1. By the first law of thermodynamics,

$dQ = dU - dW$, where here $dW = -PdV$.

For heat added at fixed volume, $dW = 0$, so

$$dQ = C_V dT = dU \Rightarrow C_V = \frac{dU}{dT} \Rightarrow dU = C_V dT$$

For heat added at fixed pressure:

$$dQ = C_P dT = dU + PdV = C_V dT + PdV$$

From the ideal gas law, $PV = Nk_B T$, so

$$d(PV) = PdV + VdP = Nk_B dT$$

At fixed pressure, $VdP = 0$, so $PdV = Nk_B dT$.

Plugging this in:

$$C_P dT = C_V dT + Nk_B dT$$

$$\Rightarrow C_P - C_V = Nk_B$$

2. Heat capacity at fixed $\vec{D}$:

$$C_{\vec{D}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{D}} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)\Big|_{\vec{D}}$$

We can similarly consider the heat capacity at fixed $\vec{E}$:

$$C_{\vec{E}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{E}} = -T\left(\frac{\partial^2 \tilde{F}}{\partial T^2}\right)_{\vec{E}}$$

## Application: heat capacity in linear dielectric media

a. We now consider the special case of a linear dielectric medium, so that $\vec{D} = \epsilon\vec{E}$. For simplicitly, we take $\epsilon$ to be homogeneous across the medium. We then also have $\delta\vec{D} = \epsilon\,\delta\vec{E}$, so

assumes no explicit dependence of $\epsilon$ on $\vec{E}$ (which is the case for linear medium)

$$\delta U = T\delta S + \frac{1}{4\pi}\int_V dV\,\frac{\vec{D}\cdot\delta\vec{D}}{\epsilon}$$

$$= T\delta S + \frac{1}{4\pi}\,\delta\left[\int_V dV\,\frac{D^2}{2\epsilon}\right]$$

since $\delta D^2 = \delta(\vec{D}\cdot\vec{D}) = 2\vec{D}\cdot\delta\vec{D}$.

in general, $D$ varies in space; we leave out this explicit dependence for notational convenience

If we want to consider a system at fixed temperature instead of fixed entropy, we can use Helmholtz free energy $F$ instead of $U$:

$$\delta F = -S\,dT + \frac{1}{4\pi}\,\delta\left[\int dV\,\frac{D^2}{2\epsilon}\right]$$

Let us say that we start at $\vec{D} = 0$ and then increase $\vec{D}$ to some final value $\vec{D}_F$. Then:

$$F(T, D_F) - F(T, 0) = \frac{1}{4\pi}\int_V dV\,\frac{D_F^2}{2\epsilon} > 0$$

(For normal materials, $\epsilon > 1$, since polarization induced along $\vec{E}$ field)

$$\Rightarrow F(T,D) = F(T,0) + \frac{1}{4\pi}\int_V dV \frac{D^2}{2\epsilon}$$

b. This equation gives us the necessary information to determine how $\vec{D}$ affects the balance of energy in the system. For instance, we can find an expression for the entropy:

$$S(T,D) = -\left(\frac{\partial F}{\partial T}\right)_{\vec{D}}$$

$$= -\frac{\partial F(T,0)}{\partial T} - \frac{1}{4\pi}\left(\frac{\partial}{\partial T}\int_V dV \frac{D^2}{2\epsilon}\right)_{\vec{D}}$$

The first term is just the entropy when $\vec{D}=0$, and in the second term the temperature derivative acts just on $\epsilon$, since $\vec{D}$ is held fixed. So:

$$S(T,D) = S(T,0) + \frac{1}{4\pi}\int_V dV \frac{D^2}{2\epsilon^2}\frac{d\epsilon}{dT}$$

c. We can consider $C_{\vec{D}}$, the heat capacity at fixed $\vec{D}$.

$$C_{\vec{D}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{D}} = C_0 + \frac{1}{4\pi}\int_V dV D^2 T \frac{d}{dT}\left(\frac{1}{2\epsilon^2}\frac{d\epsilon}{dT}\right)$$

$$= C_0 - \frac{1}{4\pi}\int_V dV D^2 T \frac{d^2}{dT^2}\left(\frac{1}{2\epsilon}\right)$$

where $C_0$ is the heat capacity at zero field.

We have noted that

$$\frac{d^2}{dT^2}\left(\frac{1}{2\epsilon}\right) = -\frac{d}{dT}\left(\frac{1}{2\epsilon^2}\frac{d\epsilon}{dT}\right)$$

This tells us that $C_{\vec{D}} - C_0$ depends on the details of the temperature dependence of $\epsilon(T)$.

d. What if $\vec{E}$ is the quantity that we externally control instead of $\vec{D}$? We can then use $\tilde{F}$ instead of F. By analogy with the calculation of $F(T, D)$, we find that

$$\tilde{F}(T, E) = \tilde{F}(T, 0) - \frac{1}{4\pi}\int_V dV\, \frac{\epsilon E^2}{2}$$

Note that $-\frac{1}{4\pi}\int_V dV\, \frac{\epsilon E^2}{2} = -\frac{1}{4\pi}\int_V \frac{D^2}{2\epsilon}$, so

$$\tilde{F}(T, E) - \tilde{F}(T, 0) = -\left(F(T, D) - F(T, 0)\right)$$
$$= -\frac{1}{8\pi}\int_V dV\, \vec{E}\cdot\vec{D} = -\frac{1}{2}\sum_j \phi_j q_j$$

using our result for this integral from lecture

$F(T, D) - F(T, 0) = \frac{1}{2}\sum_j \phi_j q_j$ is just the total work required to assemble the charges $q_j$ on the conductors.

To find $S(T, E)$:

$$S(T,E) = -\left(\frac{\partial \tilde{F}}{\partial T}\right)_{\vec{E}}$$

$$= S(T,0) + \frac{1}{4\pi}\int_V dV \frac{E^2}{2}\frac{d\epsilon}{dT}$$

Note that $\int_V dV \frac{E^2}{2}\frac{d\epsilon}{dT} = \int_V dV \frac{D^2}{2\epsilon^2}\frac{d\epsilon}{dT}$, so

$S(T,D) = S(T,E)$. This makes sense, because the entropy is a general "state-function" that should not depend on whether we hold $\vec{D}$ or $\vec{E}$ fixed. The heat capacity $C_{\vec{E}}$ at constant $\vec{E}$ is

$$C_{\vec{E}} = T\left(\frac{\partial S}{\partial T}\right)_{\vec{E}} = C_0 + \frac{1}{4\pi}\int_V dV \frac{E^2}{2} T \frac{d^2\epsilon}{dT^2}$$

same value of $C_0$ since zero field means $\vec{E}$ and $\vec{D}$ are both fixed at zero

The heat capacities at constant $\vec{E}$ and $\vec{D}$ differ by an amount

$$C_{\vec{E}} - C_{\vec{D}} = \frac{T}{4\pi}\int_V dV\left[\frac{E^2}{2}\frac{d^2\epsilon}{dT^2} - \frac{D^2}{2}\frac{d}{dT}\left(\frac{1}{\epsilon^2}\frac{d\epsilon}{dT}\right)\right]$$

$$\frac{D^2}{2}\frac{d}{dT}\left(\frac{1}{\epsilon^2}\frac{d\epsilon}{dT}\right) = \frac{\epsilon^2 E^2}{2}\left[\frac{-2}{\epsilon^3}\left(\frac{d\epsilon}{dT}\right)^2 + \frac{1}{\epsilon^2}\frac{d^2\epsilon}{dT^2}\right]$$

$$= -\frac{E^2}{\epsilon}\left(\frac{d\epsilon}{dT}\right)^2 + \frac{E^2}{2}\frac{d^2\epsilon}{dT^2} \Rightarrow C_{\vec{E}} - C_{\vec{D}} = \frac{T}{4\pi}\int_V dV \frac{E^2}{\epsilon}\left(\frac{d\epsilon}{dT}\right)^2$$

## 3. Electrostriction

If we allow for volume changes,

$$\delta U = T\delta S + \frac{1}{4\pi}\int_V dV\, \vec{E}\cdot\delta\vec{D} - p\,dV \quad \text{for pressure } p$$

We consider the Gibbs free energy $G = U - TS + pV$ such that

$$\delta G = -S\,dT + V\,dp + \frac{1}{4\pi}\int_V dV\, \vec{E}\cdot\delta\vec{D}$$

To get $\delta G$ in terms of $\delta\vec{E}$, we can define

$$\tilde{G} = G - \frac{1}{4\pi}\int_V dV\, \vec{E}\cdot\vec{D}$$

so that $\delta\tilde{G} = -S\,dT + V\,dp - \frac{1}{4\pi}\int_V dV\, \vec{D}\cdot\delta\vec{E}$

Assuming a linear dielectric so that $\vec{D} = \epsilon\vec{E}$,

$$\delta\tilde{G} = -S\,dT + V\,dp - \frac{1}{4\pi}\,\delta\left[\int_V dV\, \epsilon\,\frac{E^2}{2}\right]$$

since $\delta E^2 = \delta(\vec{E}\cdot\vec{E}) = 2\vec{E}\cdot\delta\vec{E}$. Integrating the electric field from 0 to $\vec{E}$ with $T$ and $p$ held fixed, we have

$$\tilde{G}(T,p,E) = \tilde{G}(T,p,0) - \frac{1}{8\pi}\,\epsilon\int_V dV\, E^2$$

Assuming a uniform applied electric field E,

$$\tilde{G}(T,p,E) = \tilde{G}(T,p,0) - \epsilon \frac{E^2 V}{8\pi}$$

where V is the volume of the dielectric we are considering. Based on the form of $\delta\tilde{G}$,

$$V = \left(\frac{\partial \tilde{G}}{\partial p}\right)_{T,E}$$

Using this formula, the volume $V_0$ with $\vec{E}=0$ is

$$V_0 = \left(\frac{\partial \tilde{G}(T,p,0)}{\partial p}\right)_{T,E}$$

The volume V with the field $\vec{E}$ is

$$V = V_0 - \frac{E^2 V}{8\pi}\left(\frac{\partial \epsilon}{\partial p}\right)_{T,E}$$

The change in volume is

$$\frac{\Delta V}{V} = \frac{V - V_0}{V} = -\frac{E^2}{8\pi}\left(\frac{\partial \epsilon}{\partial p}\right)_{T,E}$$

4. In a dielectric, we have the relation

$\vec{\nabla}\cdot\vec{D} = 4\pi\rho_{exc}(\vec{r}) = 4\pi q\,\delta(\vec{r}) \rightarrow$ in this problem

$\vec{D} = \epsilon_x E_x \hat{x} + \epsilon_y E_y \hat{y} + \epsilon_z E_z \hat{z}$

with $E_i = -\dfrac{\partial\phi}{\partial x_i}$.

Thus:

$$\epsilon_x \frac{\partial^2\phi}{\partial x^2} + \epsilon_y \frac{\partial^2\phi}{\partial y^2} + \epsilon_z \frac{\partial^2\phi}{\partial z^2} = -4\pi q\,\delta(\vec{r})$$

Let us introduce new variables

$$x' = \frac{x}{\sqrt{\epsilon_x}},\quad y' = \frac{y}{\sqrt{\epsilon_y}},\quad z' = \frac{z}{\sqrt{\epsilon_z}}$$

Then $\dfrac{\partial}{\partial x_i} = \dfrac{\partial x_i'}{\partial x_i}\dfrac{\partial}{\partial x_i'} = \dfrac{1}{\sqrt{\epsilon_i}}\dfrac{\partial}{\partial x_i'}$

$$\Rightarrow (\nabla')^2\phi = -4\pi q\,\delta(\vec{r}),\quad \delta(\vec{r}) = \delta(x)\delta(y)\delta(z)$$

in the primed coordinates

Note that $1 = \int dx\,dy\,dz\,\delta(x)\delta(y)\delta(z) = \sqrt{\epsilon_x\epsilon_y\epsilon_z}\int dx'dy'dz'\,\delta(x)\delta(y)\delta(z)$

Also, $1 = \int dx' dy' dz' \, \delta(x')\delta(y')\delta(z')$

$$\Rightarrow \delta(x')\delta(y')\delta(z') = \delta(x)\delta(y)\delta(z)\sqrt{\epsilon_x \epsilon_y \epsilon_z}$$

$$\Rightarrow \delta(\vec{r}) = \frac{\delta(\vec{r}\,')}{\sqrt{\epsilon_x \epsilon_y \epsilon_z}}$$

So $(\nabla')^2 \phi = -\dfrac{4\pi q \delta(\vec{r}\,')}{\sqrt{\epsilon_x \epsilon_y \epsilon_y}}$

This looks just like the equation for the potential in vacuum, but with $x_i \to x_i'$ and

$q \to \dfrac{q}{\sqrt{\epsilon_x \epsilon_y \epsilon_z}}$. The solution is then

$$\phi = \frac{q}{\sqrt{\epsilon_x \epsilon_y \epsilon_z}} \frac{1}{\sqrt{(x^2/\epsilon_x) + (y^2/\epsilon_y) + (z^2/\epsilon_z)}}$$

5. a. $\ddot{x} + \frac{1}{\tau}\dot{x} + w_0^2 x + a x^2 = -\frac{e}{m}E_0 e^{-iwt}$

From lecture, the zeroth order solution (ignoring a) is:

$$x_1(t) = \frac{eE_0/m}{w^2 - w_0^2 + iw/\tau} e^{-iwt} \equiv C_1(w) e^{-iwt}$$

$x_1(t)$ is proportional to the field $E(t) = E_0 e^{-iwt}$. We will consider the next order contribution to the solution, which will be second order in the field. This second order term will therefore have the form

$$x_2(t) = C_2(w) e^{-2iwt}, \quad \text{where } C_2(w)$$

is to be determined. Plugging in and equating terms with respective time dependence going as $e^{-iwt}$ and $e^{-i2wt}$ on each side:

$$\underbrace{\left(-w^2 - i\frac{w}{\tau} + w_0^2\right)C_1(w) e^{-iwt} = -\frac{e}{m}E_0 e^{-iwt}}$$

this equation is how we got the form for $C_1(w)$ above

$$\left(-4w^2 C_2(w) - 2i\frac{w}{\tau}C_2(w) + w_0^2 C_2(w) + a\, C_1(w)^2\right) e^{-2iwt} = 0$$

$$\Rightarrow C_2(w) = \frac{-a\,C_1(w)^2}{w_0^2 - 4w^2 - 2i\frac{w}{\tau}}$$

The oscillating polarization $P(2w)$ at frequency $2w$ is

$$P(2w) = -neC_2(w) = \frac{ane^3 E_0^2/m^2}{\left(w_0^2 - w^2 - i\frac{w}{\tau}\right)^2\left(w_0^2 - 4w^2 - 2i\frac{w}{\tau}\right)}$$

So the second-order nonlinear susceptibility, defined so that $P(2w) = \chi_2(2w)E_0^2$, is

$$\chi_2(2w) = \frac{ane^3/m^2}{\left(w_0^2 - w^2 - iw/\tau\right)^2\left(w_0^2 - 4w^2 - 2i\frac{w}{\tau}\right)}$$

b. $P(2w)$ corresponds to oscillating dipoles at frequency $2w$, which will radiate electromagnetic waves at frequency $2w$.

6. a. The force on an electron is

$$\vec{F} = m\ddot{\vec{r}} = -m\omega_0^2\vec{r} - e\left(\vec{E} + \frac{\dot{\vec{r}}}{c} \times \vec{B}\right)$$

For an electric field $\vec{E}e^{-i\omega t}$, we have electron position with time dependence $\vec{r}e^{-i\omega t}$, as in class. Because of the Lorentz force term, we will get equations of motion that look different for the $x$ and $y$ directions:

$$-\omega^2 x = -\omega_0^2 x - \frac{e}{m}E_x + i\omega y\frac{eB_0}{mc}$$

$$\Rightarrow (\omega_0^2 - \omega^2)x - i\omega\omega_c y = -\frac{e}{m}E_x$$

$$-\omega^2 y = -\omega_0^2 y - \frac{e}{m}E_y + i\omega\omega_c x$$

$$\Rightarrow (\omega_0^2 - \omega^2)y + i\omega\omega_c x = -\frac{e}{m}E_y$$

The polarization $\vec{P}e^{-i\omega t}$ is such that $P_x = -n_0 e x$, $P_y = -n_0 e y$, so that

$$(\omega_0^2 - \omega^2)P_x - i\omega\omega_c P_y = \frac{n_0 e^2}{m}E_x$$

$$i\omega\omega_c P_x + (\omega_0^2 - \omega^2)P_y = \frac{n_0 e^2}{m}E_y$$

Let $E_+$ denote the component of the field with positive circular polarization, and $E_-$ denote the component of the field with negative circular polarization. We can do a similar thing for the polarization, writing $P_+$ and $P_-$. Note that:

$$\vec{E} = E_x\hat{x} + E_y\hat{y} = E_+\left(\frac{\hat{x}+i\hat{y}}{2}\right) + E_-\left(\frac{\hat{x}-i\hat{y}}{2}\right)$$

$$\Rightarrow E_x = \frac{1}{2}(E_+ + E_-)$$

$$E_y = \frac{i}{2}(E_+ - E_-)$$

Similarly,

$$P_x = \frac{1}{2}(P_+ + P_-)$$

$$P_y = \frac{i}{2}(P_+ - P_-)$$

Our equations are then

$$\frac{1}{2}(w_0^2 - w^2)(P_+ + P_-) + \frac{1}{2}ww_c(P_+ - P_-) = \frac{1}{2}\frac{n_0e^2}{m}(E_+ + E_-)$$

$$\frac{i}{2}(w_0^2 - w^2)(P_+ - P_-) + \frac{i}{2}(P_+ + P_-)ww_c = \frac{i}{2}(E_+ - E_-)\frac{n_0e^2}{m}$$

$$\Rightarrow (w_0^2 - w^2)P_+ + ww_cP_+ = \frac{n_0e^2}{m}E_+$$

$$(w_0^2 - w^2)P_- - ww_cP_- = -\frac{n_0e^2}{m}E_-$$

$$\Rightarrow P_\pm = \frac{\frac{n_0 e^2}{m} E_\pm}{w_0^2 - w^2 \pm w w_c}$$

$$\chi_{e_\pm} = \frac{P_\pm}{E_\pm}, \quad \epsilon_\pm = 1 + 4\pi \chi_{e_\pm}, \quad n_\pm^2 = \epsilon_\pm$$

$$\Rightarrow n_\pm^2 = 1 + \frac{4\pi n_0 e^2/m}{w_0^2 - w^2 \pm w w_c} \qquad \text{for } w_c = \frac{eB_0}{mc}$$

b. For + and minus circular polarization, the magnitude of the k-vector $k_\pm$ is such that

$$k_\pm^2 = n_\pm^2 \frac{w^2}{c^2} \approx \left[1 + \frac{4\pi n_0 e^2/m}{w_0^2 - w^2}\left(1 \mp \frac{w w_c}{w_0^2 - w^2}\right)\right]\frac{w^2}{c^2}$$

after Taylor expanding to first order in $B_0$.

We can write $k_\pm = k \mp \Delta k$, where $k = \frac{w}{c}\sqrt{1 + \frac{4\pi n_0 e^2/m}{w_0^2 - w^2}}$

We will find $\Delta k$ to 1st order in $B_0$.

$$k_\pm = \frac{w}{c}\sqrt{1 + \frac{4\pi n_0 e^2/m}{w_0^2 - w^2} \mp \frac{(4\pi n_0 e^2/m) w w_c}{(w_0^2 - w^2)^2}}$$

$$\approx k\left(1 \mp \frac{1}{2}\frac{w w_c (4\pi n_0 e^2/m)}{(w_0^2 - w^2)(w_0^2 - w^2 + (4\pi n_0 e^2/m))}\right)$$

$$\Rightarrow k_\pm = \frac{w}{c} n \left( 1 \mp \frac{1}{2} \frac{w w_c (4\pi n_0 e^2/m)}{(w_0^2 - w^2)(w_0^2 - w^2 + (4\pi n_0 e^2/m))} \right)$$

where $n \approx \frac{1}{2}(n_+ + n_-) \approx \sqrt{1 + \frac{4\pi n_0 e^2/m}{w_0^2 - w^2}}$

to leading order in $B_0$. Thus

$$\Delta k = \frac{w_c}{c} \frac{w^2}{w_0^2 - w^2} \frac{n(4\pi n_0 e^2/m)}{2(w_0^2 - w^2) n^2}$$

Note that $n^2 - 1 = \frac{4\pi n_0 e^2/m}{w_0^2 - w^2}$

$$\Rightarrow \Delta k = \frac{w_c}{c} \frac{w^2}{w_0^2 - w^2} \frac{n^2 - 1}{2n}$$

Let us assume that we start out at $z=0$ with

$E_x = E_0$, $E_y = 0$. Then at $z=0$,

$E_+ = E_- = E_0$, using our convention from before. Now, as the wave propagates:

$$E_x(z) = \frac{1}{2}\left(E_+(z=0) e^{i(k_+ z - wt)} + E_-(z=0) e^{i(k_- z - wt)}\right)$$

$$E_y(z) = \frac{i}{2}\left(E_+(z=0) e^{i(k_+ z - wt)} - E_-(z=0) e^{i(k_- z - wt)}\right)$$

Plugging in

$$E_x(z) = \frac{1}{2} E_0 e^{i(kz-wt)} \left(e^{-i\Delta kz} + e^{i\Delta kz}\right)$$

$$= E_0 \cos(\Delta kz)\, e^{i(kz-wt)}$$

$$E_y(z) = \frac{i}{2} E_0 e^{i(kz-wt)} \left(e^{-i\Delta kz} - e^{i\Delta kz}\right)$$

$$= E_0 \sin(\Delta kz)\, e^{i(kz-wt)}$$

So for propagation over a distance $d$, the angle of polarization is rotated by

$$\Delta\theta = \Delta k d \approx \frac{w_c d}{c} \frac{w^2}{w_0^2 - w^2} \frac{n^2-1}{2n}$$

c. If we propagate in the $-z$ direction, the sign of $z$ changes in $\cos(\Delta kz)$, $\sin(\Delta kz)$, but also the sign of $k$ and $\Delta k$ will change, since we will now take the negative square root. So after back reflection, the angle of polarization will keep rotating in the same direction.