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# Microscopic Derivation of Fluctuation Formulas for Calculating Dielectric Constants by Simulation

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A microscopic derivation using the average Maxwell electric field is given for fluctuation formulas for the dielectric constant of a simulation sample for both periodic and reaction field boundary conditions. The reaction field case is for a spherical cavity reaction field. The derivations put both boundary conditions on an equal footing of microscopic theory and the only nonrigorous part of the derivation is the assumption that the region used to average the electric field is large enough. The fluctuation formula for reaction field boundary conditions is rather different from that used heretofore. The method is applied to a subregion of an isolated spherical system.

**KEY WORDS:** Dipoles; boundary conditions; electrostatics.

## 1. INTRODUCTION

Much confusion exists in the literature over the precise status of various boundary conditions that can be applied to the electrostatic interactions between the particles of a finite simulation sample of a polar fluid. The two most popular forms of boundary conditions are periodic boundary conditions and reaction field boundary conditions. Periodic boundary conditions have been condemned for introducing artificial long-range dipole–dipole correlations into the system(1,2) and methods of implementing them have been improperly understood.(3) Reaction field boundary conditions, because they surround the sample with a continuous dielectric medium of dielectric constant not equal to that of the system, may also be criticized

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for inducing physically inappropriate long-range dipole–dipole correlations. The point of this paper is to show that these criticisms are irrelevant to the calculation of static dielectric constants, by deriving a fluctuation formula for the dielectric constant from the Hamiltonian (plus boundary conditions) for the system. Along the way it is possible to clear up some misconceptions in standard derivations. The theory assumes only that the simulation sample is large enough.

For a polar system the dielectric constant is the constant $\varepsilon$ in the equation

$$\varepsilon \mathbf{E}_{\mathrm{AV}} = \mathbf{E}_{\mathrm{AV}} + 4\pi \mathbf{p}_{\mathrm{AV}} \tag{1}$$

where $\mathbf{p}_{\mathrm{AV}}$ is the average polarization density in some region $\Omega$ and $\mathbf{E}_{\mathrm{AV}}$ is the average of the microscopic electric field over that region. The polarization that is averaged to give $\mathbf{p}_{\mathrm{AV}}$ is that resulting from applying an external constant electric field $\mathbf{e}_0$ to a system of which $\Omega$ is a subregion. The electric field that is averaged is the sum of $\mathbf{e}_0$ plus the electric field at the point concerned due to all the dipoles in the system. To obtain $\varepsilon$ as a property of the bulk material, it is first necessary to let the system become infinite and then, after this limit is taken, to let the region $\Omega$ become infinite.

In a simulation sample, which is necessarily finite, such careful juggling of limiting processes is obviously not possible. Nevertheless, there is an electric field defined at any point in the system, and a polarization density. The definition of the electric field at a point $\mathbf{r}$ in a dipolar system of $N$ molecules of dipole moment $\boldsymbol{\mu}_j$ at $\mathbf{r}_j$, $1 \leqslant j \leqslant N$, is

$$\mathbf{E}(\mathbf{r}) = \mathbf{e}_0 - \sum_{j=1}^{N} (\boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j}) \nabla_{\mathbf{r}} \psi(\mathbf{r}, \mathbf{r}_j; x) \tag{2}$$

where $\psi(\mathbf{r}, \mathbf{r}_j; x)$ is the solution of a Poisson equation with the boundary condition $x$ applied. On the other hand, the electrostatic energy of the system is

$$H_{\mathrm{ES}}(\mathbf{e}_0; x) = \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} (\boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j})(\boldsymbol{\mu}_k \cdot \nabla_{\mathbf{r}_k}) \psi(\mathbf{r}_k, \mathbf{r}_j; x) - \mathbf{e}_0 \cdot \mathbf{M} \tag{3}$$

where

$$\mathbf{M} = \sum_{j=1}^{N} \boldsymbol{\mu}_j \tag{4}$$

is the net dipole moment of the system and $\mathbf{e}_0$ is an constant applied external electric field. Thus, it is clear that once the Hamiltonian for the simulation sample has been defined precisely, with the effects of electrostatic boundary conditions on the sample included, the electric field at a point $\mathbf{r}$ in the sample is also defined.

In a simulation, the Hamiltonian may be conveniently written

$$H(\mathbf{e}_0, x) = H_{\mathrm{SR}} + H_{\mathrm{ES}}(\mathbf{0}; x) - \mathbf{e}_0 \cdot \mathbf{M} \tag{5}$$

for the boundary condition $x$, where $H_{\mathrm{SR}}$ is the sum of all the short-ranged interactions between the molecules. The average polarization density $\langle \mathbf{p}(\Omega) \rangle_{\mathbf{e}_0;x}$ of some subregion $\Omega$ [with volume $V(\Omega)$] of the simulation cube of side $L$ may be written

$$\langle \mathbf{p}(\Omega) \rangle_{\mathbf{e}_0;x} = \frac{\int d(1) \cdots \int d(N)\, [\mathbf{M}(\Omega)/V(\Omega)] \exp[-\beta H(\mathbf{0}; x) + \beta \mathbf{e}_0 \cdot \mathbf{M}]}{\int d(1) \cdots \int d(N) \exp[-\beta H(\mathbf{0}; x) + \beta \mathbf{e}_0 \cdot \mathbf{M}]} \tag{6}$$

where

$$\mathbf{M}(\Omega) = \sum_{\substack{j=1 \\ \mathbf{r}_j \in \Omega}}^{N} \boldsymbol{\mu}_j \tag{7}$$

is the net dipole moment of the region $\Omega$. Equation (6) may be expanded in powers of $\mathbf{e}_0$. The result can be written as

$$\begin{aligned} 4\pi \langle \mathbf{p}(\Omega) \rangle_{\mathbf{e}_0;x} &= 4\pi \langle \mathbf{p}(\Omega) \rangle_{\mathbf{0};x} + \frac{9y\gamma(\Omega)\{\langle \mathbf{M}(\Omega)\mathbf{M} \rangle_{\mathbf{0};x} - \langle \mathbf{M}(\Omega) \rangle_{\mathbf{0};x} \langle \mathbf{M} \rangle_{\mathbf{0};x}\} \cdot \mathbf{e}_0}{N\mu^2} + O(\mathbf{e}_0^2) \end{aligned} \tag{8}$$

where

$$\gamma(\Omega) = L^3/V(\Omega) \tag{9}$$

$$y = 4\pi\rho\mu^2/9kT \tag{10}$$

is a dimensionless measure of the strength of the dipolar interactions, and $\rho = N/L^3$ is the number density of particles in the system. Assuming that the system is not ferroelectric, so that $\langle \mathbf{M}(\Omega) \rangle_{\mathbf{0};x} = \mathbf{0}$, we find that Eq. (6) reduces to

$$4\pi \langle \mathbf{p}(\Omega) \rangle_{\mathbf{e}_0;x} = 3y\gamma(\Omega) \frac{\langle \mathbf{M}(\Omega) \cdot \mathbf{M} \rangle_{\mathbf{0};x} \mathbf{e}_0}{N\mu^2} + O(\mathbf{e}_0^2) \tag{11}$$

It is precisely this form for the average polarization in a system that must be related to the expectation of the electric field. Relation (11) is exact and to calculate the dielectric constant in the thermodynamic limit, it must be studied first in the limit $N \to \infty$, $L \to \infty$ with $N/L^3 = \rho$ kept fixed, and then $\Omega \to \infty$.

In a boundary condition $x$, the potential $\psi(\mathbf{r}, \mathbf{r}_k; x)$ is a solution of

$$\nabla_{\mathbf{r}}^2 \psi(\mathbf{r}, \mathbf{r}_k; x) = -4\pi\delta(\mathbf{r} - \mathbf{r}_k) \tag{12}$$

with the boundary condition $x$ applied. The solution may be written in the form$^{(4)}$

$$\psi(\mathbf{r}, \mathbf{r}_k; x) = \frac{1}{|\mathbf{r} - \mathbf{r}_k|} + H(\mathbf{r}, \mathbf{r}_k; x) \tag{13}$$

where $H(\mathbf{r}, \mathbf{r}_k; x)$ is a continuously differentiable function of $\mathbf{r}$ and $\mathbf{r}_k$ in the region on which the solution is sought. The electric field at a point $\mathbf{r}$ in his region, for a configuration $C = \{\boldsymbol{\mu}, \mathbf{r}_1, ..., \boldsymbol{\mu}_N, \mathbf{r}_N\}$ of the molecules, is

$$\mathbf{E}(\mathbf{r}; x) = \mathbf{e}_0 - \sum_{j=1}^{N}{}^{*} (\boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j}) \nabla_{\mathbf{r}} \psi(\mathbf{r}, \mathbf{r}_j; x) \tag{14}$$

where the asterisk on the sum means that the $|\mathbf{r} - \mathbf{r}_j|^{-1}$ part of $\psi(\mathbf{r}, \mathbf{r}_j; x)$ is omitted when $\mathbf{r} = \mathbf{r}_j$. In configuration $C$, the average electric field in a region $\Omega$ is given by

$$\mathbf{E}(\Omega; x) = \frac{1}{V(\Omega)} \int_\Omega d^3\mathbf{r}\, \mathbf{E}(\mathbf{r}; x) \tag{15}$$

Using (13) and (14), we obtain from this

$$\begin{aligned} \mathbf{E}(\Omega; x) = \mathbf{e}_0 &- \sum_{j=1}^{N} \boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j} \int_\Omega \nabla_{\mathbf{r}} H(\mathbf{r}, \mathbf{r}_j; x)\, d^3\mathbf{r} \\ &- \sum_{j=1}^{N} (\boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j}) \int_\Omega \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}_j|}\, d^3\mathbf{r} \end{aligned} \tag{16}$$

The first set of integrals in (16) may be simplified using Gauss' theorem in the form

$$\int_\Omega \nabla_{\mathbf{r}} f(\mathbf{r})\, d^3\mathbf{r} = \int_{\partial\Omega} f(\mathbf{r})\, \hat{\mathbf{n}}(\mathbf{r})\, d^2\mathbf{r} \tag{17}$$

where $\hat{\mathbf{n}}(\mathbf{r})$ is the unit outward normal at $\mathbf{r}$ o the surface $\partial\Omega$ of $\Omega$. Gauss' theorem applies because $H(\mathbf{r}, \mathbf{r}_j; x)$ is continuously differentiable in $\mathbf{r}$. The second set of integrals in (16) cannot be treated in this way immediately because the integrand of each is singular at $\mathbf{r}=\mathbf{r}_j$. Thus, a sphere $S_\delta(j)$ of radius $\delta$ is constructed around each $\mathbf{r}_j$. Then

$$\int_\Omega \nabla_\mathbf{r} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, d^3\mathbf{r}$$

$$= \int_{\Omega|S_\delta(j)} \nabla_\mathbf{r} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, d^3\mathbf{r} + \int_{S_\delta(j)} \nabla_\mathbf{r} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, d^3\mathbf{r} \tag{18}$$

The integrand in the second integral in (18) is $(\mathbf{r}-\mathbf{r}_j)/|\mathbf{r}-\mathbf{r}_j|^3$, so this second integral can be written using the substitution $\mathbf{t}=\mathbf{r}-\mathbf{r}_j$ as

$$\int_0^\delta dt \int_0^\pi \sin\theta\, d\theta \int_{-\pi}^\pi d\phi\, (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

which is zero. The first integral in (18) has a continuously differentiable integrand and so may be written using (17) as

$$\int_{\partial\Omega} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, \hat{\mathbf{n}}(\mathbf{r})\, d^2\mathbf{r} - \int_{\partial S_\delta(j)} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, \hat{\mathbf{n}}(\mathbf{r})\, d^2\mathbf{r} \tag{19}$$

The integral over $\partial S_\delta(j)$ may now be written as

$$\delta \int_0^\pi \sin\theta\, d\theta \int_{-\pi}^\pi d\phi\, (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

which is also zero. Thus

$$\int_\Omega \nabla_\mathbf{r} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, d^3\mathbf{r} = \int_{\partial\Omega} \frac{1}{|\mathbf{r}-\mathbf{r}_j|}\, \hat{\mathbf{n}}(\mathbf{r})\, d^2\mathbf{r} \tag{20}$$

This rather labored calculation seems necessary since it is sometimes [e.g., Ref. 5, Eq. (8.3D)] carried out wrongly. This analysis gives

$$\mathbf{E}(\Omega; x) = \mathbf{e}_0 - \sum_{j=1}^{N} (\boldsymbol{\mu}_j \cdot \nabla_{\mathbf{r}_j}) \int_{\partial\Omega} \psi(\mathbf{r}, \mathbf{r}_j; x)\, \hat{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r} \tag{21}$$

## 2. PERIODIC BOUNDARY CONDITIONS

The periodic boundary conditions (PBC) used here are those introduced by de Leeuw *et al.*$^{(6)}$ The cubic simulation cell of side $L$ is replicated to make a large sphere of periodic copies, with the region exterior to the sphere being a dielectric continuum of dielectric constant $\varepsilon'$.

The sphere of copies has radius $R$ and may be called $S(R)$. The relevant Poisson equation is then

$$\nabla_{\mathbf{r}}^2 \psi(\mathbf{r}, \mathbf{r}_k; \text{PBC}, \varepsilon') = -4\pi \sum_{L\mathbf{n} \in S(R)} \delta(\mathbf{r} - \mathbf{r}_k - L\mathbf{n}) \tag{22}$$

with the usual electrostatic conditions applying at the sphere surface.

For $R$ large but finite, an expansion for the solution may be developed in inverse powers of $R$,[7,8] and in the limit $R \to \infty$ the solution in the original simulation cell is

$$\psi(\mathbf{r}, \mathbf{r}_k; \text{PBC}, \varepsilon') = \frac{1}{L} \psi_{\text{PER}} \left( \frac{\mathbf{r} - \mathbf{r}_k}{L} \right) + \frac{4\pi}{L^3(2\varepsilon' + 1)} \mathbf{r} \cdot \mathbf{r}_k \tag{23}$$

where

$$\psi_{\text{PER}}(\mathbf{r}) = \sum_{\mathbf{n}} \frac{\operatorname{erfc}(\alpha |\mathbf{n} + \mathbf{r}|)}{|\mathbf{n} + \mathbf{r}|} + \sum_{\mathbf{m} \neq \mathbf{0}} \frac{\exp(-\pi^2 \mathbf{m}^2/\alpha^2)}{\pi \mathbf{m}^2} \exp(2\pi i \mathbf{m} \cdot \mathbf{r}) \tag{24}$$

is a periodic function of period 1 in each of the components of $\mathbf{r}$. The two sums in (24) over all vectors with integer components are absolutely convergent for $\alpha > 0$, so that $\psi_{\text{PER}}(\mathbf{r})$ is properly defined. This correct solution to the potential-theory problem in these boundary conditions cannot be derived from a Fourier transform of the solution of an infinite system. The representation (13) for this potential may be obtained by noting that the $\mathbf{n} = \mathbf{0}$ term of $\psi_{\text{PER}}(\mathbf{r})$ gives a contribution

$$1/|\mathbf{r} - \mathbf{r}_k| - \operatorname{erf}(\alpha |\mathbf{r} - \mathbf{r}_k|/L)/|(\mathbf{r} - \mathbf{r}_k)|$$

to $\psi(\mathbf{r}, \mathbf{r}_k; \text{PBC}, \varepsilon')$. It is sensible to use the simulation cell (SC) as the averaging region.

This gives

$$\mathbf{E}(\text{SC}; \text{PBC}, ') = \mathbf{e}_0 - \frac{4\pi}{2\varepsilon' + 1} \frac{\mathbf{M}}{L^3} \tag{25}$$

since the surface integral over the simulation cell surface of $L^{-1} \hat{\mathbf{n}} \psi_{\text{PER}}((\mathbf{r} - \mathbf{r}_k)/L)$ [cf. Eq. (21)] is zero because the contributions of opposite plane surfaces of the cell cancel by the periodicity. If the canonical expectation of both sides of Eq. (25) is taken, the result

$$\langle \mathbf{E}(\text{SC}; \text{PBC}, \varepsilon') \rangle_{\mathbf{e}_0; \text{PBC}, \varepsilon'} = \mathbf{e}_0 - \frac{1}{2\varepsilon' + 1} 4\pi \langle \mathbf{p}(\text{SC}) \rangle_{\mathbf{e}_0; \text{PBC}, \varepsilon'} \tag{26}$$

is obtained. Using Eq. (11), it follows that

$$4\pi\langle \mathbf{p}(\mathrm{SC})\rangle_{\mathbf{e}_0;\mathrm{PBC},\varepsilon'} = 3y\,\frac{\langle \mathbf{M}^2\rangle_{\mathbf{0};\mathrm{PBC},\varepsilon'}}{N\mu^2}\,\mathbf{e}_0 \tag{27}$$

Using the assumption that the simulation cell is large enough to identify the average electric field in (26) with the $\mathbf{E}_{\mathrm{AV}}$ of Eq. (1) then gives

$$\frac{(\varepsilon-1)(2\varepsilon'+1)}{2\varepsilon'+\varepsilon} = 3y\,\frac{\langle \mathbf{M}^2\rangle_{\mathbf{0};\mathrm{PBC},\varepsilon'}}{N\mu^2} \tag{28}$$

a result originally derived be a semimacroscopic argument by de Leeuw *et al.*[6] The only assumptions used in this derivation are that the thermodynamic limit of $\varepsilon$ in $(\mathrm{PBC}, \varepsilon')$ geometry is the same as for free space geometry, and that the sample SC is large enough to make the identification of $\langle \mathbf{E}(\mathrm{SC};\, \mathrm{PBC}, \varepsilon')\rangle_{\mathbf{e}_0;\mathrm{PBC},\varepsilon'}$ with $\mathbf{E}_{\mathrm{AV}}$.

## 3. REACTION FIELD BOUNDARY CONDITIONS

In reaction field boundary conditions, the energy of (or forces on) a dipole $\boldsymbol{\mu}_j$ at $\mathbf{r}_j$ can be calculated by surrounding the dipole with a sphere of radius $R_c$ with center at $\mathbf{r}_j$, filling the region exterior to the sphere with a dielectric continuum of dielectric constant $\varepsilon'$ and ignoring the interaction of dipoles $\boldsymbol{\mu}_k$ at $\mathbf{r}_k$ for which $|\mathbf{r}-\mathbf{r}_k| > R_c$. The relevant Poisson equation is

$$\begin{aligned} &\nabla_{\mathbf{r}}^2 \psi(\mathbf{r}, \mathbf{r}_k;\, \mathrm{RF}, R_c, \varepsilon') \\ &\quad = \begin{cases} -4\pi\delta(\mathbf{r}-\mathbf{r}_k) & \text{if } |\mathbf{r}_{jk}| \leqslant R_c \\ 0 & \text{if } |\mathbf{r}_{jk}| > R_c \end{cases} \end{aligned} \tag{29}$$

with the usual electrostatic boundary conditions at $|\mathbf{r}| = R_c$. The solution to this electrostatic problem is found by taking spherical coordinates along $\mathbf{r}_{jk}$ and is

$$\begin{aligned} &\psi(\mathbf{r}, \mathbf{r}_k;\, \mathrm{RF}, R_c, \varepsilon') \\ &= \begin{cases} \dfrac{1}{|\mathbf{r}-\mathbf{r}_k|} - \dfrac{2(\varepsilon'-1)}{R_c} \displaystyle\sum_{l=0}^{\infty} \left(\frac{r\,|\mathbf{r}_{kj}|}{R_c^2}\right)^{l} \frac{l+1}{(l+1)\varepsilon'+l}\, P_l(\cos\theta) \\ \qquad \text{if } |\mathbf{r}_{kj}| \leqslant R_c \\ 0 \qquad \text{if } |\mathbf{r}_{kj}| > R_c \end{cases} \end{aligned} \tag{30}$$

For point dipoles, the dipole interaction is

$$\phi(j, k; \mathrm{RF}, R_c, \varepsilon') = \begin{cases} \boldsymbol{\mu}_j \cdot \dfrac{1 - 3\hat{\mathbf{r}}_{jk}\hat{\mathbf{r}}_{jk}}{|\mathbf{r}_{jk}|^3} \cdot \boldsymbol{\mu}_k - \dfrac{2(\varepsilon' - 1)}{R_c^3(2\varepsilon' + 1)} \boldsymbol{\mu}_j \cdot \boldsymbol{\mu}_k \\ \quad \text{if} \quad |\mathbf{r}_{jk}| \leqslant R_c \\ 0 \quad \text{if} \quad |\mathbf{r}_{jk}| > R_c \end{cases} \tag{31}$$

The singular part of this potential [cf. Eq. (13)] is obvious. The problem of averaging the electric field in this case is a little more complicated than in (PBC, $\varepsilon'$) boundary conditions. The field must be averaged in each sphere and the result averaged over the spheres. In the sphere $S(R_c, j)$ about $\mathbf{r}_j$, Eqs. (21) and (30) give

$$\mathbf{E}(S(R_c, j); \mathrm{RF}, R_c, \varepsilon') = \mathbf{e}_0 - \frac{1}{2\varepsilon' + 1} 4\pi \mathbf{p}(S(R_c, j)) \tag{32}$$

where in configuration $C$, $\mathbf{p}(S(R_c, j))$ is the polarization density in the sphere of radius $R_c$, center $\mathbf{r}_j$, namely

$$\mathbf{p}(S(R_c, j)) = \sum_{\substack{k=1 \\ |\mathbf{r}_{kj}| \leqslant R_c}}^{N} \boldsymbol{\mu}_k / V(R_c, j) \tag{33}$$

The canonical expectation of Eq. (32) then gives

$$\langle \mathbf{E}(S(R_c, j); \mathrm{RF}, R_c, \varepsilon') \rangle_{\mathbf{e}_0; \mathrm{RF}, R_c, \varepsilon'} = \mathbf{e}_0 - \frac{1}{2\varepsilon' + 1} 4\pi \langle \mathbf{p}(S(R_c, j)) \rangle_{\mathbf{e}_0; \mathrm{RF}, R_c, \varepsilon'} \tag{34}$$

At the same time, Eq. (11) gives

$$4\pi \langle \mathbf{p}(S(R_c, j)) \rangle_{\mathbf{e}_0; \mathrm{RF}, R_c, \varepsilon'} = 3y\gamma(S(R_c, j)) \frac{\langle \mathbf{M}(S(R_c, j)) \cdot \mathbf{M} \rangle_{0, \mathrm{RF}, R_c, \varepsilon'}}{N\mu^2} \mathbf{e}_0 \tag{35}$$

with

$$\gamma(S(R_c, j)) = 3L^3/4\pi R_c^3 \tag{36}$$

The relations may be averaged over $j$. Defining

$$\mathbf{M}(R_c)=\frac{1}{N}\sum_{j=1}^{N}\left\{\sum_{\substack{k=1\\|\mathbf{r}_{kj}|\leqslant R_c}}^{N}\boldsymbol{\mu}_k\right\} \tag{37}$$

$$4\pi\bar{\mathbf{p}}(R_c)=3y\,\frac{3L^3}{4\pi R_c^3}\,\frac{\langle\mathbf{M}(R_c)\cdot\mathbf{M}\rangle_{\mathbf{0};\mathrm{RF},R_c,\varepsilon'}}{N\mu^2}\,\mathbf{e}_0 \tag{38}$$

and $\bar{\mathbf{E}}$ as the average of the field on the left side of Eq. (34) gives

$$\bar{\mathbf{E}}=\mathbf{e}_0-\frac{1}{2\varepsilon'+1}\,\bar{\mathbf{p}}(R_c) \tag{39}$$

On the assumption that $R_c$ is large enough, and using its largest possible value, $L/2$, the identification of $\bar{\mathbf{E}}$ with $\mathbf{E}_{\mathrm{AV}}$ gives, from

$$\frac{(\varepsilon-1)(2\varepsilon'+1)}{2\varepsilon'+\varepsilon}=3y\,\frac{6}{\pi}\,\frac{\langle\mathbf{M}(R_c)\cdot\mathbf{M}\rangle_{\mathbf{0};\mathrm{RF};R_c,\varepsilon'}}{N\mu^2} \tag{40}$$

This fluctuation formula is similar to that used in recent studies using the reaction field,(5,9,10) but with a significant difference. Here the fluctuation quantity is $\langle\mathbf{M}(R_c)\cdot\mathbf{M}\rangle$ and not $\langle\mathbf{M}^2\rangle$ or $\langle\mathbf{M}(R_c)^2\rangle$. Patey *et al.*(10) have shown that results for $\varepsilon$ using $\langle\mathbf{M}^2\rangle$ can be quite different from results using $\langle\mathbf{M}(R_c)^2\rangle$, with volume scaling properly accounted for. Thus, the correct formula (40) for (RF, $R_c$, $\varepsilon'$) boundary conditions will give yet a third answer, but perhaps one that can be better trusted.

## 4. ISOLATED SPHERE BOUNDARY CONDITION

Some recent work by Hesse-Bezot *et al.*(2) and Levesque and Weis(11) treated a large set of dipoles confined to a sphere $S(R)$ of radius $R$ with a Lennard-Jones potential at the sphere boundary to contain the particles. They considered spherical subregions $S(R_a, \mathbf{r}_0)$, with center $\mathbf{r}_0$, radius $R_a$, to carry out averages over the field. These spheres were entirely within $S(R)$. To obtain more reliable statistical estimates, they in fact averaged the result over $\mathbf{r}_0$.

The relevant Poisson equation in this case is

$$\nabla_{\mathbf{r}}^2\psi(\mathbf{r},\mathbf{r}_k;0)=-4\pi\delta(\mathbf{r}-\mathbf{r}_k) \tag{41}$$

with the boundary condition $\psi\rightarrow 0$ as $|\mathbf{r}|\rightarrow\infty$. The solution is then

$$\psi(\mathbf{r},\mathbf{r}_k;0)=1/|\mathbf{r}-\mathbf{r}_k| \tag{42}$$

The dipole–dipole interaction is then the standard free space one. Inserting (42) in (21) gives for the average electric field in $S(R_a, \mathbf{r}_0)$

$$\mathbf{E}(S(R_a, \mathbf{r}_0); 0) = \mathbf{e}_0 - \frac{4\pi}{3}\mathbf{p}(S(R_a, \mathbf{r}_0)) - \sum_{\substack{j=1 \\ \mathbf{r}_j \notin S(R_a, \mathbf{r}_0)}}^{N} [\mathsf{I} - 3\hat{\mathbf{r}}_{j,0}\hat{\mathbf{r}}_{j,0}] \cdot \frac{\boldsymbol{\mu}_j}{|\mathbf{r}_{j,0}|^3} \tag{43}$$

where $\mathbf{r}_{j,0} = \mathbf{r}_j - \mathbf{r}_0$. It may now be noted that

$$4\pi \langle \mathbf{p}(S(R_a, \mathbf{r}_0)) \rangle_{\mathbf{e}_0, 0} = 3y\gamma(S(R_a, \mathbf{r}_0)) \frac{\langle \mathbf{M}(S(R_a, \mathbf{r}_0) \cdot \mathbf{M} \rangle_{\mathbf{0};0}}{N\mu^2} \mathbf{e}_0 \tag{44}$$

where

$$\gamma(S(R_a, \mathbf{r}_0)) = R^3/R_a^3 \tag{45}$$

The canonical expectation of (43) is not easy to evaluate. The third term on the right-hand side is replaced by assuming the region outside $S(R_a, \mathbf{r}_0)$ to be a dielectric continuum of dielectric constant $\varepsilon$, which responds to the net dipole moment of the region $S(R_a, \mathbf{r}_0)$ and thereby contributes to the electric field in that region. This assumption then gives

$$\frac{(\varepsilon - 1)[(\varepsilon + 2)(2\delta + 1) - 2(R_a/R)^3(1 - \varepsilon)^2]}{3\varepsilon(\varepsilon + 2)} = 3y\gamma(S(R_a, \mathbf{r}_0)) \frac{\langle \mathbf{M}(R_a) \cdot \mathbf{M} \rangle_{\mathbf{0};0}}{N\mu^2} \tag{46}$$

where $\mathbf{M}(R_a)$ is an average of $\mathbf{M}(S(R_a, \mathbf{r}_0))$ over a range of values $\mathbf{r}_0$. The expectation on the right-hand side of (46) is not precisely that used.(2,11) More important is the assumption that the external region can be treated as a uniform continuum. The geometry may also be implemented with the spherical sample immersed in a dielectric continuum of dielectric constant $\varepsilon'$, with appropriate changes to the left-hand side of (46) and a reaction field term in the Hamiltonian. The derivation of a fluctuation formula is interesting, since it does not really assume that $\varepsilon$ is independent of boundary conditions in the thermodynamic limit. The boundary condition used is the physically observed one. It does make the same assumption that the derivations in other boundary conditions make, that the averaging region chosen will be large enough. Also, this fluctuation formula makes an explicit extra assumption about the behavior of those dipoles exterior to the averaging region. Without further analysis, the status of the fluctuation formula (46) must remain unresolved.

## 5. DISCUSSION

The derivations of fluctuation formulas here are useful in tha they make quite clear what violence is being done to the electrostatics of an infinite, isolated system when a particular boundary condition is used to model it. The fluctuation formulas for periodic boundary conditions and reaction field boundary conditions [Eqs. (8) and (40), respectively] have exactly the same microscopic theoretical basis. The only question as to their viability as reliable ways of calculating dielectric constants is whether the system is large enough. That is a matter for simulation experiment.

The basis for the fluctuation formula for the isolated spherical system is not so sound, for while no violence at all is done to the electrostatic interactions in calculating the configurations, a specific semimacroscopic model is used in interpreting the fluctuations. This inconsistency between the Hamiltonian and the fluctuation formula does not occur in periodic boundary conditions or reaction field boundary conditions.

The rosy picture of an equivalent theoretical basis for both periodic and reaction field boundary conditions should not be allowed to obscure several rather difficult problems with reaction field boundary conditions. First, because of the spherical cutoff in the dipole–dipole interaction, a molecular dynamics simulation will not conserve energy. The kinetic energy must be regularly rescaled. This can have unknown effects on the resulting averages. Neumann *et al.*(9) have tried using a cubic cutoff and included the reaction field in the inside of the corresponding cube. However, this reaction field can only be evaluated approximately. Adams and Adams(12) have shown that dielectric constant estimates can be very sensitive to small changes in the reaction field potential, so that the approximate cubic reaction boundary condition may not be entirely reliable. A second difficulty arises when systems of molecules carrying charge distributions with a net dipole moment are to be studied. Here terms from all values of $l$ in the series (30) for $\psi(\mathbf{r}, \mathbf{r}_k;\, \mathrm{RF}, R_c, \varepsilon')$ contribute to the Hamiltonian. It is not at all clear that the resulting simulation will be any easier or faster to implement than a periodic boundary condition simulation, where fast, reliable numerical techniques are available. Finally, with such molecular systems a molecule may be partly inside the cutoff sphere and partly outside, which will lead to rather unphysical interactions near the cutoff.

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