Lecture 2. Nonlinear susceptibility

Learning objectives:

1. Classic harmonic oscillator model

2. Anharmonic model $\begin{cases} \text{Non-centrosymmetric media} \\ \text{Centrosymmetric media} \end{cases}$

$\chi^{(2)}$ and $\chi^{(3)}$ are related to $\chi^{(1)}$

Recap: last lecture:

$$\mathcal{P}(t) = \epsilon_0 \chi^{(1)} E(t) + \epsilon_0 \chi^{(2)} E^2(t) + \epsilon_0 \chi^{(3)} E^3(t) + \cdots$$

$$\underbrace{\epsilon_0 \chi^{(1)} E(t)}_{P^{(1)}} \quad \underbrace{\epsilon_0 \chi^{(2)} E^2(t)}_{P^{(2)}} \quad \underbrace{\epsilon_0 \chi^{(3)} E^3(t)}_{P^{(3)}}$$

At $E \sim E_{at}$, $P^{(1)} \sim P^{(2)}$

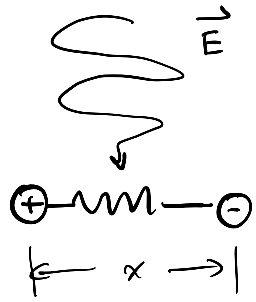
$\chi^{(1)} \sim \chi^{(2)} E_{at}$ — inner atom E-field

$$\Rightarrow \begin{cases} \chi^{(2)} \sim \dfrac{\chi^{(1)}}{E_{at}} \\[2ex] \chi^{(3)} \sim \dfrac{\chi^{(1)}}{E_{at}^2} \end{cases}$$

<u>What can be the more rigorous relation between</u>

<u>$\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$?</u>

1. Classic harmonic oscillator model.



dipole moment: $p = qx$

Equation of motion: $F = m\dfrac{d^2\tilde{x}}{dt^2}$

$$F = \underbrace{-eE}_{\text{EM}} - \underbrace{m\omega_0^2\tilde{x}}_{\text{restoring}} - \underbrace{2m\gamma\frac{d\tilde{x}}{dt}}_{\text{damping}} = m\frac{d^2\tilde{x}}{dt^2} \quad ①$$

Assume the input field:

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c., \text{ plug in } ①.$$

Solutions: $\tilde{x}(\omega_1) = -\dfrac{eE_1}{m(\omega_0^2-\omega_1^2-2i\omega_1\gamma)}$

$\tilde{x}(\omega_2) = \dfrac{-eE_2}{m(\omega_0^2-\omega_2^2-2i\omega_2\gamma)}$ $\longrightarrow$ Define as D

Or. $\tilde{x}^{(1)}(\omega_j) = -\dfrac{e}{m}\cdot\dfrac{E_j}{D(\omega_j)}$ $\quad j = 1.2\ldots$

Displacement

How to calculate the susceptibility? $\chi^{(1)}$

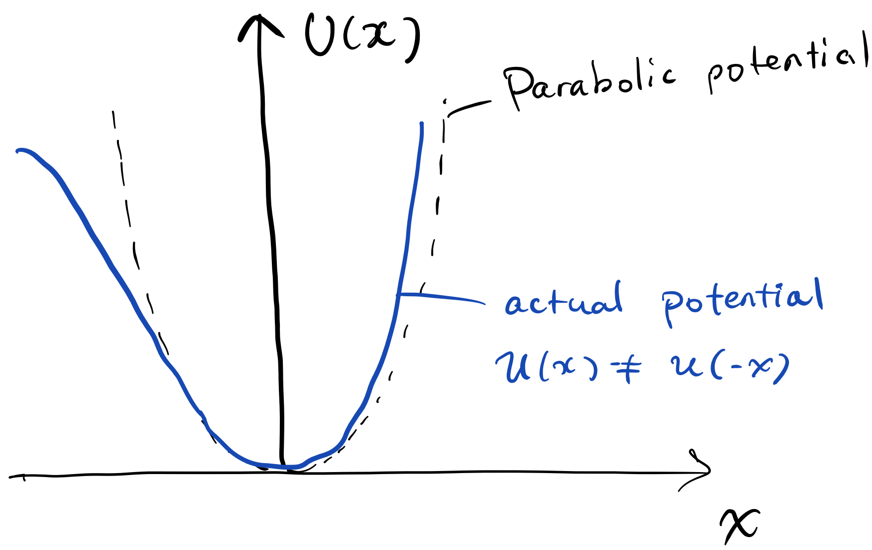
Defiaiton of polarization :

$$P^{(1)}(\omega_j) = \epsilon_0 \chi^{(1)}(\omega_j) E(\omega_j) = -Ne\, x^{(1)}(\omega_j)$$

$$\boxed{\chi^{(1)}(\omega_j) = \frac{Ne^2}{m\epsilon_0 D(\omega_j)}}$$

2. Anharmonic oscillator model

① Non-centrosymmetric media



Strength of nonlinearity

$$U(\tilde{x}) = -\int F_{restoring} \cdot dx = \underbrace{\frac{1}{2} m\omega_0^2 \tilde{x}^2}_{\text{even}} + \underbrace{\frac{1}{3} m a \tilde{x}^3}_{\text{odd}}$$

$$F_{restoring} = -\frac{dU(x)}{dx} = -m\omega_0^2 x - m a x^2$$

E.O.M.:

$$\frac{d^2x}{dt^2} + 2\gamma \frac{dx}{dt} + \omega_0^2 x + a x^2 = \frac{-e\tilde{E}(t)}{m}$$

Assuming input field:

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c.$$

No general solution! Use the perturbation theory (same as the Q.M.)

$$\ddot{x} + 2\gamma \ddot{x} + \omega_0^2 x + a x^2 = -\lambda e E(t)/m \quad ①$$

coupling strength 0 → 1
set to be 1 at the end.

Solution: $x = \underline{\lambda} x^{(1)} + \underline{\lambda^2} x^{(2)} + \underline{\lambda^3} x^{(3)} + \dots$, plug in ①

Match the λ, λ^2 and λ^3 terms to make sure it is a solution

We have:

$$\begin{cases} \ddot{x}^{(1)} + 2\gamma \dot{x}^{(1)} + \omega_0^2 x^{(1)} = -\dfrac{eE(t)}{m} & \text{— linear} \\ \ddot{x}^{(2)} + 2\gamma \dot{x}^{(2)} + \omega_0^2 x^{(2)} + a (x^{(1)})^2 = 0 & \\ \ddot{x}^{(3)} + 2\gamma \dot{x}^{(3)} + \omega_0^2 x^{(3)} + 2a\, x^{(1)} x^{(2)} = 0. & \\ \vdots \end{cases} \quad \left.\right\} \text{nonlinear}$$

Since for the linear case,

$$x^{(1)}(\omega_j) = -\frac{e}{m}\frac{E_j}{D(\omega_j)} \leftarrow \omega_0^2 - \omega_j^2 - 2i\omega\gamma$$

We know the input contains ω_1 and ω_2.

So $(x^{(1)})^2$ contains $\pm 2\omega_1$ $\pm 2\omega_2$, $\pm(\omega_1+\omega_2)$ $\pm(\omega_1-\omega_2)$

At ω_1, the second eq. can be written as:

$$\ddot{x}^{(2)} + 2\gamma \dot{x}^{(2)} + \omega_0^2 x^{(2)} = \frac{-a\left(\frac{eE_1}{m}\right)^2 e^{-2i\omega_1 t}}{D^2(\omega_1)}$$

Assuming solution: $x^{(2)}(t) = x^{(2)}(2\omega_1)e^{-2i\omega_1 t}$

$$\Rightarrow \quad x^{(2)}(2\omega_1) = \frac{-a\left(\frac{e}{m}\right)^2 E_1^2}{D(2\omega_1)\, D^2(\omega_1)}$$

$$x^{(2)}(2\omega_2) = \frac{-a(e/m)^2 E_2^2}{D(2\omega_2)\, D^2(\omega_2)}$$

$$x^{(2)}(\omega_1+\omega_2) = \frac{-2a\left(\frac{e}{m}\right)^2 E_1 E_2}{D(\omega_1+\omega_2)\, D(\omega_1)\, D(\omega_2)}$$

$$x^{(2)}(\omega_1-\omega_2) = \frac{-2a\left(\frac{e}{m}\right)^2 E_1 E_2^*}{D(\omega_1-\omega_2)\, D(\omega_1)\, D(\omega_2)}$$

$$x^{(2)}(0) = \frac{-2a\left(\frac{e}{m}\right)^2 E_1 E_1^*}{D(0)\, D(\omega_1)\, D(-\omega_1)} + \frac{-2a\left(\frac{e}{m}\right)^2 E_2 E_2^*}{D(0)\, D(\omega_2)\, D(-\omega_2)}$$

Next, calculate $\chi^{(2)}(2\omega_1, \omega_1, \omega_1)$

$$P^{(2)}(2\omega_1) = \epsilon_0 \chi^{(2)}(2\omega_1, \omega_1, \omega_1)\, E(\omega_1)^2$$

$-Nex^{(2)}(2\omega_i)$

$$\Rightarrow \chi^{(2)}(2\omega_1, \omega_1, \omega_1) = \frac{N\left(\frac{e^3}{m^2}\right)a}{\epsilon_0\, D(2\omega_1)\, D^2(\omega_1)}$$

$$= \frac{\epsilon_0^2 m a}{N^2 e^3} \chi^{(1)}(2\omega_1) \left[\chi^{(1)}(\omega_1)\right]^2$$

Similarly, we can write

$\chi^{(2)}(\omega_1+\omega_2, \omega_1, \omega_2)$ $\chi^{(2)}(\omega_1-\omega_2, \omega_1, \omega_2)$ $\chi^{2}(0, \omega_1, -\omega_1)$

$$\begin{cases} \chi^{(2)}(2\omega_1, \omega_1, \omega_1) = \dfrac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(2\omega_1) \left[\chi^{(1)}(\omega_1)\right]^2 \\ \chi^{(2)}(\omega_1+\omega_2, \omega_1, \omega_2) = \dfrac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1+\omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2) \quad \text{(SFG)} \\ \chi^{(2)}(\omega_1-\omega_2, \omega_1, \omega_2) = \dfrac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1-\omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_2) \quad \text{(DFG)} \\ \chi^{(2)}(0, \omega_1, -\omega_1) = \dfrac{\epsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(0) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_1) \end{cases}$$

Miller's rule:

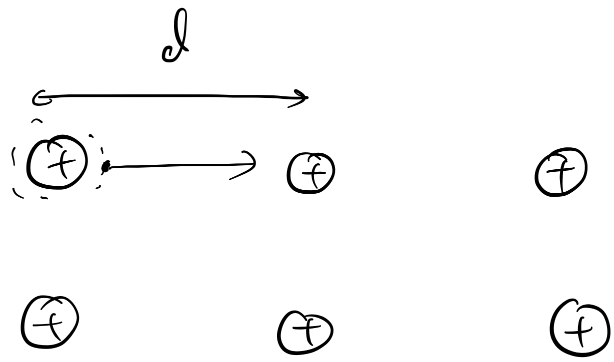
For all non-centrosymmetric crystals,

$$\boxed{\frac{\chi^{(2)}(\omega_1+\omega_2, \omega_1, \omega_2)}{\chi^{(1)}(\omega_1+\omega_2)\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)} \simeq \text{Constant.}}$$

$$\Rightarrow \frac{\overbrace{m}^{\text{electron mass}} \overset{?}{a} \epsilon_0^2}{\underbrace{N^2}_{\sim 10^{22}\,\text{cm}^{-3} \text{ for all matter.}} e^3} \simeq \text{Constant}$$

How to calculate the nonlinear restoring force term a?

Lattice



When e^- displacement is comparable to d, linear and non linear restoring force would be comparable.

i.e. $m\omega_0^2 d = m a d^2$.

$$\Rightarrow \quad a = \frac{\omega_0^2}{d}$$

roughly the same for all solids

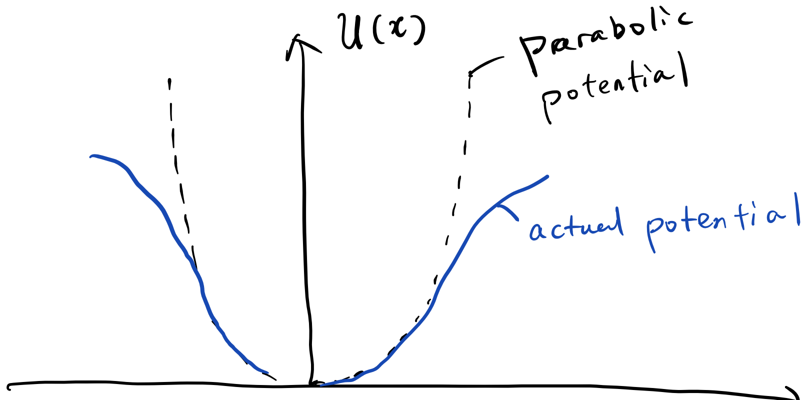
$$\chi^{(2)}(\omega_1+\omega_2, \omega_1, \omega_2) = \frac{\overbrace{N}^{1/d^3}(e^3/m^2)\,\overbrace{a}^{\omega_0^2/d}}{\epsilon_0 \underbrace{D(\omega_1+\omega_2)}_{\omega_0^2}\underbrace{D(\omega_1)}_{\omega_0^2}\underbrace{D(\omega_2)}_{\omega_0^2}}$$

$$\simeq \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4}$$

$\omega_0 = 1\times10^6$ rad/s, $d = 3\,\text{Å}$. $e = 1.6\times10^{-19}$ C $m = 9.1\times10^{-31}$ kg

$$\boxed{\chi^{(2)} \doteq 6.9\times10^{-12}\ \text{m/V}}$$

② Centrosymmetric media.



strength

$$U(x) = -\int F_{restoring} \cdot dx = \frac{1}{2} m \omega_0^2 x^2 - \frac{1}{4} m b\, x^4$$

$$F_{restoring} = -\frac{dU(x)}{dx} = -m\omega_0^2 x + m b x^3$$

E.O.M.

$$\ddot{\tilde{x}} + 2\gamma \dot{\tilde{x}} + \omega_0^2 \tilde{x} - b\tilde{x}^3 = -\frac{e\tilde{E}(t)}{m}. \quad ①$$

Assume the input field:

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + c.c.$$

$$= \sum_n E(\omega_n) e^{-i\omega_n t}$$

Perturbation theory:

$$\tilde{x}(t) = \lambda \tilde{x}^{(1)}(t) + \lambda^2 x^{(2)}(t) + \lambda^3 x^3(t) + \dots$$, plug in ①

We get

$$\begin{cases} \ddot{\tilde{x}}^{(1)} + 2\gamma \dot{\tilde{x}}^{(1)} + \omega_0^2 \tilde{x}^{(1)} = \dfrac{-e\tilde{E}(t)}{m} & ② \\ \ddot{\tilde{x}}^{(2)} + 2\gamma \dot{\tilde{x}}^{(2)} + \omega_0^2 \tilde{x}^{(2)} = 0 & ③ \\ \ddot{\tilde{x}}^{(3)} + 2\gamma \dot{\tilde{x}}^{(3)} + \omega_0^2 \tilde{x}^{(3)} - b x^{(1)3} = 0 & ④ \end{cases}$$

damped, not driven
$\tilde{x}^{(2)} \doteq 0$

let $x^{(1)}(t) = \sum_n x^{(1)}(\omega_n) e^{-i\omega_n t}$.

④ becomes:

$$\ddot{x}^{(3)} + 2\gamma \dot{x}^{(3)} + \omega_0^2 x^{(3)} = -\sum_{mnp} \frac{be^3 [E(\omega_m) E(\omega_n)] E(\omega_p)}{m^3 D(\omega_m) D(\omega_n) D(\omega_p)} e^{-i(\omega_m+\omega_n+\omega_p)t}$$

Assume solution is in the form:

$$\tilde{x}^{(3)}(t) = \sum_q x^{(3)}(\omega_q) e^{-i\omega_q \cdot t}$$

$$x^{(3)}(\omega_q) = -\sum_{m,n,p} \frac{be^3 [E(\omega_m) E(\omega_n)] E(\omega_p)}{m^3 D(\omega_q) D(\omega_m) D(\omega_n) D(\omega_p)}$$

Recall $P_i^{(3)}(\omega_q) = \epsilon_0 \sum_{jkl} \sum_{mnp} \chi^{(3)}_{ijkl}(\omega_q, \omega_m, \omega_n, \omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$

$$\Rightarrow \chi^{(3)}_{ijkl}(\omega_q, \omega_m, \omega_n\ \omega_p)$$

$$= \frac{b m \epsilon_0^3}{3N^3 e^4}\left[\chi^{(1)}(\omega_q)\,\chi^{(1)}(\omega_m)\,\chi^{(1)}(\omega_n)\,\chi^{(1)}(\omega_p)\right]$$

$$\cdot\left[\delta_{ij}\delta_{kl} + \delta_{ij}\delta_{jl} + \delta_{ij}\delta_{jk}\right]$$

when $x \sim d$, $\underbrace{m\omega_0^2 d}_{\text{linear}} = \underbrace{m b d^3}_{\text{nonlinear}}$

$$\Rightarrow d = \frac{\omega_0^2}{d^2}$$

$$\chi^{(3)} \simeq \frac{N b e^4}{\epsilon_0 m^3 \omega_0^8} = \frac{e^4}{\epsilon_0 m^3 \underset{7\times10^{15}\,\text{rad/s}}{\omega_0^6}\, \underset{3\,\text{Å}}{d^5}}. \simeq 344\ \text{pm}^2/\text{V}^2$$