Simulating Nanoscale Dielectric Response

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(Received 25 November 2005; published 13 June 2006)

We introduce a constrained energy functional to describe dielectric response. We demonstrate that the local functional is a generalization of the long-ranged Marcus energy. Our reformulation is used to implement a cluster Monte Carlo algorithm for the simulation of dielectric media. The algorithm avoids solving the Poisson equation and remains efficient in the presence of spatial heterogeneity, nonlinearity, and scale dependent dielectric properties.

The response of dielectric materials leads to important modifications of the bare electrostatic energy of charges [1]. Even on *microscopic* scales many important qualitative insights result from the application of the *macroscopic* laws of electrostatics. For example, a large part of the solvation free energy of an ion in water is understood in terms of the Born self energy of an ion, $q^2/8\pi a\epsilon$ where ϵ is the macroscopic dielectric constant of the solvent and a an atomic scale; similarly many essential features of ion channels can be explained by a continuum description of high dielectric channels through low dielectric membranes [2,3].

On the nanometer scale the dielectric response is, in general, nonlocal [4], $\mathbf{D_r} = \int \epsilon_{\mathbf{r},\mathbf{r}'}\mathbf{E_{r'}} \, d^3\mathbf{r}'$, where $\mathbf{D}$ is the electric displacement and $\mathbf{E}$ the electric field. In Fourier space the field energy of a homogeneous fluid is given by

$$U_{\text{elec}} = \sum_q \epsilon(q)\frac{\mathbf{E}^2(q)}{2}, \qquad (1)$$

where $\epsilon(q)$ is now a scale dependent dielectric constant with $\mathbf{D}(q) = \epsilon(q)\mathbf{E}(q)$. If we take water as an example [5] we learn that starting from $\epsilon \sim 80$ at $q = 0$, the dielectric constant of water drops to $\epsilon = 20$ at a wavelength which is comparable to the Bjerrum length of a monovalent ion (7 Å); below a wavelength of ~ 5 Å ϵ diverges and becomes *negative*. Moreover, many situations of practical interest require the inclusion of nonlinear effects such as dielectric saturation or surface ordering and alignment [6].

Recently, we introduced an algorithm which permits the calculation of electrostatic interactions in heterogeneous *local* dielectric media without solving the Poisson equation [7]. The idea is to generate long-ranged electrostatic interactions *dynamically* via local interactions between charges, the medium and the electric field. On first sight, it seems straightforward to replace the field energy $U = \int(\mathbf{D_r}^2/2\epsilon_{\mathbf{r}})d^3\mathbf{r}$ used in Ref. [7] by Eq. (1). However, this approach is fundamentally flawed: the method would

allow one to treat *unphysical* systems with $0 < \epsilon(q) < 1$ [4] while becoming unstable for real materials in which the dielectric constant becomes negative.

In this Letter we present a generalization of the Marcus energy for polarizable media [8] written in terms of the true, independent thermodynamic variables in the problem [4,9]: the electric polarization of the medium, $\mathbf{P}$, and the displacement, $\mathbf{D}$. We show that our formalism is capable of reproducing the full range of the linear dielectric response seen in nature including negative dielectric constants [4,9]. In addition, we demonstrate that the same techniques can be used to study nonlinear or polar dielectrics at similar computational cost. The important feature is the use of a cluster algorithm [10] for the equilibration of the field degrees of freedom.

We now introduce the energy functional. There are two contributions to the energy of a dielectric medium. Firstly, the energy density $\mathbf{E}^2/2 = (\mathbf{D} - \mathbf{P})^2/2$ of the electric field; secondly, an elastic polarization energy, $G(\mathbf{P})$, due to short-ranged interactions between molecules. We start by expressing G as a general quadratic function of $\mathbf{P}$ with a *short-ranged kernel* $K_{\mathbf{r},\mathbf{r}'}$ which we describe more fully below. In a heterogeneous system K varies from place to place in the sample; it contains *all* the material properties. Thus,

$$U = \int \frac{(\mathbf{D_r} - \mathbf{P_r})^2}{2} d^3\mathbf{r} + \int \frac{\mathbf{P_r} K_{\mathbf{r},\mathbf{r}'}\mathbf{P_{r'}}}{2} d^3\mathbf{r} d^3\mathbf{r}'. \qquad (2)$$

We use units with $\epsilon_0 = 1$ and periodic boundary conditions. Furthermore, $\mathbf{D}$ is constrained by Gauss's law, $\text{div}\mathbf{D} - \rho = 0$. In the following we demonstrate the equivalence of our formalism to the standard theory of dielectric media [11–13].

We first work at zero temperature; this will allow us to calculate the relationship between the dielectric constant $\epsilon(q)$ defined in Eq. (1) and the kernel $K(q)$ in Eq. (2). We minimize Eq. (2) subject to the constraint of Gauss's law with the help of a Lagrange multiplier ϕ. We consider the

stationary points of the functional

$$A = U - \int d^3\mathbf{r}\,\phi(\text{div}\mathbf{D} - \rho). \qquad (3)$$

We will pass rather freely between the full integral form, Eq. (2) and an operator notation in which all components of a field are grouped in a single vector and K is a matrix. The variational equations are

$$\delta\phi: \text{div}\mathbf{D} - \rho = 0; \qquad \delta\mathbf{P}: \mathbf{P} - \mathbf{D} + K\mathbf{P} = \mathbf{0};$$
$$\delta\mathbf{D}: \mathbf{D} - \mathbf{P} + \text{grad}\phi = \mathbf{0}. \qquad (4)$$

We indeed find from the variational equations that if we define $\mathbf{E} \equiv \mathbf{D} - \mathbf{P}$ then the relation between the polarization and the electric field is $\mathbf{P} = \chi\mathbf{E}$, where $\chi = K^{-1}$ is the susceptibility to the electric field, $\mathbf{E} = -\text{grad}\phi$. We now solve Eq. (4) for $\mathbf{P}$ in terms of $\mathbf{D}$ and substitute in Eq. (2). We find Eq. (1) with

$$\epsilon(q) = 1 + K^{-1}(q). \qquad (5)$$

We have reproduced all the standard relations between $\mathbf{E}$, $\mathbf{P}$, ϕ, and $\mathbf{D}$ of electrostatics, as well as the energy Eq. (1) which should be the *minimum* of the functional Eq. (2). Similarly, we can show that our Ansatz is equivalent to the Marcus polarization functional [8,11,12]: we use Eq. (4) to eliminate the constrained field $\mathbf{D}$ and express Eq. (2) in terms of the polarization $\mathbf{P}$ and the *bare* electric field $\mathbf{E}_0 = -\text{grad}\phi_0$ generated by the free charges in vacuum: $\nabla^2\phi_0 = -\rho$,

$$U_p = \frac{1}{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{\text{div}\mathbf{P_r}\text{div}\mathbf{P_{r'}}}{|\mathbf{r} - \mathbf{r}'|} - \int \mathbf{E}_0 \cdot \mathbf{P}\,d^3\mathbf{r}$$
$$+ \frac{1}{2}\int \mathbf{P_r}K_{\mathbf{r},\mathbf{r}'}\mathbf{P_{r'}}d^3\mathbf{r}\,d^3\mathbf{r}' + \int\frac{\mathbf{E}_0^2}{2}d^3\mathbf{r}. \qquad (6)$$

It is instructive to rewrite Eq. (6) in the operator notation:

$$U_p = \frac{1}{2}\mathbf{P}(T + K)\mathbf{P} - \mathbf{E}_0 \cdot \mathbf{P} + \frac{\mathbf{E}_0^2}{2}. \qquad (7)$$

T denotes $|q\rangle\langle q| \longrightarrow -\frac{3|\mathbf{r}\rangle\langle\mathbf{r}|-1}{4\pi r^3} + \frac{I}{3}\delta(\mathbf{r})$ in real space. The field $\mathbf{P}$ interacts with itself via the long-ranged dipole-dipole potential.

We now consider the stability of the functional Eq. (2) for $q \neq 0$, in order to check that the energy is a true minimum, not just a stationary point. The longitudinal constraint of Eq. (3) freezes $\mathbf{D}$; only fluctuations of $\mathbf{P}$ are free. The coefficient of $\mathbf{P}^2$ in Eq. (2) is $V_q(\mathbf{P}) = \mathbf{P}(1 + K)\mathbf{P}/2$. In order for fluctuations in $\mathbf{P}$ to be bounded (so that the ground state is stable) we require that eigenvalues of $(1 + K)$ are positive. Now express $V_q(\mathbf{P})$ in terms of the field $\mathbf{E}$ and eliminate K for ϵ using Eq. (5):

$$V_q(\mathbf{E}) = \frac{\epsilon(q)[\epsilon(q) - 1]}{2}\mathbf{E}^2 > 0. \qquad (8)$$

Stability implies that $\epsilon(q)[\epsilon(q) - 1] > 0$, so that $\epsilon \geq 1$ or $\epsilon \leq 0$. The expression Eq. (8) is indeed that given in

Ref. [9] for the effective potential of the electric field. Stable modes with $\epsilon(q) < 0$ (such as those seen in water) correspond to $-1 < K(q) < 0$. We conclude that our constrained energy Eq. (2) is capable of reproducing the full range of dielectric response seen in nature and leads to the correct band of forbidden response functions $0 < \epsilon(q) < 1$ where the system becomes thermodynamically unstable: in electrostatics there can be no equivalent of diamagnetic response, which seems plausible from the conventional energy Eq. (1).

We now generalize to finite temperatures and study the partition function

$$Z = \int d\mathbf{P}d\mathbf{D}e^{-\beta U}\prod_{\mathbf{r}}\delta(\text{div}\mathbf{D}(\mathbf{r}) - \rho(\mathbf{r})). \qquad (9)$$

We integrate over $\mathbf{P}$ or $\mathbf{D}$ to find the finite temperature generalizations of Eqs. (1) and (6): The $\mathbf{P}$ degrees of freedom are Gaussian, when we integrate over them we find the constrained partition function

$$Z = \frac{1}{\sqrt{|1 + K|}}\int d\mathbf{D}e^{-\beta\int(\mathbf{D}^2/2\epsilon)d^3\mathbf{r}}\prod_{\mathbf{r}}\delta(\text{div}\mathbf{D} - \rho) \qquad (10)$$

where we have dropped unimportant numerical prefactors. This constrained integral over $\mathbf{D}$ was studied in detail in Ref. [7]. When dielectric properties are local, so that $K(\mathbf{r}, \mathbf{r}') = \kappa(\mathbf{r})I\delta(\mathbf{r} - \mathbf{r}')$, Eq. (10) describes particles interacting through an electrostatic potential which is a solution to the Poisson equation, $\text{div}(\epsilon\text{grad}\phi) = -\rho$, with $\epsilon(\mathbf{r}) = 1 + 1/\kappa(\mathbf{r})$. In addition it gives the Keesom potential between fluctuating, classical dipoles.

Rather than integrating over $\mathbf{P}$ we integrate over $\mathbf{D}$ in Eq. (9): the δ-function constraint is imposed using the identity $2\pi\delta(x) = \int e^{i\phi x}d\phi$. The integral over $\mathbf{D}$ is then Gaussian, as is that subsequently performed over ϕ. We find $Z = \int d\mathbf{P}e^{-\beta U_p}$. U_p is the energy of Eq. (6). This is our principal formal result. It shows that with the energy functional Eq. (2) integrating over the constrained field $\mathbf{D}$ generates results which are equivalent to using the long-ranged Marcus functional Eq. (6).

The treatment of the stability of the field $\mathbf{P}$ requires generalization at finite temperature: We must distinguish between the longitudinal and transverse parts of the operator K when $q \neq 0$: $K_{l|t}$. From Eq. (2) we calculate the fluctuations of the polarization field. Longitudinal fluctuations give $\beta S(\mathbf{q}) = \beta\langle\delta\mathbf{P}\cdot\delta\mathbf{P}\rangle_l(\mathbf{q}) = 1/[1 + K_l(\mathbf{q})]$ whereas for the two transverse modes $\beta\langle\delta\mathbf{P}\cdot\delta\mathbf{P}\rangle_t(\mathbf{q}) = 2/K_t(\mathbf{q})$, so that the eigenvalues of K_t must also be positive. Combining these two expressions we find the fluctuations in $\mathbf{P}$ for small q:

$$\beta\langle\delta\mathbf{P}\cdot\delta\mathbf{P}\rangle_{q\to 0} = \frac{1}{(1 + K_l)} + \frac{2}{K_t} \to \frac{(2\epsilon + 1)(\epsilon - 1)}{\epsilon},$$
$$\beta\langle\delta\mathbf{P}^2\rangle_{q=0} = \frac{3}{K(0)} = 3(\epsilon - 1), \qquad (11)$$

where we have used the fact that K becomes isotropic at small q. These expressions are familiar from the Kirkwood theory of dielectrics [14] and will be used to extract dielectric constants from our simulations. Using these expressions is always numerically challenging since they link the dielectric properties to *fluctuations* in the polarization field. Accurate results require simulations which are many times longer than the equilibration time.

By choosing appropriate kernels K we can introduce semimicroscopic models of dielectric media with a great variety of dielectric properties. A systematic approach is to use a Landau-Ginsburg expansion of the free energy for the polarization field [15]. The lowest order terms (corresponding to a linear theory $G = \mathbf{P}K\mathbf{P}/2$) are given by

$$G = \frac{1}{2} \int \{\kappa \mathbf{P}^2 + \kappa_t (\mathrm{curl}\mathbf{P})^2 + \kappa_l (\mathrm{div}\mathbf{P})^2\} d^3\mathbf{r}. \quad (12)$$

Eigenvalues of K_l are $(\kappa + \kappa_l q^2)$, transverse eigenvalues are $(\kappa + \kappa_t q^2)$. The dispersion laws split at $O(q^2)$. Stability implies that κ, κ_l, and κ_t must all be positive. From Eq. (5) the dielectric constant is $\epsilon(q) = \{1 + 1/(\kappa + \kappa_l q^2)\}$. It falls off monotonically with wave vector.

Until now we have worked with linear media, which as we have shown analytically reproduce the standard theory of dielectric media. However our approach is *not* limited to linear models. Consider soft Langevin dipoles where the length constraint is imposed by an energy function $G = \int \gamma(\mathbf{P}^2 - P_0^2)^2 d^3\mathbf{r}$. Dipoles with long-ranged interactions described by the operator T in Eq. (7) have long been used [16] to describe polar solvents. In contrast to linear models, they exhibit a saturation of the polarization degrees of freedom when interacting with strongly charged objects. To generate, in addition, scale dependent dielectric effects we include derivative terms in the free energy:

$$G = \int \left\{ \gamma(\mathbf{P}^2 - P_0^2)^2 + \frac{\kappa_l (\mathrm{div}\mathbf{P})^2}{2} + \frac{\alpha(\mathrm{grad\,div}\mathbf{P})^2}{2} \right\} d^3\mathbf{r}. \quad (13)$$

We are particularly interested in the case $\kappa_l < 0$ in order to produce systems with $\epsilon(q) < 0$, together with $\alpha > 0$, necessary for stability at large wave vectors. At interfaces other contributions to G such as $\int \mathrm{grad}\kappa \cdot \mathbf{P} d^3\mathbf{r}$ select a preferred direction for the polarization and can be used to study ordering by surfaces. We leave such considerations, however, to future work. In our first simulations we used $\alpha = -0.4\kappa_l$, $P_0^2 = 7.5/\gamma$.

We discretize the fields on a simple cubic lattice of side L so that $\mathbf{E}$ and $\mathbf{P}$ are associated with the $3L^3$ links. The constrained field $\mathbf{D}$ is sampled by a cluster (worm) algorithm [10,17] invented to study quantum spin models. We sample $\mathbf{P}$ with the Metropolis algorithm. The worm modifies a large cluster of $O(L^3)$ $\mathbf{D}$ variables while conserving $\mathrm{div}\mathbf{D}$. We define a sweep as $3L^3$ Monte Carlo tries for $\mathbf{P}$ and one worm for $\mathbf{D}$. We measure $\beta S(\mathbf{q})$ and determine $\epsilon(\mathbf{q}) = 1/[1 - \beta S(\mathbf{q})]$. The results are plotted for several

sets of parameters in Fig. 1. Passage of $\beta S(\mathbf{q})$ through 1 gives rise to poles in the dielectric properties, leading to some of the major qualitative features known in water: First, a long wavelength dielectric constant satisfying $\epsilon(0) > 1$; second, a band of wavevectors with negative dielectric constant; third, convergence of ϵ to 1 for large q.

A central point of this Letter is the demonstration of the computational efficiency of our approach. In the following we compare a linear, nonlocal model Eq. (12), a heterogeneous, linear, local model, and a nonlinear model consisting of soft Langevin dipoles Eq. (13). We determine equilibration times with a blocking method [18]: Starting from $N = 2^n$ recordings, $x(t)$, one calculates an estimate of the mean and standard error for blocks of data of length $b = 2^m$ with $0 \le m < n$. We studied the dynamics of variable $x(t) = \mathbf{P}^2(t, q = 0)$, used to measure the $q = 0$ dielectric constant through Eq. (11). Blocking analysis leads to a monotonically increasing estimate of the standard error, in $\langle x \rangle$, $\sigma(b)$. When b the block size has reached the autocorrelation time of the simulation the standard error converges to $\sigma^2 = 2\tau_{\mathrm{int}}\langle \delta x^2 \rangle / N$, where τ_{int} is the integrated autocorrelation time. We calculated the blocking curves for various values of system size and model parameters, Fig. 2. Systems of different size L have blocking curves which superpose with no rescaling of the data; the relaxation time (in sweeps) of the algorithm is independent of the system size. When we modify the dielectric properties we need to rescale both horizontal and vertical axes to superpose data. We find that the scaling variables are $N\sigma^2(b)/\chi_0\langle \delta x^2 \rangle$ as a function of b/χ_0 where χ_0 is the
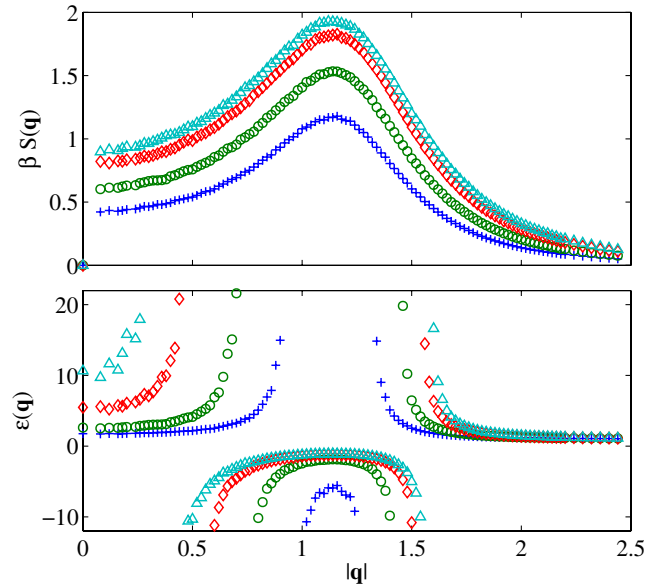

FIG. 1 (color online). Dielectric constant deduced from polarization fluctuations for the dielectric Eq. (13). $L = 64$. Data plotted as a function of $|\mathbf{q}|$ with $|\mathbf{q}|^2 = 2\sum_i(1 - \cos q_i)$. (γ, κ_l) are $+$ $(5, -2.3)$, $\bigcirc$ $(2.5, -1.5)$, $\diamond$ $(1, -1.0)$, $\triangle$ $(0.5, -0.9)$. Four days simulation per curve on a Pentium-4 processor.
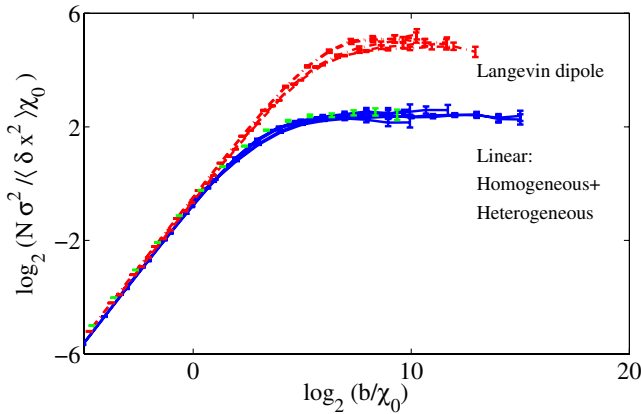
FIG. 2 (color online).   Scaled statistical error as a function of scaled blocking factor. Curves for $L = 10, 13, 18$ and simulations of $N = 2^{22}$ sweeps. Linear: Eq. (12), $\kappa = 1.0, 0.1, 0.03, 0.015$, $\kappa_t = 0$, $\kappa_l = \kappa/8$. Nonlinear (blue online): Eq. (13). $\gamma = 2, 1, 0.4$, $\alpha = \kappa_l = 0$ scaled with χ_0. Heterogenous linear with $L = 18$ where $\kappa = 0.25$ for $0 < z \le l/2$ and $\kappa = 0.02$ for $L/2 < z < L$ scaled with $\chi_0 = 50$.

$q = 0$ susceptibility; for the heterogeneous system we used the appropriate χ_0 for the large ϵ region. Thus the simulation is slowed by a factor χ_0 when dielectric properties change. For $\chi_0 = 1$ $\tau_{\text{int}} \sim 2$ sweeps when simulating with a simple quadratic energy for the polarization fluctuations. When using the soft Langevin dipole the simulation is approximately 6 times slower.

In a set of tests our Monte Carlo algorithm performed 20 times faster than a conventional molecular dynamics code [19] applied to a simple cubic grid of dipoles [16], that is to an *explicit* lattice model of a dielectric medium corresponding to Eq. (13) without the divergence terms. Experience [20,21] shows that the inherent advantages of the formulation in terms of local fields are not lost in off-lattice molecular dynamics implementations. We therefore believe that the present work opens the way to the development of more realistic implicit solvents models for (bio)-molecular simulations.

The appearance of a long time scale in high dielectric media can be understood as being due to the large ratio of the amplitude of transverse to longitudinal fluctuations $2(1 + K^{-1}) = 2\epsilon$, which splits the experimental longitudinal and transverse relaxation time scales [22]. This same splitting limits the efficiency of our algorithm. $O(\epsilon)$ sweeps are needed to fully equilibrate the system and to generate the Keesom—van der Waals interactions. Note, however, that the autocorrelation time of the longitudinal modes which are important for interactions between charges remains $O(1)$ sweeps even when the transverse and $q = 0$ modes are slow.

To conclude, we have shown that a generalization of the Marcus functional for polarizable media (in the style of Landau-Ginsburg) provides a natural framework for discussing dielectric response on the nanometer scale, and that the long-range electrostatic interactions in heterogeneous, nonlinear, and nonlocal dielectric media can be simulated with constrained energy functionals for the fields. This method is to be contrasted with generalized Born methods which use approximate solutions of electrostatics in heterogenous dielectric media [23]. The present work provides a natural link between macroscopic theory and microscopic models of dielectric materials.

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