

The goal of this document is to derive the general form of effective polarization (6.92) and magnetization (6.100) counting all orders of multipole moments.

For this, we use the tensor notation for the Taylor expansion of  $f(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn})$  around  $\mathbf{x} - \mathbf{x}_n$ :

$$f(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn}) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \underbrace{\mathbf{x}_{jn}^{\otimes k} \cdot (\nabla^{\otimes k} f)(\mathbf{x} - \mathbf{x}_n)}_{\equiv f_{jn}^{(k)}(\mathbf{x}, t)} \quad (1)$$

In the following, we will use the simplified writing  $\nabla^{\otimes k} f$  while keeping in mind that it is to be evaluated at  $\mathbf{x} - \mathbf{x}_n$ .

Obviously  $f_{jn}^{(0)}(\mathbf{x}, t) = f(\mathbf{x} - \mathbf{x}_n)$  and for  $k \geq 1$ ,

$$f_{jn}^{(k)}(\mathbf{x}, t) = \mathbf{x}_{jn}^{\otimes k} \cdot \nabla^{\otimes k} f = (\mathbf{x}_{jn} \cdot \nabla) [\mathbf{x}_{jn}^{\otimes (k-1)} \cdot \nabla^{\otimes (k-1)} f] = (\mathbf{x}_{jn} \cdot \nabla) f_{jn}^{(k-1)}(\mathbf{x}, t) = \nabla \cdot [\mathbf{x}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t)] \quad (2)$$

Note we have used the fact that  $\mathbf{x}_{jn}$  is independent of the observation point  $\mathbf{x}$  so it does not interact with  $\nabla$ .

Thus the average microscopic charge density for a given molecule  $n$  is

$$\begin{aligned} \langle \eta_n(\mathbf{x}, t) \rangle &= \left\langle \sum_{j(n)} q_j \delta(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn}) \right\rangle = \sum_{j(n)} q_j f(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn}) \\ &= \sum_{j(n)} q_j f(\mathbf{x} - \mathbf{x}_n) + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j f_{jn}^{(k)}(\mathbf{x}, t) \\ &= \langle q_n \delta(\mathbf{x} - \mathbf{x}_n) \rangle + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j f_{jn}^{(k)}(\mathbf{x}, t) \end{aligned} \quad (3)$$

With the microscopic Maxwell equation (6.70)

$$\epsilon_0 \nabla \cdot \mathbf{E} = \langle \eta(\mathbf{x}, t) \rangle = \langle \eta_{\text{free}}(\mathbf{x}, t) \rangle + \sum_{n(\text{mol})} \langle \eta_n(\mathbf{x}, t) \rangle \quad (4)$$

and the macroscopic Maxwell equation

$$\nabla \cdot \mathbf{D} = \underbrace{\langle \eta_{\text{free}}(\mathbf{x}, t) \rangle + \sum_{n(\text{mol})} \langle q_n \delta(\mathbf{x} - \mathbf{x}_n) \rangle}_{\text{total macroscopic charge density}} \quad (5)$$

we can obtain

$$\begin{aligned} \nabla \cdot (\mathbf{D} - \epsilon_0 \mathbf{E}) &= - \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j f_{jn}^{(k)}(\mathbf{x}, t) \quad \text{by (2)} \\ &= \nabla \cdot \left[ \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \sum_{j(n)} q_j \mathbf{x}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t) \right] \end{aligned} \quad (6)$$

This enables us to identify

$$\mathbf{D} - \epsilon_0 \mathbf{E} = \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \underbrace{\sum_{j(n)} q_j \mathbf{x}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t)}_{\equiv \mathbf{q}_n^{(k)}(\mathbf{x}, t)} \quad (7)$$

as the effective macroscopic polarization  $\mathbf{P}_{\text{eff}}$ . Its  $k = 1$  order gives the usual polarization

$$\sum_{n(\text{mol})} \mathbf{q}_n^{(1)} = \sum_{n(\text{mol})} \mathbf{p}_n f(\mathbf{x} - \mathbf{x}_n) = \left\langle \sum_{n(\text{mol})} \mathbf{p}_n \delta(\mathbf{x} - \mathbf{x}_n) \right\rangle = \mathbf{P} \quad (8)$$

and the higher order multipole moments generate additional terms, for example  $k = 2$

$$-\frac{1}{2} \sum_{n(\text{mol})} \mathbf{q}_n^{(2)} = -\frac{1}{2} \sum_{n(\text{mol})} \sum_{j(n)} q_j \mathbf{x}_{jn} \sum_{\beta} (\mathbf{x}_{jn})_{\beta} \left( \frac{\partial f}{\partial x_{\beta}} \right) (\mathbf{x} - \mathbf{x}_n) \quad (9)$$

which is consistent with the second order term given in (6.92).

On the other hand, for effective magnetization, let's consider the microscopic average current density.

$$\langle \mathbf{j}(\mathbf{x}, t) \rangle = \left\langle \sum_{j(\text{free})} q_j \mathbf{v}_j \delta(\mathbf{x} - \mathbf{x}_j) \right\rangle + \underbrace{\left\langle \sum_{n(\text{mol})} \sum_{j(n)} q_j (\mathbf{v}_{jn} + \mathbf{v}_n) \delta(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn}) \right\rangle}_{\langle \mathbf{j}_{\text{bnd}}(\mathbf{x}, t) \rangle} \quad (10)$$

where the second term denotes the average current density produced by the bound charges, which is

$$\begin{aligned} \langle \mathbf{j}_{\text{bnd}}(\mathbf{x}, t) \rangle &= \sum_{n(\text{mol})} \sum_{j(n)} q_j (\mathbf{v}_{jn} + \mathbf{v}_n) f(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_{jn}) \\ &= \sum_{n(\text{mol})} \sum_{j(n)} q_j (\mathbf{v}_{jn} + \mathbf{v}_n) \left[ f(\mathbf{x} - \mathbf{x}_n) + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} f_{jn}^{(k)}(\mathbf{x}, t) \right] \\ &= \sum_{n(\text{mol})} \sum_{j(n)} q_j \mathbf{v}_n f(\mathbf{x} - \mathbf{x}_n) + \sum_{n(\text{mol})} \sum_{j(n)} q_j \mathbf{v}_{jn} f(\mathbf{x} - \mathbf{x}_n) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j (\mathbf{v}_{jn} + \mathbf{v}_n) f_{jn}^{(k)}(\mathbf{x}, t) \end{aligned} \quad (11)$$

whose first term is just the macroscopic current density attributed to the bound charges

$$\sum_{n(\text{mol})} q_n \mathbf{v}_n f(\mathbf{x} - \mathbf{x}_n) = \left\langle \sum_{n(\text{mol})} q_n \mathbf{v}_n \delta(\mathbf{x} - \mathbf{x}_n) \right\rangle \quad (12)$$

Inserting (11) back into (10) gives

$$\begin{aligned} \langle \mathbf{j}(\mathbf{x}, t) \rangle &= \overbrace{\left\langle \sum_{j(\text{free})} q_j \mathbf{v}_j \delta(\mathbf{x} - \mathbf{x}_j) \right\rangle}^{\text{total macroscopic current density } \mathbf{J}(\mathbf{x}, t)} + \left\langle \sum_{n(\text{mol})} q_n \mathbf{v}_n \delta(\mathbf{x} - \mathbf{x}_n) \right\rangle + \\ &\quad \underbrace{\sum_{n(\text{mol})} \sum_{j(n)} q_j \mathbf{v}_{jn} f(\mathbf{x} - \mathbf{x}_n) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j (\mathbf{v}_{jn} + \mathbf{v}_n) f_{jn}^{(k)}(\mathbf{x}, t)}_{\equiv \mathbf{R}(\mathbf{x}, t)} \end{aligned} \quad (13)$$

With the microscopic Maxwell equation (6.70)

$$\frac{1}{\mu_0} \nabla \times \mathbf{B} - \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} = \langle \mathbf{j}(\mathbf{x}, t) \rangle = \mathbf{J}(\mathbf{x}, t) + \mathbf{R}(\mathbf{x}, t) \quad (14)$$

and the macroscopic Maxwell equation

$$\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{J}(\mathbf{x}, t) \quad (15)$$

we have

$$\nabla \times \left( \frac{\mathbf{B}}{\mu_0} - \mathbf{H} \right) = \mathbf{R}(\mathbf{x}, t) - \frac{\partial}{\partial t} (\mathbf{D} - \epsilon_0 \mathbf{E}) \quad (16)$$

Our goal is to find  $\mathbf{M}_{\text{eff}}$  such that

$$\mathbf{R}(\mathbf{x}, t) - \frac{\partial}{\partial t} (\mathbf{D} - \epsilon_0 \mathbf{E}) = \nabla \times \mathbf{M}_{\text{eff}} \quad (17)$$

which will allow us to write

$$\frac{\mathbf{B}}{\mu_0} - \mathbf{H} = \mathbf{M}_{\text{eff}} \quad (18)$$

hence interpreted as the effective magnetization.

Define

$$\mu_n^{(k)}(\mathbf{x}, t) = \frac{k}{k+1} \sum_{j(n)} q_j (\mathbf{x}_{jn} \times \mathbf{v}_{jn}) f_{jn}^{(k-1)}(\mathbf{x}, t) \quad (19)$$

as the  $k$ -th order molecular magnetization for molecule  $n$ . Compare with (6.95), we see  $\mathbf{m}_n$  is just  $\boldsymbol{\mu}_n^{(1)}$ .

The claim we want to prove is that (17) holds if

$$\mathbf{M}_{\text{eff}} = \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \boldsymbol{\mu}_n^{(k)}(\mathbf{x}, t) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \mathbf{q}_n^{(k)}(\mathbf{x}, t) \times \mathbf{v}_n \quad (20)$$

The interpretation of the first term of (20) is the magnetization contribution from all of the multipole moments within the molecule, and the second term is the magnetization contribution from all of the multipole moments in response to the molecule's motion as a whole. Note in the special case of bulk motion where  $\mathbf{v}_n = \mathbf{v}$  for all  $n$ , by (7), the second term of (20) just gives  $(\mathbf{D} - \epsilon_0 \mathbf{E}) \times \mathbf{v}$ , and (20) is the same as (6.100) when we truncate the first term to  $k = 1$ .

Another comment is that even though  $\mathbf{q}_n^{(k)}$  and  $\boldsymbol{\mu}_n^{(k)}$  are both defined using  $f_{jn}^{(k-1)}(\mathbf{x}, t)$ , they are eventually the same as some multi-order partial derivatives of the average of molecule multipole moment times  $\delta(\mathbf{x} - \mathbf{x}_n)$ , hence represent the average attribute of the medium.

Writing out the components of LHS of (17) gives (note the first sum starts from  $k = 0$  now after some merging)

$$\text{LHS}_{(17)} = \sum_{n(\text{mol})} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_n f_{jn}^{(k)}(\mathbf{x}, t) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \frac{\partial \mathbf{q}_n^{(k)}(\mathbf{x}, t)}{\partial t} \quad (21)$$

And for RHS of (17)

$$\text{RHS}_{(17)} = \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times \boldsymbol{\mu}_n^{(k)}(\mathbf{x}, t) + \sum_{n(\text{mol})} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times [\mathbf{q}_n^{(k)}(\mathbf{x}, t) \times \mathbf{v}_n] \quad (22)$$

To prove (17), it is sufficient to drop the sum over all molecules in (21) and (22) and prove for each  $n$

$$\begin{aligned} & \overbrace{\sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t)}^{L_1} + \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_n f_{jn}^{(k)}(\mathbf{x}, t)}^{L_2} + \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \frac{\partial \mathbf{q}_n^{(k)}(\mathbf{x}, t)}{\partial t}}^{L_3} \\ &= \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times \boldsymbol{\mu}_n^{(k)}(\mathbf{x}, t)}_{R_1} + \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times [\mathbf{q}_n^{(k)}(\mathbf{x}, t) \times \mathbf{v}_n]}_{R_2} \end{aligned} \quad (23)$$

With vector identity

$$\nabla \times (\mathbf{a} \times \mathbf{b}) = \mathbf{a}(\nabla \cdot \mathbf{b}) - \mathbf{b}(\nabla \cdot \mathbf{a}) + (\mathbf{b} \cdot \nabla) \mathbf{a} - (\mathbf{a} \cdot \nabla) \mathbf{b} \quad (24)$$

we can expand  $R_2$  as

$$R_2 = \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \mathbf{v}_n [\nabla \cdot \mathbf{q}_n^{(k)}(\mathbf{x}, t)]}^{R_{21}} + \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} (\mathbf{v}_n \cdot \nabla) \mathbf{q}_n^{(k)}(\mathbf{x}, t)}^{R_{22}} \quad (25)$$

Due to (2), we see  $R_{21} = L_2$ , so what's remaining to prove is

$$\underbrace{\sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t)}_{L_1} + \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \frac{\partial \mathbf{q}_n^{(k)}(\mathbf{x}, t)}{\partial t}}_{L_3} = \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times \boldsymbol{\mu}_n^{(k)}(\mathbf{x}, t)}_{R_1} + \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} (\mathbf{v}_n \cdot \nabla) \mathbf{q}_n^{(k)}(\mathbf{x}, t)}_{R_{22}} \quad (26)$$

Note that in  $L_3$ ,

$$\begin{aligned} \frac{\partial \mathbf{q}_n^{(k)}(\mathbf{x}, t)}{\partial t} &= \frac{\partial}{\partial t} \left[ \sum_{j(n)} q_j \mathbf{x}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t) \right] \\ &= \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t) + \sum_{j(n)} q_j \mathbf{x}_{jn} \frac{\partial}{\partial t} [\mathbf{x}_{jn}^{\otimes(k-1)} \cdot \nabla^{\otimes(k-1)} f] \\ &= \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t) + \sum_{j(n)} q_j \mathbf{x}_{jn} \left\{ \left[ \frac{\partial \mathbf{x}_{jn}^{\otimes(k-1)}}{\partial t} \right] \cdot \nabla^{\otimes(k-1)} f \right\} + \\ &\quad \sum_{j(n)} q_j \mathbf{x}_{jn} \left\{ \mathbf{x}_{jn}^{\otimes(k-1)} \cdot \frac{\partial}{\partial t} [\nabla^{\otimes(k-1)} f] \right\} \end{aligned} \quad (27)$$

Since for any function  $g(\mathbf{x} - \mathbf{x}_n)$ ,

$$\frac{\partial g(\mathbf{x} - \mathbf{x}_n)}{\partial t} = -\mathbf{v}_n \cdot (\nabla g)(\mathbf{x} - \mathbf{x}_n) = -[(\mathbf{v}_n \cdot \nabla)g](\mathbf{x} - \mathbf{x}_n) \quad (28)$$

the third term of (27) becomes

$$-\sum_{j(n)} q_j \mathbf{x}_{jn} \left\{ \mathbf{x}_{jn}^{\otimes(k-1)} \cdot [(\mathbf{v}_n \cdot \nabla)(\nabla^{\otimes(k-1)} f)] \right\} = -(\mathbf{v}_n \cdot \nabla) \mathbf{q}_n^{(k)}(\mathbf{x}, t) \quad (29)$$

With (27),(29) inserted into (26), we see  $R_{22}$  can be canceled from both sides and what is remaining to prove is

$$\begin{aligned} & \overbrace{\sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t)}^{L_1} + \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k-1)}(\mathbf{x}, t)}^{L_4} + \overbrace{\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sum_{j(n)} q_j \mathbf{x}_{jn} \left\{ \left[ \frac{\partial \mathbf{x}_{jn}^{\otimes(k-1)}}{\partial t} \right] \cdot \nabla^{\otimes(k-1)} f \right\}}^{L_5} \\ &= \underbrace{\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times \mu_n^{(k)}(\mathbf{x}, t)}_{R_1} \end{aligned} \quad (30)$$

Observe that

$$\begin{aligned} L_1 + L_4 &= \sum_{k=0}^{\infty} \left[ \frac{(-1)^k}{k!} + \frac{(-1)^{k+1}}{(k+1)!} \right] \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t) \\ &= \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j \mathbf{v}_{jn} f_{jn}^{(k)}(\mathbf{x}, t) \quad \text{drop } k=0 \text{ term and use (2)} \\ &= \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j \mathbf{v}_{jn} [\mathbf{x}_{jn} \cdot \nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] \end{aligned} \quad (31)$$

and  $L_5$  has vanishing  $k=1$  term, so shifting the index  $k$  by one gives

$$\begin{aligned} L_5 &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k+1)!} \sum_{j(n)} q_j \mathbf{x}_{jn} \left[ \left( \frac{\partial \mathbf{x}_{jn}^{\otimes k}}{\partial t} \right) \cdot \nabla^{\otimes k} f \right] \\ &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k+1)!} \sum_{j(n)} q_j \mathbf{x}_{jn} k \left\{ [\mathbf{v}_{jn} \otimes \mathbf{x}_{jn}^{\otimes(k-1)}] \cdot \nabla^{\otimes k} f \right\} \\ &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{(k+1)!} \sum_{j(n)} q_j \mathbf{x}_{jn} k (\mathbf{v}_{jn} \cdot \nabla) f_{jn}^{(k-1)}(\mathbf{x}, t) \\ &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j \mathbf{x}_{jn} [\mathbf{v}_{jn} \cdot \nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] \end{aligned} \quad (32)$$

Thus

$$\begin{aligned} L_1 + L_4 + L_5 &= \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j \left\{ \mathbf{v}_{jn} [\mathbf{x}_{jn} \cdot \nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] - \mathbf{x}_{jn} [\mathbf{v}_{jn} \cdot \nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] \right\} \\ &= \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j [\nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] \times (\mathbf{v}_{jn} \times \mathbf{x}_{jn}) \end{aligned} \quad (33)$$

where we have used

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c}) \mathbf{b} - (\mathbf{a} \cdot \mathbf{b}) \mathbf{c} \quad (34)$$

Then (30) is finally proved since

$$\begin{aligned} R_1 &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \nabla \times \left[ \frac{k}{k+1} \sum_{j(n)} q_j (\mathbf{x}_{jn} \times \mathbf{v}_{jn}) f_{jn}^{(k-1)}(\mathbf{x}, t) \right] \\ &= \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \cdot \frac{k}{k+1} \sum_{j(n)} q_j [\nabla f_{jn}^{(k-1)}(\mathbf{x}, t)] \times (\mathbf{x}_{jn} \times \mathbf{v}_{jn}) = L_1 + L_4 + L_5 \end{aligned} \quad (35)$$