mathcal{D})}
\]

\[
\frac{\partial \mathcal{D}}{\partial \rho} = 0 \quad \frac{\partial E}{\partial \mathcal{D}} > 0
\]

stability requires

\[
\frac{\partial E}{\partial \mathcal{D}^2} > 0 \quad \frac{\partial \mathcal{D}}{\partial \rho^2} > 0
\]
§ 18 Problem critical pt. dielectric in an electric field.

\[ (18.9) \quad \sigma = \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T = \left( \frac{\partial^2 \varepsilon}{\partial \rho^2} \right)_T - \frac{E^2}{8\pi} \left( \frac{\partial^2 \varepsilon}{\partial \rho^2} \right)_T. \]

From Eq. (10.18),
\[ \left( \frac{\partial \varepsilon}{\partial \rho} \right)_T = \frac{1}{\rho} \left( \frac{\partial p}{\partial \rho} \right)_T. \]

\[ \rho = \rho(p, T) \text{ is EOS in absence of field.} \]

Thus,
\[ \frac{1}{\rho} \left( \frac{\partial p}{\partial \rho} \right)_T = \frac{E^2}{8\pi} \left( \frac{\partial^2 \varepsilon}{\partial \rho^2} \right)_T. \]

For stability, must also have
\[ \left( \frac{\partial^2 \varepsilon}{\partial \rho^2} \right)_T = \left( \frac{\partial^2 p}{\partial \rho^2} \right)_T = 0. \]

Hence,
\[ \left( \frac{\partial p}{\partial \rho} \right)_{T, E} \bigg|_{E=0} + \left( \frac{\partial^2 p}{\partial \rho^2} \right)_{T, E} \bigg|_{\rho=0} = \frac{\partial^2 p}{\partial T \partial \rho}. \]

\[ \Delta T = \left( \frac{\partial p}{\partial \rho} \right)_{T, E} \bigg|_{\rho=0} = \frac{\partial^2 p}{\partial T \partial \rho} \bigg|_{\rho=0}. \]
§19 Ferroelectrics

It is known that pyroelectric and non-pyroelectric properties are connected through a second-order phase transition. Near this transition, ferroelectric properties are observed.

\[ \text{All pyroelectrics are piezo electric.} \]

\[ \text{piezo pyro (non pyro) have } D \approx 0 \text{ but} \]

\[ \text{Bred \theta \text{ and } E_0 \text{ (E)} \text{ (E)} \text{ (E)} \text{ (E)} \text{ (E)}} \text{.} \]

\[ \text{in an ordinary pyro x-ray, change of polar direction involves considerable reorientation of lattice} \]

\[ \text{very high energy barrier} \]

New Curie pt. arrangement of atoms mostly stable between pyro Curie pt. \( \text{small spontaneous polarization} \)

\[ \text{change in direction of \text{pol} \text{ar} \text{ o} \text{ri} \text{t} \text{a} \text{t} \text{ion} \text{)} \text{ requires \text{a} slight \text{re} \text{or} \text{ien} \text{t} \text{ation \text{)} \text{ in \text{ the}} \text{ lattice} \text{)} \text{.} \]

\[ \text{ferroelectric axis} \text{ determined by the structure} \]

\[ D \text{ non pyro electric phase lower at Curie pt. In some cases, it is uniquely determined.} \]

\[ \text{emergent spontaneous polarization dependent upon static field.} \]

\[ \text{some cases: symmetry of the non-pyroelectric phase may allow spontaneous} \]

\[ \text{polarization in any preferred equivalent direction.} \]

\[ \text{Ferroelectricity in form of general decay of 2nd order phase transistions.} \]

\[ \text{Thermodynamic stability} \]

\[ \text{D is stable (unstable) in nonpyroelectic (pyroelectic)phase.} \]

\[ \theta \text{ must have } D \text{ is zero when } \text{D and E is no field present).} \]
\[
\Phi - \Phi_0 = \frac{1}{8\pi} \frac{1}{\varepsilon(\Phi)} D \cdot D
\]

where \( D \) is the electric displacement and \( \varepsilon(\Phi) \) is the dielectric constant as a function of \( \Phi \).

**Coord axes principal axes by \( \varepsilon_{ij} \)**

\[
\varepsilon_{ii} = \frac{1}{8\pi} \left( \frac{1}{\varepsilon(\Phi)} \frac{D_x^2}{\varepsilon(\Phi)} + \frac{1}{\varepsilon(\Phi)} \frac{D_y^2}{\varepsilon(\Phi)} + \frac{1}{\varepsilon(\Phi)} \frac{D_z^2}{\varepsilon(\Phi)} \right)
\]

\( D = 0 \) corresponds to \( \varepsilon = \infty \) if \( \frac{1}{\varepsilon(\Phi)} \) all positive.

Pyroelectric phase can only be formed when one of these three coefficients changes sign. \( \varepsilon(\Phi) \) goes from \(-\infty\) to \(+\infty\).

\( \frac{1}{\varepsilon(\Phi)} \) vanishes at a transition point.

If \( \varepsilon(x) \neq \varepsilon(y) \neq \varepsilon(z) \), only one of the coefficients \( \frac{1}{\varepsilon(\Phi)} \) vanishes and the ferroelectric axis is uniquely defined.

Since \( \frac{1}{\varepsilon(\Phi)} \) is small, keep quadratic term (2 axis along z axis equivalent).

\[
\Phi = \Phi_0 + \frac{1}{8\pi \varepsilon(\Phi)} D_x^2 + \frac{B}{16\pi} D_z^4
\]

\( B > 0 \) at \( T = \Theta \) for stability. There at \( D_x = 0 \) and in the neighborhood of that point.

Near \( \Theta \),

\[
\frac{1}{\varepsilon(\Phi)} = 1/(\varepsilon(T-\Theta)) \quad \text{as} \quad \varepsilon(T-\Theta)^{-1}
\]

\( \varepsilon(\Phi) \) diverges inversely as \( T-\Theta \).

\[
\varepsilon(\Phi) = 1/\varepsilon(T-\Theta)
\]

\[
\frac{1}{10^{-3}} \text{ cm}^{-1}
\]

\[
\frac{1}{30^{-10} - 10^{-8}} \text{ cm}^{-1}
\]

\[
\frac{1}{10^{-3}} \text{ cm}^{-1}
\]
\[ E_z = \frac{4\pi}{3} \frac{\partial P}{\partial D_z} = \frac{2(T-\Theta)}{B} D_z + B D_z^3 \] (19,4) Heflin and Funk

In the pyroelectric phase \((T-\Theta) > 0\), \(D_z = 0\) for \(E_z = 0\).

As \(E_z\) increases at given \(T-\Theta\), \(D_z\) first increases linearly

\[ D_z = (E_z/B)^{1/2} \]

eventually for large enough \(E_z\).

Linear relationship between \(E_z\) and \(D_z\) also ceases to be valid for small enough \(T-\Theta\); small \(E_z\) large \(D_z\); large \(D_z\) requires higher order terms.

For \(T < \Theta\) (pyro) \(D_z = 0\) cannot correspond to a stable state. For \(E_z = 0\), induction has a nonzero value

\[ -\kappa(T-\Theta) = B D_z^2 \]

\[ D_z = \left\{ \frac{\kappa(T-\Theta)}{B} \right\}^{1/2} (\pm) \]

\[ D_{z0} = \pm \sqrt{\frac{\kappa(T-\Theta)}{B}} \]

Points for dielectric.

Spontaneous polar \( P_{z0} = D_{z0}/4\pi \) goes as \(\sqrt{T-\Theta}\) near Curie point.

"dielectric constant" of pyroelectric phase \(dP_z/dE_z\) for \(E_z = 0\).

\[ 1 = \left\{ \kappa(T-\Theta) + 3B D_z^2 \right\} \frac{dD_z^2}{dE_z^2} \]

\[ \frac{dD_z}{dE_z} = \frac{1}{2\kappa(T-\Theta)} \left[ \sqrt{\kappa(T-\Theta)} - \kappa(T-\Theta) \right] \]

\[ \epsilon(2) = \frac{1}{d(T-\Theta)} \] in the nonpyroelectric phase.

The Curie point.
\[ S = - \left( \frac{\partial \Theta}{\partial T} \right)_D = S_0 - \frac{\kappa}{8\pi} \rho \frac{\partial^2 \rho}{\partial \Theta \partial \tilde{T}} \quad \text{fourth order term can be neglected} \]

in nonpyrophase \( S = S_0 \)

pyro phase \( S = S_0 - \frac{\kappa}{8\pi} \frac{\kappa (\Theta - T)}{B} \)

\[ S = S_0 - \frac{\kappa}{8\pi B} (\Theta - T) \]

specific heat

\[ T \frac{\partial S}{\partial T} = C_p = C_{p_0} + T \frac{\partial^2 \rho}{\partial \Theta \partial \tilde{T}} \to C_{p_0} + \frac{\Theta \kappa}{8\pi B} \]

specific heat, nonpyroelectric phase in the case \( T = \Theta \).

If the transition takes place at \( E_z = 0 \)

it is accompanied by a sudden change in the specific heat

as happens in ordinary 2nd order phase transitions, \( C > C_{p_0} \)

**Fig. 13** \( D_z (E_z) \)

\[ E_z = \kappa (T - \Theta) D_z + B D_z^3 \]

specific heat increases when pyroelectricity appears.
\[
\frac{\partial E_z}{\partial \theta} = 0
\]

\[
E_z = -\frac{\alpha z^2 (\theta - 7)^3}{\beta z^2 (\theta - 7)^3}
\]

\[
\alpha \approx 1.5 - B + 3B^2
\]

\[
0 = \alpha (\theta - 7) + 3B^2
\]

\[
\frac{\partial E_z}{\partial \theta} = 0
\]