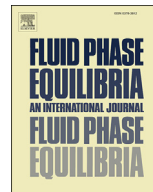




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## Electric-field mapped averaging for the dielectric constant

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## ABSTRACT

We examine the performance of mapped averaging for the computation of the dielectric constant in application to the TIP4P water potential. We compare the efficiency of conventional and mapped averaging in terms of the difficulty ratio, considering four temperatures (500 K, 650 K, 1300 K, and 1800 K) and densities from  $10^{-6}$  g/cm<sup>3</sup> to 1.0 g/cm<sup>3</sup>. We consider differences in the methods also with respect to correlation of samples, and system-size effects. Results for 650 K are compared to experimental data as represented by a correlation for the dielectric constant from the literature, with deviations of up to 25% observed. Significant advantage in efficiency is seen for the mapped-averaging approach at high temperature and low density, while being marginally less efficient at liquid-like densities. We also examine the simulation data against results from a dielectric virial series to third order in density, and suggest that an even better mapped-averaging method may be developed from consideration of pairwise interactions of the molecular dipoles.

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## 1. Introduction

Solution properties have long attracted the attention of researchers in chemical thermodynamics [1–4]. Molecular models of electrolytes and aqueous solutions rely on a proper treatment of electrostatics for an accurate description of solution behavior. A key property relating to these considerations is the dielectric constant, or relative permittivity. Models of water that aim to be used for studies of solutions should give attention to whether the dielectric constant is predicted well. It characterizes how well a solvent screens the interactions of charges with each other, and thereby has an appreciable effect on the general behavior of solutions. Indeed, considerable attention has been given to evaluation of the dielectric properties for various water models via molecular simulation [5–8]. The dielectric constant is related to the fluctuations in the mean square total dipole moment in the absence of an external electric field [9,10]. It is considered one of the more difficult properties for calculation by molecular simulation; long-range electrostatic effects are relevant, and like all fluctuation-based quantities, averaging tends to converge slowly.

To aid calculation of precise values of dielectric constant, we developed a formulation of mapped averaging (MA) [11,12] for its evaluation. Mapped averaging is a new, general method for

reformulation of the ensemble averages in statistical mechanics. Given a property approximation based in statistical mechanical theory, the MA framework derives new ensemble averages that represent exactly the error in the theory. If the starting theory is reasonably accurate, the correction given by the averages can be evaluated with good precision, because it eliminates fluctuations related to the known approximate behavior. We have had good success in application of this idea to evaluation of properties of atomic crystals, where a harmonic treatment provides a suitable starting point [12–14]; the simulations then give directly the anharmonic contributions to properties.

Our application of MA to evaluate the dielectric constant from molecular simulation builds on knowledge of fluctuations in non-interacting dipoles, such that the simulation measures only contributions in excess of this. Presently we consider only rigid, non-polarizable dipoles interacting with an external field  $\mathbf{E}$ . When presenting the general MA framework [11], we used application to the dielectric constant as one of several brief examples illustrating the effectiveness of the approach. We performed simulations of the Stockmayer model (Lennard-Jones with point dipole), and showed that MA at low density yields results that are much more precise than conventional averaging with the same amount of computation.

In this paper, we consider application to a more realistic molecular model, the TIP4P potential for water. This model has three charged sites and one LJ site, which means there are ten pairs of interaction between each pair of molecules, and no explicit dipole-

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dipole interaction is employed. We examine the effectiveness of MA for such a system. We focus on calculation of the dielectric constant of water in supercritical states. One reason is that most previous simulation studies of the dielectric constant of water considered the liquid state, so we provide new data as a byproduct of the study. Additionally, in the supercritical conditions the non-interacting dipole starting point is more appropriate, and the approach may be anticipated to be more effective. We compare the performance of MA and the conventional approach by consideration of the difficulty. Also we examine other performance-related features that we did not consider in previous work, in particular the rate of decay of correlations, and system-size effects. In applications to the anharmonic behavior of crystals, we found large differences between conventional and mapped averaging with regard to these issues. We also compare our simulation results with experimental data as represented by a correlation.

The formalism and simulation details of MA for calculation of the dielectric constant are presented in Sec. 2 and results are given in Sec. 3. In Section 4, we summarize the findings and consider paths for future development of the MA method for evaluation of the dielectric constant.

## 2. Formalism and simulation details

### 2.1. Ensemble averages

We consider molecules with a fixed dipole moment,  $|\mu_i| \equiv \mu_D$ . The energy of interaction with external field  $\mathbf{E}$  is:

$$U_E = -\mathbf{E} \cdot \mathbf{M}, \quad (1)$$

where  $\mathbf{M} = \sum_i \mu_i$  is the total dipole moment (here and below,  $i$  sums over all  $N$  molecules in the system). The dielectric constant is given in terms of the second derivative of the free energy  $A$  with respect to the field  $\mathbf{E}$ , which yields directly the conventional form for the ensemble average:

$$\nabla_{\mathbf{E}}^2(\beta A) = -\beta^2 (\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2) \quad (2)$$

This is what we will refer to as the conventional averaging approach for evaluating the dielectric constant. For the isotropic and homogeneous systems we consider, there is no permanent dipole moment ( $\langle \mathbf{M} \rangle \equiv 0$ ), so we average just  $\mathbf{M}^2$ .

The MA formulation for this derivative is developed as follows (additional detail is available in Ref. [11]). We derive the mapping under an assumption that the probability of a configuration is that for independent dipoles in a  $z$ -directed field  $\mathbf{E} = (0, 0, E)$ . This assumption leads us to define the following:

$$p(\Omega; E) = \exp(-\beta U_E) = \prod_i p_1(z_i; E) \quad (3a)$$

$$p_1(z_i; E) = \exp(\beta \mu_D E z_i) \quad (3b)$$

$$q(E) \equiv \int d\Omega p(\Omega; E) = (q_1(E))^N \quad (3c)$$

$$q_1(E) = \int_{-1}^1 dz_i p_1(z_i; E) = 2 \sinh(\beta \mu_D E) / (\beta \mu_D E) \quad (3d)$$

Here,  $\Omega$  is the vector of orientations for all  $N$  molecules, and  $z_i$  is the  $z$ -component of the orientation of dipole  $i$ . These approximations to

the true Boltzmann weight and partition function are used in a type of conservation equation to derive the mapping, which is given via a generalized “rotational velocity”  $v_i^E$  (the  $E$  superscript indicates that this velocity describes change in orientation with respect to a changing field  $E$ , rather than time):

$$\frac{\partial}{\partial E} \left( \frac{p_1(z_i; E)}{q_1(E)} \right) + \frac{\partial}{\partial z_i} \left( \frac{p_1(z_i; E)}{q_1(E)} v_i^E \right) = 0. \quad (4)$$

The mapping given by solution of this formula keeps the ratio  $p_1/q_1$  constant (in the Lagrangian frame) as  $E$  is varied. If the independent-dipole approximation is valid, then the formula for the change in free energy with  $E$  (as derived below) would be expressed in terms of an average having no fluctuations, yielding a result with perfect precision. To the extent the system does not obey the independent-dipole approximation, there will be fluctuations in the average; however, while some imprecision is introduced, there is no loss of accuracy.

Solution to Eq. (4) with the boundary condition  $v_i^E(z_i = 1) = 0$  yields:

$$v_i^E = \frac{1}{2} \beta \mu_D (1 - z_i^2) \quad (5)$$

The second derivative of the free energy is then [11]:

$$\beta A_{EE} = -\langle J_{EE} - J_E^2 \rangle + \langle \beta U_{EE} \rangle - \text{Var}[J_E - \beta U_E] \quad (6)$$

where subscripts indicate derivatives with respect to  $E$ . The Jacobian derivatives are given in terms of the mapping as

$$J_E = \nabla \cdot \mathbf{v}^E, \quad (7a)$$

$$J_{EE} - J_E^2 = \nabla \cdot \mathbf{v}_E^E + \mathbf{v}^E \cdot \nabla (\nabla \cdot \mathbf{v}^E), \quad (7b)$$

and the configurational-energy derivatives are

$$\beta U_E = -\mathbf{M}_z - \mathbf{v}^E \cdot \boldsymbol{\tau} \quad (8a)$$

$$\beta U_{EE} = -(\mathbf{v}_E^E + \mathbf{v}^E \cdot \nabla \mathbf{v}^E) \cdot \boldsymbol{\tau} + \mathbf{v}^E \cdot \phi \cdot \mathbf{v}^E - 2\mathbf{v}^E \cdot \boldsymbol{\tau}_E, \quad (8b)$$

where  $\boldsymbol{\tau}$  is the  $3N$ -dimensional vector of the components of the torque on all molecules, and  $\phi$  is the  $3N \times 3N$  Hessian for the energy with respect to the orientations; also, the  $\nabla$  operator here is the  $3N$ -dimensional vector of orientation derivatives.

We repeat this derivation for fields in the  $x$  and  $y$  directions, respectively, and sum over all three directions to obtain the final MA expression for the second derivative [11]:

$$\begin{aligned} \nabla_{\mathbf{E}}^2(\beta A) = & -N\beta^2 \mu_D^2 + \frac{\beta^4}{4} \left\langle \left| \sum_{i=1}^N \boldsymbol{\tau}_i \times \boldsymbol{\mu}_i \right|^2 \right\rangle - \frac{\beta^3}{4} \left\langle \sum_{i=1}^N \sum_{j=1}^N (\nabla_i \cdot \boldsymbol{\tau}_j) \right. \\ & \times (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) - \boldsymbol{\mu}_j \cdot \nabla_i \boldsymbol{\tau}_j \cdot \boldsymbol{\mu}_i \left. \right\rangle \end{aligned} \quad (9)$$

where  $\boldsymbol{\tau}_i$  is the torque on molecule  $i$ , and  $\nabla_i$  is the gradient with respect to the molecule- $i$  orientation. Equation (9) is clearly separated into two parts. The first term in this expression is the Clausius-Mossotti-Debye result [15], which describes fluctuations of independent dipoles. The remaining terms represent the correction to this approximate form, given as ensemble averages that will be small and precise to the extent that the independent-

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