ELECTRIC-FIELD MAPPED AVERAGING FOR NON-INTERACTING AND INTERACTING DIPOLES

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1. Non-interacting dipoles

We first briefly review the formulation for $\mathbf{v}^{\mathbf{E}}$ for non-interacting dipoles (the case in our JCTC paper). The energy function for ideal dipoles under electric field is

$$u = \mathbf{E} \cdot \mathbf{M} = -E_z \mu \sum_i^N \cos\theta_i. \tag{1}$$

μ is the dipole moment, $\mathbf{E}$ is the electric field and $\mathbf{M} = \sum_i \boldsymbol{\mu}_i$ is the the total dipole polarization obtained by summation of all the dipoles; the latter equality in (1) assumes that $\mathbf{E}$ has non-zero component in the z direction only. For the mapping coordinate, we define $z_i = \cos\theta_i$, the z-component of the unit dipole vector of molecule i as oriented in a given configuration, so $-1 \le z_i \le 1$. An approximate $p(\boldsymbol{\mu}, \mathbf{E})$ is formed from this energy function. Specifically, we identify $p_1(z_i, E_z) = \exp(\beta\mu E_z z_i)$, for which $q_1(E_z) = \int p_1(z_i, E_z) dz_i = \sinh(\beta\mu E_z)/(\beta\mu E_z)$. Solution of Eq. (12) in the JCTC mapped-averaging paper with boundary condition $v_i^{E_z} = 0$ for $z = 1$ yields (for $E_z \to 0$):

$$\begin{aligned} v_i^{E_z} &= \frac{1}{2}\beta\mu(1 - z_i^2) \\ &= \frac{1}{2}\beta\mu \sin^2\theta_i. \end{aligned} \tag{2}$$

Similarly, we can get mapping for x and y components of $\mathbf{E}$.

2. Interacting dipoles

Now we try to use similar approach to get $\mathbf{v}^{\mathbf{E}}$ for interacting dipoles, with energy function $u = u_E + u_{DD}$, where

$$u_{\mathrm{E}} = -\mu \mathbf{E} \cdot (\hat{\mathbf{e}}_1 + \hat{\mathbf{e}}_2) \tag{3a}$$

$$u_{\mathrm{DD}} = \frac{\mu^2}{r^3} \left(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2 - 3 \left(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{r}} \right) \left(\hat{\mathbf{e}}_2 \cdot \hat{\mathbf{r}} \right) \right), \tag{3b}$$

where $\hat{\mathbf{e}}_i$ is the unit vector for the orientation of the dipole on molecule i. We focus on just one dipole pair, with the idea that the same result will be applied to a sum of pairs (the approach isn't entirely straightforward, and has to be handled in a way similar to how we

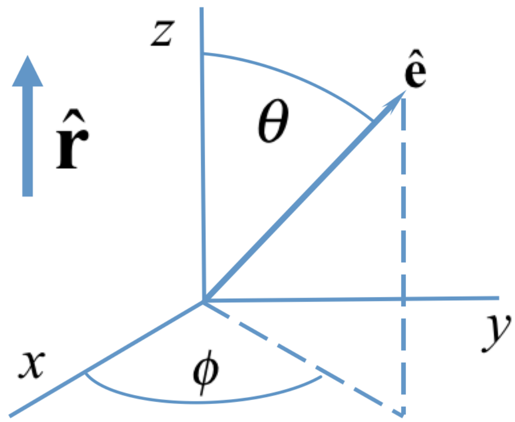

FIGURE 1. Coordinates describing dipole orientation $\hat{\mathbf{e}}$. z axis is defined to be parallel with $\hat{\mathbf{r}}$, the unit vector specifying the direction from one dipole to the other.

treated pair interactions when getting the pressure; we omit details of this larger context and focus just on the mapping now).

We adopt the coordinate system illustrated in Fig. 1. In terms of the coordinates defined there, the energy functions are

$$\begin{aligned} u_{\mathrm{E}} =& -\mu\left[E_x(\sin\theta_1\cos\phi_1+\sin\theta_2\cos\phi_2)+E_y(\sin\theta_1\sin\phi_1+\sin\theta_2\sin\phi_2)\right. \\ & \left.+E_z(\cos\theta_1+\cos\theta_2))\right] \end{aligned} \tag{4a}$$

$$u_{\mathrm{DD}} =\frac{\mu^2}{r^3}\left[\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)-2\cos\theta_1\cos\theta_2\right]. \tag{4b}$$

Presently we'll consider mapping only orientation coordinates. In the more complete case, we would map the separation distance r as well, and include the non-dipole interaction in u.

The weight function p is defined as the Boltzmann factor for the pair:

$$p = \exp\left[-\beta(u_E+u_{DD})\right] \tag{5a}$$

and q is the integral over the mapping coordinates,

$$q = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_{-1}^{1} d(\cos\theta_1) \int_{-1}^{1} d(\cos\theta_2) p(\theta_1,\theta_2,\phi_1,\phi_2). \tag{5b}$$

We consider mapping for E_z, E_x and E_y separately. The full free-energy derivative will be obtained by summing these three terms. Let us start with E_z. The mapping equation is

$$\frac{\partial}{\partial E_z}\left(\frac{p}{q}\right) + \nabla\cdot\left(\frac{p}{q}\mathbf{v}^{E_z}\right) = 0; \tag{6}$$

or, equivalently

$$\frac{\partial p}{\partial E_z} - \frac{p}{q}\frac{\partial q}{\partial E_z} + \nabla\cdot\left(p\mathbf{v}^{E_z}\right) = 0. \tag{7}$$

We note that

$$\frac{\partial p}{\partial E_z} = \beta\mu(\cos\theta_1 + \cos\theta_2)p \tag{8a}$$

$$\frac{\partial q}{\partial E_z} = \beta\mu\int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_{-1}^{1} d(\cos\theta_1)\int_{-1}^{1} d(\cos\theta_2)(\cos\theta_1+\cos\theta_2)p(\theta_1,\theta_2,\phi_1,\phi_2) \tag{8b}$$

The divergence operator for these coordinates is written here for a general vector $\mathbf{A}$ defined in the $(\theta_1, \theta_2, \phi_1, \phi_2)$ space:

$$\begin{aligned}\nabla\cdot\mathbf{A} =& \frac{1}{\sin\theta_1}\frac{\partial}{\partial\theta_1}\left(A_{\theta_1}\sin\theta_1\right) + \frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\left(A_{\theta_2}\sin\theta_2\right)\\ &+ \frac{1}{\sin\theta_1}\frac{\partial A_{\phi_1}}{\partial\phi_1} + \frac{1}{\sin\theta_2}\frac{\partial A_{\phi_2}}{\partial\phi_2}\end{aligned} \tag{9}$$

In the present application, $\mathbf{A} = p\mathbf{v}^{E_z}$, and our aim is to evaluate the $(\theta_1, \theta_2, \phi_1, \phi_2)$ components of $\mathbf{v}^{E_z}$. The necessary "initial condition" is that $\mathbf{v}^{E_z} \equiv 0$ for $\theta_1 = \theta_2 = 0$.

We can perhaps make progress by taking advantage of some features of the problem:

- The problem is underspecified, so we can satisfy (7) by separating it into parts involving only some of the variables, and solving these independently. We would aim to have a separate equation for each component of $\mathbf{v}^{E_z}$.
- We need $\mathbf{v}^{E_z}$ and its E_z derivative only for the limit $E_z \to 0$, so we can expand $\exp(-\beta u_{\mathrm{E}})$ to say, second order (perhaps first is enough).
- We can similarly expand $\exp(-\beta u_{\mathrm{DD}})$, considering that r may be large, and $u_{\mathrm{DD}} = O(r^{-3})$. We would then generate a solution for $\mathbf{v}^{E_z}$ as a series in $1/r$. The first term should be the non-interacting result, Eq. (2).
- We can try a solution in which we assume no mapping of ϕ_1, ϕ_2 ($A_{\phi_1} = A_{\phi_2} = 0$).

2.1. **Poisson equation.** We define $\psi(\theta_1, \theta_2)$ such that

$$\frac{\partial\psi}{\partial\theta_1} = p\mathbf{v}^{E_z}_{\theta_1}\sin\theta_1\sin\theta_2 \tag{10a}$$

$$\frac{\partial\psi}{\partial\theta_2} = p\mathbf{v}^{E_z}_{\theta_2}\sin\theta_1\sin\theta_2 \tag{10b}$$

Assume for now that $\mathbf{v}^{E_z}_{\phi_1} = \mathbf{v}^{E_z}_{\phi_2} = 0$. We multiply (7) through by $\sin\theta_1 \sin\theta_2$, then in terms of ψ we have a Poisson equation

$$\begin{aligned}\frac{\partial^2\psi}{\partial\theta_1^2} + \frac{\partial^2\psi}{\partial\theta_2^2} &= \sin\theta_1 \sin\theta_2 \left(-\frac{\partial p}{\partial E_z} + \frac{p}{q}\frac{\partial q}{\partial E_z} \right) \\ &= p(\theta_1, \theta_2) \sin\theta_1 \sin\theta_2 \left(-\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_z \right) \end{aligned} \tag{11}$$

where $Q_z \equiv (1/q)\partial q/\partial E_z$, and depends only on r. Note that $p(\theta_1, \theta_2)$ is given by (4) and (5a).

What to do for boundary conditions? From (10), clearly we have $\partial\psi/\partial\theta_1 = \partial\psi/\partial\theta_2 = 0$ for θ_1 or θ_2 equal to 0 or π. What else do we need?

3. Heisenberg models

The Heisenberg model is a lattice model similar to the Ising model, but with spins that take on a full range of orientations (rather than just ‘up’ and ‘down’). Instead of (3), the potential is

$$u_{\mathrm{E}} = -\mu\mathbf{E} \cdot (\hat{\mathbf{e}}_1 + \hat{\mathbf{e}}_2) \tag{12a}$$

$$u_{\mathrm{DD}} = -J\left(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2\right), \tag{12b}$$

where J is the coupling constant.

3.1. **2 dimensions.**

In 2D, the orientation is specified by the angle θ, in which case (12) is

$$u_{\mathrm{E}} = -\mu\left[E_x(\cos\theta_1 + \cos\theta_2) + E_y(\sin\theta_1 + \sin\theta_2)\right] \tag{13a}$$

$$u_{\mathrm{DD}} = -J\cos(\theta_2 - \theta_1). \tag{13b}$$

Equation (5a) for p is unchanged, but for q we have

$$q = \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 p(\theta_1, \theta_2), \tag{14}$$

and in place of (8b) we have

$$\frac{\partial q}{\partial E_x} = \beta\mu \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 (\cos\theta_1 + \cos\theta_2) p(\theta_1, \theta_2) \tag{15a}$$

$$\frac{\partial q}{\partial E_y} = \beta\mu \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 (\sin\theta_1 + \sin\theta_2) p(\theta_1, \theta_2) \tag{15b}$$

Now the divergence operator is, in place of (9):

$$\nabla \cdot \mathbf{A} = \frac{\partial A_{\theta_1}}{\partial\theta_1} + \frac{\partial A_{\theta_2}}{\partial\theta_2} \tag{16}$$

with $\mathbf{A}$ representing $p\mathbf{v}^{E_x}$. The balance equation that we need to solve is, for E_x mapping (E_y mapping is similar, but with sin in place of cos):

$$\frac{\partial A_{\theta_1}}{\partial\theta_1} + \frac{\partial A_{\theta_2}}{\partial\theta_2} = -\beta\mu(\cos\theta_1 + \cos\theta_2)p + \frac{p}{q}\frac{\partial q}{\partial E_x} \tag{17}$$

or, writing all θ dependences explicitly

$$\frac{\partial A_{\theta_1}}{\partial \theta_1} + \frac{\partial A_{\theta_2}}{\partial \theta_2} = \left(-\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x\right) e^{\beta J \cos(\theta_2 - \theta_1) + \beta\mu E_x (\cos\theta_1 + \cos\theta_2)} \tag{18}$$

(Q_x is independent of θ_1 and θ_2). We can put this in the Poisson form by defining

$$\frac{\partial \psi}{\partial \theta_1} = A_{\theta_1} \tag{19a}$$

$$\frac{\partial \psi}{\partial \theta_2} = A_{\theta_2}; \tag{19b}$$

however, we do not have an explicit requirement for the boundary condition, compared to $\partial\psi/\partial\theta = 0, \theta = 0, \pi$ used above. We do still satisfy the requirement that the integral of the right-hand side of (18) is zero. The boundary condition that we can specify *a priori* is $A_{\theta_1} = A_{\theta_2} = 0$ when $\theta_1 = \theta_2 = 0$.

As an aside, let us note that we can reformulate the balance equation to change how p enters into it. Going from (7), we write

$$\nabla \cdot \mathbf{v}^{E_x} + \frac{1}{p}\mathbf{v}^{E_x} \cdot \nabla p = -\frac{\partial \ln p}{\partial E_x} + Q_x(E_x).$$

$$\nabla \cdot \mathbf{v}^{E_x} + \mathbf{v}^{E_x} \cdot \nabla \ln p = -\frac{\partial \ln p}{\partial E_x} + Q_x(E_x). \tag{20}$$

So, for example, (17) would become

$$\begin{aligned}\frac{\partial v_{\theta_1}^{E_x}}{\partial \theta_1} + \frac{\partial v_{\theta_2}^{E_x}}{\partial \theta_2} - v_{\theta_1}^{E_x}[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)] \\ - v_{\theta_2}^{E_x}[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)] = -\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x,\end{aligned} \tag{21}$$

or, in terms of ψ

$$\begin{aligned}\frac{\partial^2 \psi}{\partial \theta_1} + \frac{\partial^2 \psi}{\partial \theta_2} - \frac{\partial \psi}{\partial \theta_1}[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)] \\ - \frac{\partial \psi}{\partial \theta_2}[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)] = -\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x,\end{aligned} \tag{22}$$

3.1.1. *Stream-function approach.* Alternatively, we define χ such that

$$v_{\theta_1}^{E_x} = \frac{\partial \chi}{\partial \theta_2} \tag{23a}$$

$$v_{\theta_2}^{E_x} = -\frac{\partial \chi}{\partial \theta_1}, \tag{23b}$$

then for (21) we have

$$\begin{aligned}-\frac{\partial \chi}{\partial \theta_2}[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)] + \frac{\partial \chi}{\partial \theta_1}[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)] \\ = -\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x,\end{aligned} \tag{24}$$

We cannot satisfy this equation in the limiting case of $\theta_1 = \theta_2 = 0$, where $v_{\theta_1} = v_{\theta_2} = 0$. Instead, we define

$$v_{\theta_1}^{E_x} = \frac{\partial \chi}{\partial \theta_2} - \beta\mu \sin\theta_1 + \frac{1}{2}\theta_1 Q_x \tag{25a}$$

$$v_{\theta_2}^{E_x} = -\frac{\partial \chi}{\partial \theta_1} - \beta\mu \sin\theta_2 + \frac{1}{2}\theta_2 Q_x, \tag{25b}$$

then

$$\begin{aligned} &\left(\frac{\partial \chi}{\partial \theta_2} - \beta\mu\sin\theta_1 + \frac{1}{2}\theta_1 Q_x\right)\left[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)\right] \\ &+ \left(-\frac{\partial \chi}{\partial \theta_1} - \beta\mu\sin\theta_2 + \frac{1}{2}\theta_2 Q_x\right)\left[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)\right] \\ &= 0 \end{aligned} \tag{26}$$

This can be rearranged to have the same form as (24), but with a different right-hand side.

3.2. **Back to 3D.** Here's a summary of how the equations are modified for the 3D case.

- Eq. (20) is still the starting point, but we need to interpret the ∇ operator for 3D rotation, thus:

$$\nabla \ln p = \sum_{i=1}^{2} \frac{\partial \ln p}{\partial \theta_i}\hat{\boldsymbol{\theta}}_i + \frac{1}{\sin\theta_i}\frac{\partial \ln p}{\partial \phi_i}\hat{\boldsymbol{\phi}}_i \tag{27a}$$

$$\nabla \cdot \mathbf{v} = \sum_{i=1}^{2} \frac{1}{\sin\theta_i}\frac{\partial}{\partial \theta_i}(\mathbf{v}_{\theta_i}\sin\theta_i) + \frac{1}{\sin\theta_i}\frac{\partial \mathbf{v}_{\phi_i}}{\partial \phi_i} \tag{27b}$$

- $\ln p = -\beta(u_{\mathrm{E}} + u_{\mathrm{DD}})$, where u_{E} and u_{DD} are given by Eq. (4) rather than (13).

This needs to be done for all three components, E_x, E_y, and E_z. As with the 2D case, we can treat these all independently, and focus on one at a time. So as a start we can again aim to get solutions that are 0th and 1st order in E_x while taking $E_y = E_z = 0$; then obtain analogous solutions likewise for E_y and E_z (actually E_z might be simplest and most similar to 2D, so that would be the best place to start).