Computing Induced Charge in Inhomogeneous Dielectric Media

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August 19, 2003

1   Introduction

The calculation of the electrostatic potential in a dielectric medium is a fundamental aspect of many scientific problems, and in some applications (particle simulations, for example) can be the rate-limiting step. One method to compute the electrostatic potential is to solve the Poisson equation for the system given the density of the source charges and the (inhomogeneous) dielectric coefficient. An alternative approach is to use superposition, considering the fields of all the charges in the system, including the charges induced in the dielectric medium by the source charges present in the system. It is this method that was recently considered by Allen, Hansen, and Melchionna who derived an efficient method for computing the induced charge using a variational (functional minimization) approach [1] and applied it to particle simulations [2]. Using this approach we describe a computationally inexpensive method that *directly* computes the induced charge.

2 Theory

Allen *et al.* [1] considered a domain D that contains the dielectric medium with dielectric coefficient $\varepsilon(\mathbf{r})$ at location $\mathbf{r} \in D$. The functional Allen *et al.* derived to determine the induced charge as a function of location is given by several volume integrations:

$$I_2[h] = \frac{1}{2} \int_D \int_D h(\mathbf{r}) h(\mathbf{r}') G(\mathbf{r} - \mathbf{r}') \, d\mathbf{r}' d\mathbf{r} \tag{1}$$
$$- \frac{1}{2} \varepsilon_0 \int_D \int_D h(\mathbf{r}') G(\mathbf{r} - \mathbf{r}') \nabla \cdot (\chi \nabla \psi_e) \, d\mathbf{r}' d\mathbf{r}$$
$$- \frac{1}{2} \varepsilon_0 \int_D \int_D h(\mathbf{r}') \psi_e(\mathbf{r}) \nabla \cdot (\chi \nabla G(\mathbf{r} - \mathbf{r}')) \, d\mathbf{r}' d\mathbf{r}$$
$$- \frac{1}{2} \int_D \int_D \int_D h(\mathbf{r}') h(\mathbf{r}'') G(\mathbf{r} - \mathbf{r}') \nabla \cdot (\chi \nabla G(\mathbf{r} - \mathbf{r}'')) \, d\mathbf{r}'' d\mathbf{r}' d\mathbf{r}$$

where $G(\mathbf{r})$ is the Green's function for the domain D, ψ_e is the electrostatic potential due to the source charges in the system of uniform dielectric 1, and

$$\chi(\mathbf{r}) = \varepsilon(\mathbf{r}) - 1 \tag{2}$$

is the local susceptibility of the medium. The induced charge $\rho_{\text{ind}}(\mathbf{r})$ resulting from the source charges is determined by minimizing $I_2[h]$ with respect to

$$h(\mathbf{r}) = \rho_{\text{ind}}(\mathbf{r}). \tag{3}$$

To determine $h(\mathbf{r})$ and therefore the induced charge profile we will solve the extremum condition

$$\frac{\delta I_2}{\delta h(\mathbf{r})} = 0 \tag{4}$$

where

$$\frac{\delta I_2}{\delta h(\mathbf{r})} = \int_D h(\mathbf{r}') G(\mathbf{r} - \mathbf{r}') \, d\mathbf{r}' - \varepsilon_0 \int_D G(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'} \cdot [\chi(\mathbf{r}') \nabla_{\mathbf{r}'} \psi_e(\mathbf{r}')] \, d\mathbf{r}' \tag{5}$$
$$- \int_D \int_D h(\mathbf{r}'') G(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'} \cdot [\chi(\mathbf{r}') \nabla_{\mathbf{r}'} G(\mathbf{r}' - \mathbf{r}'')] \, d\mathbf{r}' d\mathbf{r}''.$$

Allen *et al.* proved this condition yielded the required functional minimum. With the relation

$$\nabla \cdot (f \nabla g) = \nabla f \cdot \nabla g + f \nabla^2 g \tag{6}$$

and the definitions of the Green's function

$$\nabla_{\mathbf{r}''}^2 G \left(\mathbf{r}'' - \mathbf{r}' \right) = -\delta \left(\mathbf{r}'' - \mathbf{r}' \right) \tag{7}$$

and the electrostatic potential due to the source charge density $\rho \left(\mathbf{r} \right)$

$$\varepsilon_0 \nabla^2 \psi_e \left(\mathbf{r} \right) = -\rho \left(\mathbf{r} \right), \tag{8}$$

this may be rewritten as

$$\int_D h \left(\mathbf{r}' \right) \left[\varepsilon \left(\mathbf{r}' \right) G \left(\mathbf{r} - \mathbf{r}' \right) - \int_D G \left(\mathbf{r} - \mathbf{r}'' \right) \nabla_{\mathbf{r}''} \varepsilon \left(\mathbf{r}'' \right) \cdot \nabla_{\mathbf{r}''} G \left(\mathbf{r}'' - \mathbf{r}' \right) d\mathbf{r}'' \right] d\mathbf{r}'$$
$$= \varepsilon_0 \int_D G \left(\mathbf{r} - \mathbf{r}' \right) \nabla_{\mathbf{r}'} \varepsilon \left(\mathbf{r}' \right) \cdot \nabla_{\mathbf{r}'} \psi_e \left(\mathbf{r}' \right) d\mathbf{r}' - \int_D \left[\varepsilon \left(\mathbf{r}' \right) - 1 \right] \rho \left(\mathbf{r}' \right) G \left(\mathbf{r} - \mathbf{r}' \right) d\mathbf{r}'. \tag{9}$$

This equation may be further simplified by considering by considering both the *function* and *functional* described by Eq. (9):

$$F \left[h \left(\mathbf{r}' \right) \right] \left(\mathbf{r} \right) = \int_D h \left(\mathbf{r}' \right) g \left(\mathbf{r} \right) d\mathbf{r}' - f \left(\mathbf{r} \right) \tag{10}$$

where $g \left(\mathbf{r} \right)$ is the expression in square brackets in the first integral in Eq. (9) while $f \left(\mathbf{r} \right)$ is the right-hand side (RHS) of Eq. (9). Then $F \left[h \left(\mathbf{r}' \right) \right] \left(\mathbf{r} \right)$ is both a *function* of $\mathbf{r}$ and a *functional* of $h \left(\mathbf{r}' \right)$. It is $h \left(\mathbf{r}' \right)$ that we wish to determine under the constraint

$$F \left(\mathbf{r} \right) = 0 \tag{11}$$

for all $\mathbf{r}$. Since $F \left(\mathbf{r} \right)$ is identically 0, it follows that, as a function,

$$\nabla_{\mathbf{r}}^2 F \left(\mathbf{r} \right) = 0 \tag{12}$$

for all $\mathbf{r}$. Thus we have the identity that

$$0 = \nabla_{\mathbf{r}}^2 F \left[h \left(\mathbf{r}' \right) \right] \left(\mathbf{r} \right) = \int_D h \left(\mathbf{r}' \right) \nabla_{\mathbf{r}}^2 g \left(\mathbf{r} \right) d\mathbf{r}' - \nabla_{\mathbf{r}}^2 f \left(\mathbf{r} \right) \tag{13}$$

3

or

$$\int_D h\left(\mathbf{r}'\right) \nabla_{\mathbf{r}}^2 g\left(\mathbf{r}\right) d\mathbf{r}' = \nabla_{\mathbf{r}}^2 f\left(\mathbf{r}\right). \tag{14}$$

Applying this identity and Eq. (7) to Eq. (9) gives

$$h\left(\mathbf{r}\right)\varepsilon\left(\mathbf{r}\right) - \int_D h\left(\mathbf{r}'\right) \nabla_{\mathbf{r}}\varepsilon\left(\mathbf{r}\right) \cdot \nabla_{\mathbf{r}}G\left(\mathbf{r} - \mathbf{r}'\right) d\mathbf{r}'$$

$$= \varepsilon_0 \nabla_{\mathbf{r}}\varepsilon\left(\mathbf{r}\right) \cdot \nabla_{\mathbf{r}}\psi_e\left(\mathbf{r}\right) - \left[\varepsilon\left(\mathbf{r}\right) - 1\right]\rho\left(\mathbf{r}\right). \tag{15}$$

It is this equation that we propose to discretize and solve for $h\left(\mathbf{r}\right)$ to determine the induced charge profile. Although this equation is general for forms of the function $\varepsilon\left(\mathbf{r}\right)$, we will considering the case of sharp dielectric interfaces for discrete, point source charges. This case has been considered in other contexts (as described below), but we note that the general equation (15) for non-sharp dielectric interfaces has, to our knowledge, not been previously derived.

2.1   Discrete, point source charges

When the source charges are point charges in discrete locations, the source charge density is given by

$$\rho\left(\mathbf{r}\right) = \sum_k z_k e \delta\left(\mathbf{r} - \mathbf{x}_k\right) \tag{16}$$

where source charge k with valence z_k is located at $\mathbf{x}_k$, e is the elementary charge, and δ is the Dirac delta function. Because these charges are point charges and have no surface area, the induced charge around each charge k is localized at the position of the charge $\mathbf{x}_k$ and has density [3]

$$-z_k e\left[\varepsilon\left(\mathbf{x}_k\right) - 1\right]\delta\left(\mathbf{r} - \mathbf{x}_k\right) \tag{17}$$

if the dielectric is locally uniform around the source charge. Therefore, the contribution to h from the induced charge around the source charges (SC) is

$$h_{\mathrm{SC}}\left(\mathbf{r}\right) = -\sum_k z_k e\left[\varepsilon\left(\mathbf{x}_k\right) - 1\right]\delta\left(\mathbf{r} - \mathbf{x}_k\right). \tag{18}$$

4

Substituting this into Eq. (15) gives that

$$h\left(\mathbf{r}\right)\varepsilon\left(\mathbf{r}\right) - \int_{D} h\left(\mathbf{r}'\right)\nabla_{\mathbf{r}}\varepsilon\left(\mathbf{r}\right)\cdot\nabla_{\mathbf{r}}G\left(\mathbf{r}-\mathbf{r}'\right)d\mathbf{r}' = \varepsilon_0\nabla_{\mathbf{r}}\varepsilon\left(\mathbf{r}\right)\cdot\nabla_{\mathbf{r}}\psi_e\left(\mathbf{r}\right) \qquad (19)$$

where

$$\varepsilon_0\nabla^2\psi_e\left(\mathbf{r}\right) = -e\sum_k \frac{z_k}{\varepsilon\left(\mathbf{x}_k\right)}\delta\left(\mathbf{r}-\mathbf{x}_k\right) \qquad (20)$$

and h refers solely to the induced charge other than that around the source charges.

It is important to note that if the source charge was an ion modeled, for example, as a point charge at the center of a dielectric sphere, then the induced charge on the ion surface must also be determined [4], [5]; this would be another contribution to $h\left(\mathbf{r}\right)$ on the LHS of Eq. (9).

2.2   Sharp dielectric boundaries

One circumstance under which determining the induced charge is particularly advantageous is when the dielectric material contains only sharp boundaries that separate the medium into piecewise uniform dielectrics. Then the induced charge is a surface charge on the dielectric interfaces (if the induced charge around the source charges is not considered), and the integrals in Eq. (15) become surface integrals over the surface S of the dielectric boundaries [1]:

$$h\left(\mathbf{s}\right)\varepsilon\left(\mathbf{s}\right) - \Delta\varepsilon\left(\mathbf{s}\right)\int_{S} h\left(\mathbf{s}'\right)\nabla_{\mathbf{s}}G\left(\mathbf{s}-\mathbf{s}'\right)\cdot\mathbf{n}\left(\mathbf{s}\right)ds' = \varepsilon_0\Delta\varepsilon\left(\mathbf{s}\right)\nabla\psi_e\left(\mathbf{s}\right)\cdot\mathbf{n}\left(\mathbf{s}\right) \qquad (21)$$

where the dielectric coefficient on the boundary $\varepsilon\left(\mathbf{s}\right)$ is defined to be the arithmetic mean of the two dielectric coefficients on each side of the boundary. Futhermore, the dielectric jump $\Delta\varepsilon\left(\mathbf{s}\right)$ is the difference of the two dielectric coefficients on each side of the boundary (in the direction of the local unit normal of the surface $\mathbf{n}\left(\mathbf{s}\right)$).

To solve Eq. (21) numerically the surface S must be discretized; specifically, each discrete patch j of S is characterized by its center-of-mass $\mathbf{r}_j$, area a_j, unit normal $\mathbf{n}_j$ (this is constant

over the patch and thus the patch is planar), value of the dielectric ε_j, and value of the dielectric jump $\Delta\varepsilon_j$. Because G is the Green's function, it is known everywhere, as is its gradient. $\nabla\psi_e$ is also known because the density of the discrete, point source charges is known from Eq. (20).

The integrals in Eq. (21) are then discretized as sums over the patches i and j:

$$\sum_j h_j \left(\delta_{ij}\varepsilon_j - \Delta\varepsilon_i \frac{\partial G_{ij}}{\partial n_i} a_j \right) = \varepsilon_0 \Delta\varepsilon_i \frac{\partial \psi_i}{\partial n_i} \tag{22}$$

where δ_{ij} is the Kronecker δ,

$$\frac{\partial G_{kj}}{\partial n_k} = \nabla G\left(\mathbf{r}_k - \mathbf{r}_j\right) \cdot \mathbf{n}_k, \tag{23}$$

and

$$\frac{\partial \psi_j}{\partial n_j} = \nabla\psi_e\left(\mathbf{r}_j\right) \cdot \mathbf{n}_j. \tag{24}$$

Note that in the infinite geometry, Green's function is

$$G\left(\mathbf{r}_k - \mathbf{r}_j\right) = \frac{1}{4\pi \left|\mathbf{r}_k - \mathbf{r}_j\right|} \tag{25}$$

and therefore

$$\nabla G\left(\mathbf{r}_k - \mathbf{r}_j\right) = -\frac{1}{4\pi \left|\mathbf{r}_k - \mathbf{r}_j\right|^3} \left(\mathbf{r}_k - \mathbf{r}_j\right). \tag{26}$$

Also, for discrete charges in the infinite geometry,

$$\psi_e\left(\mathbf{r}\right) = \frac{e}{4\pi\varepsilon_0} \sum_k \frac{z_k}{\varepsilon\left(\mathbf{x}_k\right)\left|\mathbf{r} - \mathbf{x}_k\right|} \tag{27}$$

and therefore

$$\nabla\psi_e\left(\mathbf{r}_j\right) = -\frac{e}{4\pi\varepsilon_0} \sum_k \frac{z_k}{\varepsilon\left(\mathbf{x}_k\right)\left|\mathbf{r}_j - \mathbf{x}_k\right|^3} \left(\mathbf{r}_j - \mathbf{x}_k\right). \tag{28}$$

This can be written in matrix form as

$$A\mathbf{h} = \mathbf{c} \tag{29}$$

where each element of the matrix A is given by

$$A_{ij} = \delta_{ij}\varepsilon_j - \Delta\varepsilon_i \frac{\partial G_{ij}}{\partial n_i} a_j. \tag{30}$$

6

Each element of the column vector $\mathbf{h}$ is given by h_j and each element of the column vector $\mathbf{c}$ is given by

$$c_i = \varepsilon_0 \Delta \varepsilon_i \frac{\partial \psi_i}{\partial n_i}. \tag{31}$$

This the same matrix formulation used in quantum mechanical solvation programs based apparent surface charges (ASC) (see, for example, [5]) first introduced by Hoshi et al. [4].

When considering simulations of point charges, it is important to note that the source charges contribute only to the RHS $\mathbf{c}$ in Eq. (29); the only contributions to the matrix A are the dielectric profile and the Green's function. Thus the inverse of A (or any factorization of A) need only be computed *once* for a given geometry and dielectric profile. This substantially reduces computational burden to approximately N^2 operations versus N^3 for inverting the matrix at every simulation step, where N is the number of patches. We note that, in the context of ASC solvation methods, Pomelli and Tomasi have developed an algorithm that solves the matrix equation (29) with order N operations. However, they use truncated long-range electrostatic potentials to achieve this fast algorithm and such truncations have been shown to be inappropriate for simulations in more complex charged systems [7]. On the other hand, iterative methods other than those of Pomelli and Tomasi [5], [6] may yet prove to be faster than N^2 without the use of cutoff potentials [8].

Lastly, we note that because the matrix equation (29) is linear, this method may also be used to determine the coefficients of a series expansion of h [9].

3   Energy of the System

Once the induced charge has been calculated for a given set of charges, the electrostatic energy E of the system may also be calculated from the ion-ion interactions and the ion-induced charge interactions:

$$E = E_{\text{ion-ion}} + E_{\text{ion-ind}} \tag{32}$$

where, for discrete charges,

$$E_{\text{ion-ion}} = \frac{e}{2} \int \int \rho\left(\mathbf{r}'\right) \psi_e\left(\mathbf{r} - \mathbf{r}'\right) d\mathbf{r} d\mathbf{r}' \tag{33}$$

and

$$E_{\text{ion-ind}} = \frac{e}{2\varepsilon_0} \sum_j \int \int \rho\left(\mathbf{r}'\right) h\left(\mathbf{r}\right) G\left(\mathbf{r} - \mathbf{r}'\right) d\mathbf{r} d\mathbf{r}'. \tag{34}$$

In the discretized scheme, these become

$$E_{\text{ion-ion}} = \frac{e^2}{8\pi\varepsilon_0} \sum_j z_j \sum_{k \neq j} \frac{z_k}{\varepsilon\left(\mathbf{x}_k\right) \left|\mathbf{x}_j - \mathbf{x}_k\right|} \tag{35}$$

$$E_{\text{ion-ind}} = \frac{e}{2\varepsilon_0} \sum_j z_j \sum_k h_k G\left(\mathbf{r}_k - \mathbf{x}_j\right) \tag{36}$$

$$= \frac{e}{8\pi\varepsilon_0} \sum_j z_j \sum_k \frac{h_k a_k}{\left|\mathbf{r}_k - \mathbf{x}_j\right|}. \tag{37}$$

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