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 (**??**) 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

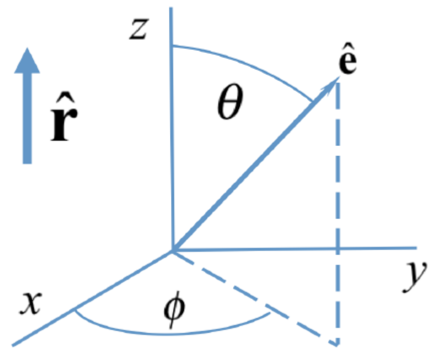

FIGURE 1. Coordinates describing dipole orientation $\hat{\mathbf{e}}$. z axis is defined to be parallel with $\hat{\mathbf{r}}$, the unit vector specifying the direction from one dipole to the other.

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. **??**. In terms of the coordinates defined there, the energy functions are

$$\begin{aligned} u_{\mathrm{E}} =& -\mu\left[E_x(\sin\theta_1\cos\phi_1+\sin\theta_2\cos\phi_2)+E_y(\sin\theta_1\sin\phi_1+\sin\theta_2\sin\phi_2)\right. \qquad (4a)\\ &\left.+E_z(\cos\theta_1+\cos\theta_2))\right] \\ u_{\mathrm{DD}} =& \frac{\mu^2}{r^3}\left[\sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2)-2\cos\theta_1\cos\theta_2\right]. \qquad (4b)\end{aligned}$$

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:

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

and q is the integral over the mapping coordinates,

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

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

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

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 (**??**) 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. (**??**).
- 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 (**??**) 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 (**??**) and (**??**).

What to do for boundary conditions? From (**??**), 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 (**??**), 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 (**??**) 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 (**??**) 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 (**??**) 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 (**??**):

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

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 (**??**) 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 (**??**), we write

$$\begin{aligned}\nabla \cdot \left(\mathbf{v}^{E_x}\right) + \mathbf{v}^{E_x} \cdot \nabla lnp &= -\frac{\partial \ln p}{\partial E_x} + \frac{1}{q}\frac{\partial q}{\partial E_x}. \\ \nabla \cdot \left(\mathbf{v}^{E_y}\right) + \mathbf{v}^{E_y} \cdot \nabla lnp &= -\frac{\partial \ln p}{\partial E_y} + \frac{1}{q}\frac{\partial q}{\partial E_y}.\end{aligned} \tag{20}$$

So, for example, (**??**) would become

$$\begin{aligned}&\frac{\partial v_{\theta_1}^{E_x}}{\partial \theta_1} + \frac{\partial v_{\theta_2}^{E_x}}{\partial \theta_2} - v_{\theta_1}^{E_x}[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)] \\ &\qquad - v_{\theta_2}^{E_x}[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)] = -\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x, \\ &\frac{\partial v_{\theta_1}^{\mathrm{Ey}}}{\partial \theta_1} + \frac{\partial v_{\theta_2}^{\mathrm{Ey}}}{\partial \theta_2} - v_{\theta_1}^{\mathrm{Ey}}\left(\beta \mathrm{J} \sin\left(\theta_1 - \theta_2\right) - \beta\mu E_y \cos\theta_1\right) \\ &\qquad - v_{\theta_2}^{\mathrm{Ey}}\left(-\beta \mathrm{J} \sin\left(\theta_1 - \theta_2\right) - \beta\mu E_y \cos\theta_2\right) = -\beta\mu\left(\sin\theta_1 + \sin\theta_2\right) + Q_y;\end{aligned} \tag{21}$$

3.1.1. *Stream-function approach x direction.* For E_x direction
We define χ such that

$$v_{\theta_1}^{E_x} = \frac{\partial \chi}{\partial \theta_2} \tag{22a}$$
$$v_{\theta_2}^{E_x} = -\frac{\partial \chi}{\partial \theta_1}, \tag{22b}$$

then for (**??**) we have

$$\begin{aligned}-\frac{\partial \chi}{\partial \theta_2}[\beta\mu E_x \sin\theta_1 - \beta J \sin(\theta_2 - \theta_1)] + \frac{\partial \chi}{\partial \theta_1}[\beta\mu E_x \sin\theta_2 + \beta J \sin(\theta_2 - \theta_1)] \\ = -\beta\mu(\cos\theta_1 + \cos\theta_2) + Q_x,\end{aligned} \tag{23}$$

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

$$v_{\theta_1}^{E_x} = \frac{\partial\chi}{\partial\theta_2} - \beta\mu\sin\theta_1 + \frac{1}{2}\theta_1 Q_x \tag{24a}$$

$$v_{\theta_2}^{E_x} = -\frac{\partial\chi}{\partial\theta_1} - \beta\mu\sin\theta_2 + \frac{1}{2}\theta_2 Q_x, \tag{24b}$$

then

$$\begin{aligned}&\left(\frac{\partial\chi}{\partial\theta_2} - \beta\mu\sin\theta_1 + \frac{1}{2}\theta_1 Q_x\right)\left[\beta\mu E_x\sin\theta_1 - \beta J\sin(\theta_2-\theta_1)\right]\\&+\left(-\frac{\partial\chi}{\partial\theta_1} - \beta\mu\sin\theta_2 + \frac{1}{2}\theta_2 Q_x\right)\left[\beta\mu E_x\sin\theta_2 + \beta J\sin(\theta_2-\theta_1)\right]\\&= 0\end{aligned} \tag{25}$$

3.1.2. *Stream-function approach Y direction.*

$$v_{\theta_1}^{\mathrm{Ey}} = \frac{\partial\chi}{\partial\theta_2} + \beta\mu\cos(\theta_1) + \frac{\theta_1}{2}Q_y \tag{26a}$$

$$v_{\theta_2}^{\mathrm{Ey}} = -\frac{\partial\chi}{\partial\theta_1} + \beta\mu\cos(\theta_2) + \frac{\theta_2}{2}Q_y, \tag{26b}$$

then

$$\begin{aligned}&\left(\frac{\partial\chi}{\partial\theta_2} + \beta\mu\cos\theta_1 + \frac{1}{2}\theta_1 Q_y\right)\left(\beta J\sin(\theta_1-\theta_2) - \beta\mu\cos\theta_1 E_y\right)\\&+\left(-\frac{\partial\chi}{\partial\theta_1} + \beta\mu\cos\theta_2 + \frac{1}{2}\theta_2 Q_y\right)\left(-\beta J\sin(\theta_1-\theta_2) - \beta\mu\cos\theta_2 E_y\right)\\&= 0\end{aligned} \tag{27}$$

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