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Simulation Calculation of Dielectric Constants: Comparison of Methods on an Exactly Solvable Model

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A mean spherical model of classical dipoles on a simple cubic lattice of side $M = 2N + 1$ sites is considered. Exact results are obtained for finite systems using periodic boundary conditions with an external dielectric constant ε' and using reaction field boundary conditions with a cutoff radius $R_c \leqslant N$ and an external dielectric constant ε'. The dielectric constant in the disordered phase is calculated using a variety of fluctuation formulas commonly implemented in Monte Carlo and molecular dynamics simulations of dipolar systems. The coupling in the system is measured by the parameter $y = 4\pi\mu^2/9kT$, where μ^2 is the fixed mean square value of the dipole moments on the lattice. The system undergoes a phase transition at $y \approx 2.8$, so that very high dielectric constants cannot be obtained in the disordered phase. The results show clearly the effects of system size, cutoff radius, external dielectric constant, and different measuring techniques on a dielectric constant estimate. It is concluded that with periodic boundary conditions, the rate of approach of the dielectric constant estimate to its thermodynamic limit is as $N^{-2/3}$ and depends only weakly on ε'. Methods of implementing reaction field boundary conditions to give rapid convergence to the thermodynamic limit are discussed.

KEY WORDS: Spherical model; dipolar systems; dielectric constant; dipolar system simulation.

1. INTRODUCTION

The calculation of dielectric constants of disordered phases of dipolar systems has been a subject of lively debate over the past 15 years.[1–17] A recent review[18] summarized many of the arguments. The problems are to convince a finite simulation sample that it is part of a very much larger system, within that sample to evaluate from the simulation an appropriate

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mean square dipole moment, and then to evaluate the dielectric constant of the system from that mean square dipole moment.

The problem of making a finite sample behave like a subsample of a larger system is the problem of the electrostatic boundary condition on the electric field of the dipoles in the sample. The problem of the mean square dipole moment breaks into two questions: (i) The mean square dipole moment of what? (ii) How to ensure that a simulation measures a long-time average or phase space average correctly? The problem of the route from mean square dipole moment averages to the dielectric constant requires an internally consistent interpretation of the physical picture of the system plus boundary conditions as a macroscopic uniform system.

Simulation results have so far concentrated on the hard-sphere point-dipole system and the Stockmayer system. Other systems have certainly been simulated, but these two are regarded as test systems for the methods being used. Comparing methods has involved comparing results obtained by different methods on the same system at the same (or nearly the same) phase points.

The purpose of this paper is to introduce a simple model of point dipoles on a lattice whose statistical mechanics can be solved exactly even for finite systems without recourse to simulation. Thus, we can give exact results for the dielectric constants (though only numerical ones) and exact results for finite systems with different boundary conditions. The behavior of the different dielectric constant estimates from a finite system may then be compared against an exact result. It is hoped that the comparisons will aid evaluation of simulation methods on more complicated systems.

The boundary conditions we consider can be called $PBC(\varepsilon')$, periodic boundary conditions with an external dielectric constant ε', and $RF(\varepsilon', R_c)$, reaction field boundary conditions with a cutoff sphere of radius R_c and an external dielectric constant ε'.

1.1. Periodic Boundary Conditions: PBC(ϵ')

In these boundary conditions we consider a simple cubic simulation cell of side length L. We construct a large spherical array of periodic copies of the sample which consists of N particles 1,..., N with dipole moment $\boldsymbol{\mu}_j$. The array is of radius R_0. A single dipole interacts with every other dipole in the sample, and every periodic copy. In addition, the region exterior to the spherical array of copies is filled with a continuous dielectric medium of dielectric constant ε'. The dipole–dipole interaction $\boldsymbol{\mu}_1 \cdot \mathbf{T}(\mathbf{r}_1 - \mathbf{r}_2) \cdot \boldsymbol{\mu}_2$ with

$$\mathbf{T}(\mathbf{r}) = -\nabla_{\mathbf{r}} \nabla_{\mathbf{r}} |\mathbf{r}|^{-1} \tag{1.1}$$

is replaced in the limit $R_0 \to \infty$ by[4]

$$\Phi_{\mathrm{PBC}}(\boldsymbol{\mu}_1, \mathbf{r}_1; \boldsymbol{\mu}_2, \mathbf{r}_2; \varepsilon') = \boldsymbol{\mu}_1 \cdot \mathbf{T}_{\mathrm{PBC}}(\mathbf{r}_1, \mathbf{r}_2; \varepsilon') \cdot \boldsymbol{\mu}_2 \tag{1.2}$$

with

$$\mathbf{T}_{\mathrm{PBC}}(\mathbf{r}_1, \mathbf{r}_2; \varepsilon') = \frac{1}{L} \nabla_{\mathbf{r}_1} \nabla_{\mathbf{r}_2} \Psi_E\left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{L}\right) - \frac{2\pi}{L^3(2\varepsilon' + 1)} \mathbf{I} \tag{1.3}$$

where $\mathbf{I}$ is the unit matrix and

$$\Psi_E(\boldsymbol{\rho}) = \sum_{\mathbf{n}} \frac{\operatorname{erfc}(\alpha|\mathbf{n} + \boldsymbol{\rho}|)}{|\mathbf{n} + \boldsymbol{\rho}|} + \sum_{\mathbf{m} \neq \mathbf{0}} \frac{\exp(-\pi^2 \mathbf{m}^2/\alpha^2)}{\pi \mathbf{m}^2} \exp(2\pi i \mathbf{m} \cdot \boldsymbol{\rho}) \tag{1.4}$$

is the periodic electrostatic potential.

1.2. Reaction Field Boundary Conditions: RF(ϵ', R_c)

In these boundary conditions the interaction of dipole $\boldsymbol{\mu}_1$ at $\mathbf{r}_1$ and $\boldsymbol{\mu}_2$ ar $\mathbf{r}_2$ is written as

$$\Phi_{\mathrm{RF}}(\boldsymbol{\mu}_1, \mathbf{r}_1; \boldsymbol{\mu}_2, \mathbf{r}_2; \varepsilon') = \begin{cases} \boldsymbol{\mu}_1 \cdot \mathbf{T}_{\mathrm{RF}}(\mathbf{r}_1, \mathbf{r}_2; \varepsilon') \cdot \boldsymbol{\mu}_2 & \text{if} \quad |\mathbf{r}_{12}^*| < R_c \\ 0 & \text{if} \quad |\mathbf{r}_{12}^*| \geqslant R_c \end{cases} \tag{1.5}$$

where

$$\mathbf{T}_{\mathrm{RF}}(\mathbf{r}_1, \mathbf{r}_2; \varepsilon') = \mathbf{T}(\mathbf{r}_{12}^*) - \frac{2\pi(\varepsilon' - 1)}{R_c^3(2\varepsilon' + 1)} \mathbf{I} \tag{1.6}$$

Here, $\mathbf{r}_{12}^*$ is the minimum image form of $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. This boundary condition was introduced by Barker and Watts.[19] A given dipole is considered to be in a sphere of radius R_c and interacts with all dipoles in that sphere. The region outside this sphere is considered to be a dielectric continuum of dielectric constant ε'. All the dipoles in the sphere polarize this dielectric and set up the reaction field on the original particle at the center of the sphere. This gives the second term in the first line of Eq. (1.5).

The dielectric constant of the material of the sample is calculated from the polarization response of the system to an infinitesimal applied electric field $\mathbf{E}_0$. The way this calculation is done must reflect the macroscopic model envisaged by the boundary conditions used. In any case, the Hamiltonian in boundary conditions χ may be written

$$\mathscr{H}_\chi(\mathbf{E}_0, \varepsilon') = \mathscr{K} + \mathscr{H}_0 + \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \boldsymbol{\mu}_j \cdot \mathbf{T}_\chi(\mathbf{r}_j, \mathbf{r}_k; \varepsilon') \cdot \boldsymbol{\mu}_k - \sum_{j=1}^{N} \mathbf{E}_0 \cdot \boldsymbol{\mu}_j \tag{1.7}$$

where $\mathscr{K}$ is the kinetic energy of the configuration and $\mathscr{H}_0$ is the potential energy of the other short-ranged interactions operating between the dipolar particles. In the canonical ensemble, the mean polarization of a subregion Ω of the sample is

$$\langle \mathbf{M}_\Omega \rangle_{\mathbf{E}_0} = \left\langle \sum_{j:\mathbf{r}_j \in \Omega} \boldsymbol{\mu}_j \right\rangle_{\mathbf{E}_0} = \frac{\int d\Gamma\, \mathbf{M}_\Omega \exp[-\beta \mathscr{H}_\chi(\mathbf{0}; \varepsilon') + \beta \mathbf{M} \cdot \mathbf{E}_0]}{\int d\Gamma \exp[-\beta \mathscr{H}_\chi(\mathbf{0}; \varepsilon') + \beta \mathbf{M} \cdot \mathbf{E}_0]} \tag{1.8}$$

Expanding the expectations on the right-hand side of Eq. (1.8) to linear terms in $\mathbf{E}_0$ and assuming that this mean subregion polarization is zero in zero field gives

$$\langle \mathbf{M}_\Omega \rangle_{\mathbf{E}_0} = \beta \{ \langle \mathbf{M}_\Omega \mathbf{M} \rangle_0 - \langle \mathbf{M}_\Omega \rangle_0 \langle \mathbf{M}_\Omega \rangle_0 \} \cdot \mathbf{E}_0 + O(\mathbf{E}_0^2) \tag{1.9}$$

In these expressions $\mathbf{M}$ is the polarization of the whole sample. The polarization density is then

$$\mathbf{p}(\Omega) = \beta \rho \gamma \mu^2 \mathbf{G}(\chi, \Omega, \varepsilon') \cdot \mathbf{E}_0 \tag{1.10}$$

where $\rho = N/L^3$, $\gamma = L^3/|\Omega|$, and

$$\mathbf{G}(\chi, \Omega, \varepsilon') = \frac{\langle \mathbf{M}_\Omega \mathbf{M} \rangle_{\mathbf{0};\chi;\varepsilon'} - \langle \mathbf{M}_\Omega \rangle_{\mathbf{0};\chi;\varepsilon'} \langle \mathbf{M} \rangle_{\mathbf{0};\chi;\varepsilon'}}{N_\Omega \mu^2} \tag{1.11}$$

with N_Ω the average number of particles in subregion Ω, $|\Omega|$ is the volume of Ω, and μ is the magnitude of the dipoles.

For periodic boundary conditions, the whole sample cell is the appropriate subregion and then the dielectric constant is given by

$$\varepsilon = \frac{2\varepsilon' + 1 + 6\varepsilon' y g(\varepsilon')}{2\varepsilon' + 1 - 3y g(\varepsilon')} \tag{1.12}$$

where

$$g(\varepsilon') = \text{trace } \mathbf{G}(PBC, L^3, \varepsilon') = \frac{1}{N\mu^2} \langle \mathbf{M}^2 \rangle \tag{1.13}$$

and $y = 4\pi\rho\mu^2/9kT$ is a dimensionless coupling parameter. This formula was derived by viewing the large array of periodic copies in two ways. The first was as a sphere of continuous medium of dielectric constant ε embedded in a medium of dielectric constant ε'. A field which was $\bar{\mathbf{E}}$ far from the sphere polarized the sphere to give a polarization density $\mathbf{p}_{MAC}$. The second was as an empty sphere so that $\bar{\mathbf{E}}$ gave the field $\mathbf{E}_0$ inside the sphere into which the array was introduced and the average polarization

$\mathbf{p}(L^3)$ calculated. The formula for ε in Eq. (1.12) results from equation $\mathbf{p}_{MAC}$ and $\mathbf{p}(L^3)$.

For reaction field boundary conditions it is not clear what subregion Ω to take. Some authors[1,2,7,10] have used the whole sample cube $\langle \mathbf{MM} \rangle$, while others[8,9] have used an average over all the spheres of radius R_c about a particle, $\langle \mathbf{M}_\Omega \mathbf{M}_\Omega \rangle$, where

$$\mathbf{M}_\Omega = \frac{1}{N} \sum_{j=1}^{N} \left\{ \sum_{\substack{k=1 \\ 0 < |\mathbf{r}_{jk}| < R_c}}^{N} \boldsymbol{\mu}_k \right\} \tag{1.14}$$

Perram and Smith[17] have argued that the appropriate response to study is that of each cutoff sphere about each particle, so that one should use $\langle \mathbf{M}_\Omega \mathbf{M} \rangle$ as in Eq. (1.11) here. This is because we can model the cutoff sphere about each particle as a continuum sphere in an external field and then compare the polarization density for that sphere with that measured in a simulation. The dielectric constant is then

$$\varepsilon = \frac{2\varepsilon' + 1 + 6\varepsilon' y g(RF, \varepsilon')}{2\varepsilon' + 1 - 3y g(RF, \varepsilon')} \tag{1.15}$$

where $g(RF, \varepsilon') = \text{trace } \mathbf{G}(RF, S_{R_c}, \varepsilon')$, S_{R_c} being the sphere of radius R_c and

$$\mathbf{G}(RF, S_{R_c}, \varepsilon') = \frac{1}{N\mu^2} \langle \mathbf{M}_\Omega \mathbf{M} \rangle \tag{1.16}$$

It is clear that there is a great range of methods to be chosen. There have been no exact calculations to give any basis for comparison. This paper gives some useful exact results. In Section 2 a lattice mean spherical model of classical dipoles is introduced and solved exactly for finite systems in all of the boundary conditions discussed here. Section 3 presents numerical results for the dielectric constant estimate as a function of system size, cutoff radius, and external dielectric constant ε'. The results and their implications for simulation studies are discussed in Section 4.

2. THE MEAN SPHERICAL MODEL

We consider a system on a simple cubic lattice $\Lambda_N = [-N, N]^{\otimes 3}$ which has $(2N+1)^3$ sites. At each site $\mathbf{n} \in \Lambda_N$, there is a three-dimensional dipole $\boldsymbol{\mu}(\mathbf{n}) \in \mathbb{R}^3$. The dipoles can have any magnitude, but the magnitudes are subject to the constraint

$$\left\langle \sum_{\mathbf{n} \in \Lambda_N} \boldsymbol{\mu}^2(\mathbf{n}) \right\rangle = (2N+1)^3 \mu^2 \tag{2.1}$$

where μ is some fixed dipole magnitude. In boundary conditions (χ, ε') the partition function for the system is

$$\mathscr{Z}(\Lambda_N, y) = \left\{ \prod_{\mathbf{n} \in \Lambda_N} \int_{\mathbb{R}^3} d^3\boldsymbol{\mu}(\mathbf{n}) \right\} \times \exp\left\{ -\tfrac{1}{2}\beta \sum_{\mathbf{n} \in \Lambda_N} \sum_{\mathbf{n}' \in \Lambda_N} \boldsymbol{\mu}(\mathbf{n}) \cdot \mathbf{T}_\chi(\mathbf{n}, \mathbf{n}'; \varepsilon') \cdot \boldsymbol{\mu}(\mathbf{n}') - \beta\lambda \left[\sum_{\mathbf{n} \in \Lambda_N} \boldsymbol{\mu}^2(\mathbf{n}) - (2N+1)^3 \mu^3 \right] \right\} \tag{2.2}$$

and λ takes the value that gives

$$\frac{\partial}{\partial \lambda} \log \mathscr{Z}(\Lambda_N, y) = 0 \tag{2.3}$$

thus ensuring that Eq. (2.1) is satisfied. The parameter y here is

$$y = 4\pi\mu^2/9kT \tag{2.4}$$

which is dimensionless (and corresponds to the standard y parameter for a continuum system with $\rho = 1$). In fact, the coupling tensors $\mathbf{T}_\chi(\mathbf{n}, \mathbf{n}'; \varepsilon')$ are periodic in all the cases we want to consider. This means that the unitary transformation

$$\hat{\boldsymbol{\mu}}(\mathbf{k}) = \sum_{\mathbf{n} \in \Lambda_N} \boldsymbol{\mu}(\mathbf{n})\, \Phi_N(\mathbf{k}, \mathbf{n}), \qquad \forall \mathbf{k} \in \Lambda_N \tag{2.5}$$

with

$$\Phi_N(\mathbf{k}, \mathbf{n}) = (2N+1)^{-3/2} \exp[2\pi i \mathbf{k} \cdot \mathbf{n}/(2N+1)] \tag{2.6}$$

will reduce the constraint Hamiltonian to the block-diagonal form

$$\beta\mathscr{H}_\chi = \beta \sum_{\mathbf{k} \in \Lambda_N} \hat{\boldsymbol{\mu}}^*(\mathbf{k}) \cdot [\lambda \mathbf{I} + \tfrac{1}{2}\hat{\mathbf{T}}_\chi(\mathbf{k}; \varepsilon')] \cdot \hat{\boldsymbol{\mu}}(\mathbf{k}) - \beta\lambda\mu^2(2N+1)^3 \tag{2.7}$$

Here $\mathbf{I}$ is the 3×3 identity matrix, and the 3×3 matrices $\hat{\mathbf{T}}_\chi$ are given by

$$\hat{\mathbf{T}}_\chi(\mathbf{k}; \varepsilon') = \sum_{\mathbf{n} \in \Lambda_N} \mathbf{T}_\chi(\mathbf{n}, \mathbf{0}; \varepsilon') \exp[2\pi i \mathbf{k} \cdot \mathbf{n}/(2N+1)] \tag{2.8}$$

To proceed further, we name the eigenvalues of $\hat{\mathbf{T}}_\chi(\mathbf{k}; \varepsilon')$ as $\{\eta_\alpha(\mathbf{k}; \chi, \varepsilon'), \alpha = 1, 2, 3\}$ and then we may evaluate the partition function. Equation (2.3) then gives

$$y = \frac{2\pi}{9} \sum_{\mathbf{k} \in \Lambda_N} \sum_{\alpha=1}^{3} \frac{1}{\lambda + \tfrac{1}{2}\eta_\alpha(\mathbf{k}; \chi, \varepsilon')} \frac{1}{(2N+1)^3} \tag{2.9}$$

This is the constraint equation for λ for the mean spherical model and the model is solvable by this simple procedure provided

$$\lambda > -\tfrac{1}{2}\eta_\alpha(\mathbf{k};\chi,\varepsilon'), \qquad \forall \mathbf{k}\in\Lambda_N, \quad 1\leqslant\alpha\leqslant 3 \tag{2.10}$$

The distribution functions are simply calculated and are

$$\frac{\langle\boldsymbol{\mu}(\mathbf{n})\,\boldsymbol{\mu}(\mathbf{n}')\rangle}{\mu^2}=\frac{2\pi}{9y}\sum_{\mathbf{k}\in\Lambda_N}\sum_{\alpha=1}^{3}\frac{\exp[2\pi i(\mathbf{n}-\mathbf{n}')\cdot\mathbf{k}/(2N+1)]}{\lambda+\tfrac{1}{2}\eta_\alpha(\mathbf{k};\chi,\varepsilon')}\frac{1}{(2N+1)^3} \tag{2.11}$$

We may now evaluate the various g-factors or fluctuation formulas. First we have

$$\begin{aligned}\frac{\langle\mathbf{MM}\rangle}{(2N+1)^3\mu^2}&=\frac{\langle\sum_{\mathbf{n}\in\Lambda_N}\boldsymbol{\mu}(\mathbf{n})\sum_{\mathbf{n}'\in\Lambda_N}\boldsymbol{\mu}(\mathbf{n}')\rangle}{(2N+1)^3\mu^2}\\&=\frac{2\pi}{9y}\sum_{\alpha=1}^{3}\frac{1}{\lambda+\eta_\alpha(\mathbf{0};\chi,\varepsilon')/2}\end{aligned} \tag{2.12}$$

and that is all we need for the case when χ is the periodic boundary condition $PBC(\varepsilon')$.

For the case of reaction field boundary conditions when $\chi = RF(\varepsilon', R_c)$ we also consider the following two g-factors which, by using the orthogonality properties of the unitary transformation, give

$$\begin{aligned}\frac{\langle\mathbf{M}_\Omega\mathbf{M}\rangle}{(4\pi/3)R_c^3\mu^2}&=\frac{\langle\sum_{|\mathbf{n}|\leqslant R_c}\boldsymbol{\mu}(\mathbf{n})\sum_{\mathbf{n}'\in\Lambda_N}\boldsymbol{\mu}(\mathbf{n}')\rangle}{(4\pi/3)R_c^3\mu^2}\\&=\left[\frac{\sum_{|\mathbf{n}|\leqslant R_c}(1)}{(4\pi/3)R_c^3\mu^2}\right]\frac{2\pi}{9y}\sum_{\alpha=1}^{3}\frac{1}{\lambda+\eta_\alpha(\mathbf{0};\chi,\varepsilon')/2}\end{aligned} \tag{2.13}$$

and

$$\begin{aligned}\frac{\langle\mathbf{M}_\Omega\mathbf{M}_\Omega\rangle}{(4\pi/3)R_c^3\mu^2}&=\frac{\langle\sum_{|\mathbf{n}|\leqslant R_c}\boldsymbol{\mu}(\mathbf{n})\sum_{|\mathbf{n}'|\leqslant R_c}\boldsymbol{\mu}(\mathbf{n}')\rangle}{(4\pi/3)R_c^3\mu^2}\\&=\frac{2\pi}{9}\frac{1}{(4\pi/3)R_c^3\mu^2}\sum_{\mathbf{k}\in\Lambda_N}H^2(\mathbf{k})\sum_{\alpha=1}^{3}\frac{1}{\lambda+\eta_\alpha(\mathbf{k};\chi,\varepsilon')/2}\end{aligned} \tag{2.14}$$

where

$$H(\mathbf{k})=\frac{1}{(2N+1)^{3/2}}\sum_{|\mathbf{n}|\leqslant R_c}\exp[2\pi i\mathbf{n}\cdot\mathbf{k}/(2N+1)] \tag{2.15}$$

Each of the above "recipes" [Eqs. (2.12)–(2.15)] has been used in the literature to calculate the g-factor. In the next section we use Eq. (2.12) to estimate the dielectric constant for $PBC(\varepsilon')$ and all three formulations to estimate the dielectric constant for $RF(\varepsilon', R_c)$.

3. RESULTS

For both $PBC(\varepsilon')$ and $RF(\varepsilon', R_c)$ the values of ε' considered were $\varepsilon' = 0,\ 1,\ \varepsilon,\ \varepsilon \pm 1,\ \infty$. The dielectric constant was calculated for values of y in the range $y = 0.5$ to $y_c \simeq 2.8$ for a variety of different N values [in the case of $PBC(\varepsilon')$] and R_c values [in the case of $RF(\varepsilon', R_c)$]. All values of y considered produced results with the same qualitative features. We have chosen $y = 2.5$ in the results presented here.

In order to analyze the results, it is appropriate to define the following two "measures" of the relative error:

$$\Delta_1(\varepsilon_1', \varepsilon_2'; N) = \frac{\varepsilon(\varepsilon_1'; N) - \varepsilon(\varepsilon_2'; N)}{\varepsilon(\infty; \infty)} \tag{3.1}$$

and

$$\Delta_2(\varepsilon'; N_1, N_2) = \frac{\varepsilon(\varepsilon'; N_1) - \varepsilon(\varepsilon'; N_2)}{\varepsilon(\infty; \infty)} \tag{3.2}$$

where $\varepsilon(\varepsilon'; N)$ is the dielectric constant. The value of $\varepsilon(\infty; \infty)$ was estimated from a least squares fit of the linear relationship between $\varepsilon(\infty; N)$ and N^{-2}.

3.1. PBC(ε')

Figure 1 shows a graph of $\varepsilon(\infty; N)$ as a function of N^{-2} at $y = 2.5$. A least squares fit of $\varepsilon(\infty; N)$ to $\alpha + \beta N^{-2}$ gives

$$\varepsilon(\infty; N) = 11.72005 - 18.2395 N^{-2} \qquad \forall N \geqslant 5 \tag{3.3}$$

Thus, the limiting value of the dielectric constant is $\varepsilon(\infty; \infty) \simeq 11.72$. Further, Eq. (3.3) indicates that surface effects have indeed been suppressed by using $PBC(\varepsilon')$. Figure 2 shows a graph of $\Delta_2(\varepsilon'; N, \infty)$ as a function of N for the six values of ε' listed above. We note that the dependence on ε' is very weak indeed.

3.2. RF(ε'; R_c)

We use the notation **MM**, $\mathbf{M}_\Omega\mathbf{M}$, and $\mathbf{M}_\Omega\mathbf{M}_\Omega$ to indicate which g-factor is being used to calculate the dielectric constant. We consider the

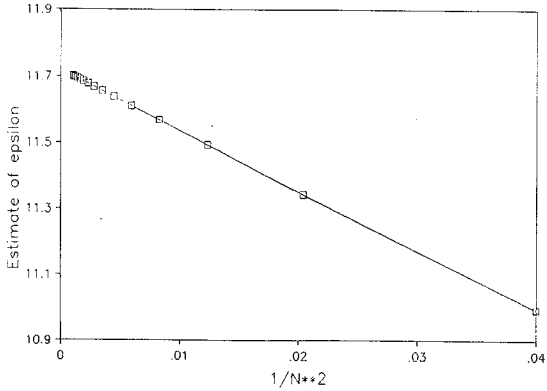


Fig. 1. Graph of $\varepsilon(\infty; N)$ versus N^{-2}.

dielectric constant as a function of cutoff radius R_c for different values of ε' at $y = 2.5$ on a lattice with side $L = 33$. Figures 3–5 illustrate the behavior of the relative dielectric constant $\Delta_2(\varepsilon'; R_c, \infty)$ under each of the three "recipes" as a function of cutoff radius R_c. All seven graphs have the same horizontal and vertical scales.

4. DISCUSSION

The results shown in Section 3 indicate that for $PCB(\varepsilon')$, $\varepsilon(\varepsilon'; N)$ is almost independent of ε'. In fact, $\Delta_1(\varepsilon_1', \varepsilon_2'; N)$ is less than 10^{-3} for side

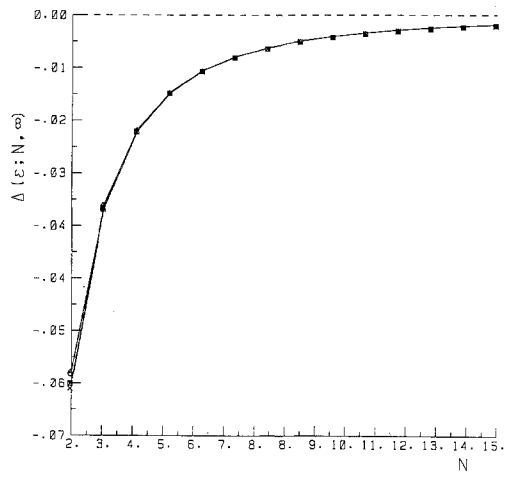
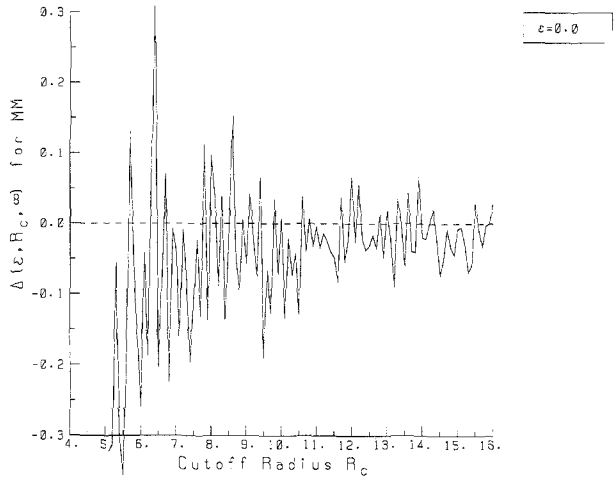


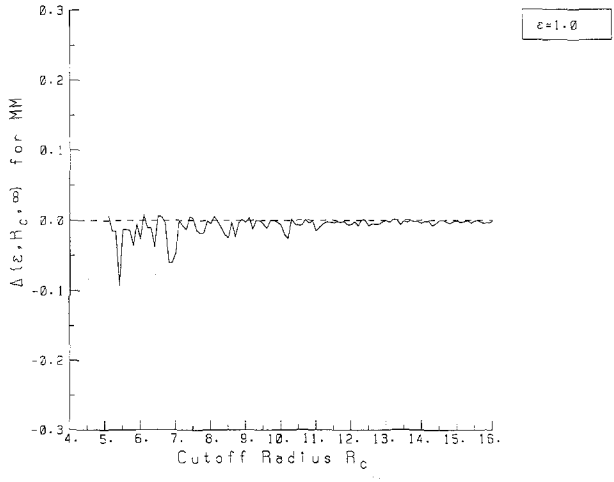
Fig. 2. Graph of $\Delta_2(\varepsilon'; N, \infty)$ versus size N for $\varepsilon' = 0, 1, \varepsilon, \varepsilon \pm 1, \infty$.

length $L \geqslant 7$. Thus, for most practical applications, the choice of ε' will not be important in the case of $PBC(\varepsilon')$, provided the boundary conditions are implemented correctly.

On the other hand, $\varepsilon(\varepsilon'; N)$ is more sensitive to the choice of the size N. The approximate relation given in Eq. (3.3) shows that the convergence to the limit is fairly slow as a function of N. In fact, to have $\Delta_2(\infty; \infty, N)$

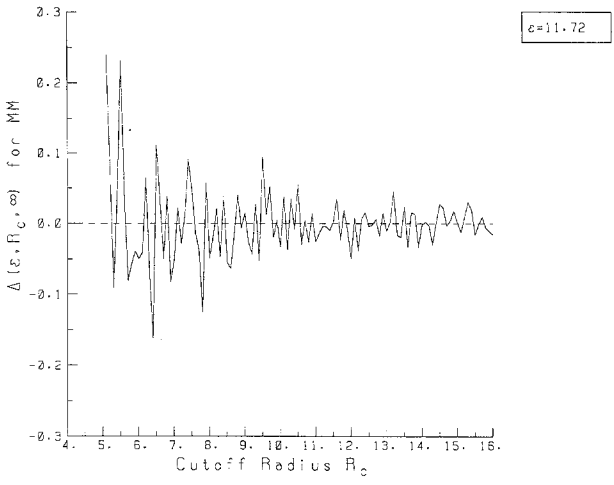


(a)

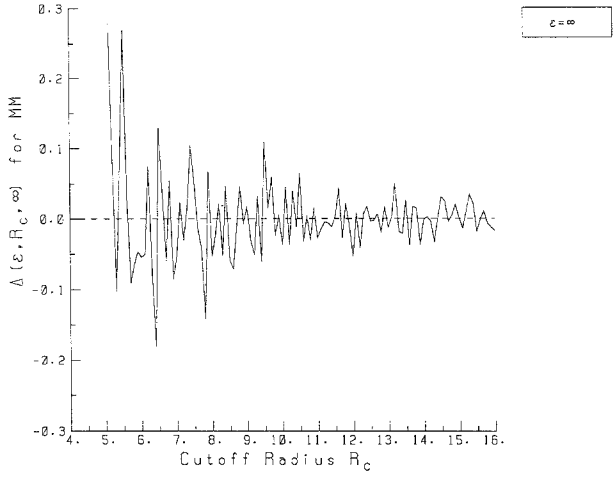


(b)

Fig. 3. Graphs of $\Delta_2(\varepsilon'; R_c, \infty)$ versus R_c at different values of ε' using the **MM** g-factor. (a) $\varepsilon' = 0.0$, (b) $\varepsilon' = 1.0$, (c) $\varepsilon' = 11.72$, (d) $\varepsilon' = \infty$.



(c)



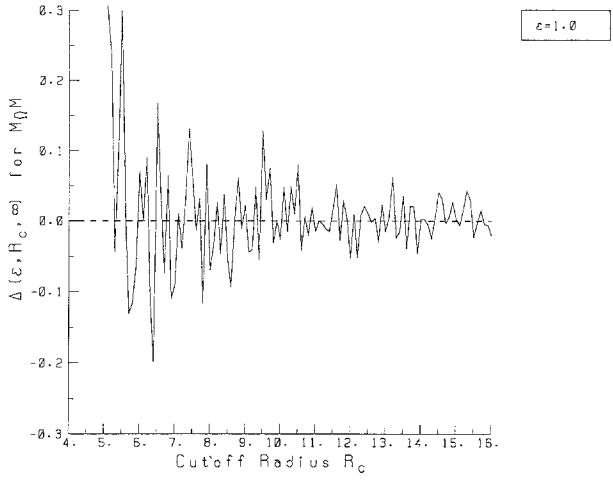
(d)

Fig. 3. (*Continued*)

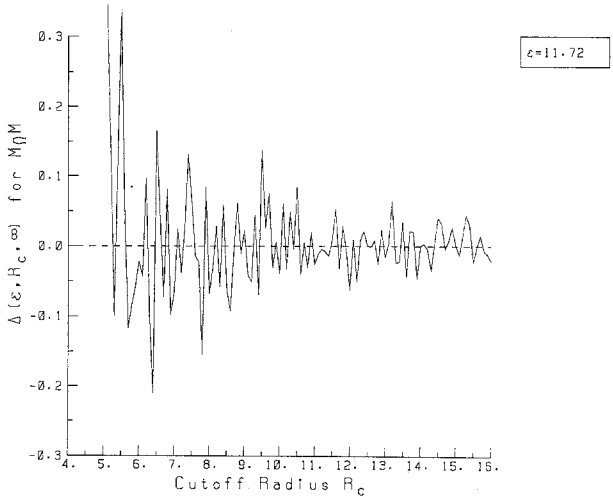
$\leqslant 10^{-2}$ requires N to be greater than 13 (20,000 dipoles). This means that for lattice systems at least, obtaining a 1% accuracy for the dielectric constant of a system from a simulation will require very much larger samples than have typically been used.

For the case of $RF(\varepsilon'; R_c)$ the dependence of the dielectric constant on ε' is much stronger than for $PBC(\varepsilon')$. $\varepsilon' = 1$ gives the fastest convergence (with cutoff) of the six ε' values considered.

For **MM**, Fig. 3 shows that $\varepsilon' = 1$ gives the fastest convergence to the dielectric constant (with cutoff). For $\varepsilon' = 0$ the dielectric constant estimates increase (on average) with cutoff radius, with estimates being 20% low for $R_c < 8$ (half the system size). For $\varepsilon' = 11.72$ and ∞, $\Delta_2(\varepsilon'; R_c, \infty)$ is less than 10% for $R_c > 8$.



(a)



(b)

Fig. 4. Graphs of $\Delta_2(\varepsilon'; R_c, \infty)$ versus R_c at different values of ε' using the $\mathbf{M}_\Omega\mathbf{M}$ g-factor. (a) $\varepsilon' = 1.0$, (b) $\varepsilon' = 11.72$.

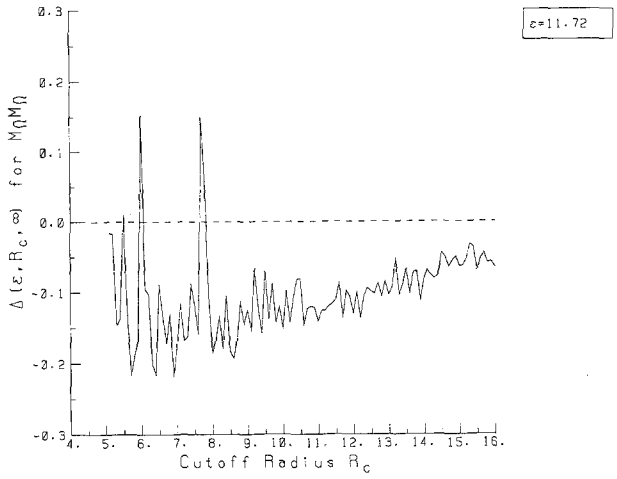


Fig. 5. Graph of $\Delta_2(\varepsilon'; R_c, \infty)$ versus R_c at $\varepsilon' = 11.72$ using the $\mathbf{M}_\Omega\mathbf{M}_\Omega$ g-factor.

For $\mathbf{M}_\Omega\mathbf{M}$, the approach to the limit is less sensitive to the choice of ε', only the $\varepsilon' = 0$ estimates differing significantly from the other ε' estimates. This observation is important because it implies that it is not necessary to know the approximate value of ε to use this recipe for the fluctuation formula. Figure 4 shows the dielectric constant estimates for $\varepsilon' = 1$ and $\varepsilon' = 11.72$. As in the case of **MM**, estimates are within 10% for $R_c > 8$.

For $\mathbf{M}_\Omega\mathbf{M}_\Omega$, the approach to the limit is poor and extremely sensitive to the choice of ε', which indicates that this route to the dielectric constant is indeed as unreliable as its "derivation" suggests. Estimates were poor for all values of ε', so only the $\varepsilon' = 11.72$ result (Fig. 5) is presented here. The values $\varepsilon' = 0, 1$ produced the worst estimates, $\varepsilon' = \infty$ gave marginally better estimates, and $\varepsilon' = 10.72, 11.72, 12.72$ gave the best results, with estimates being within 20% for $R_c > 14$ (80% of the system size).

Nonetheless, both $PBC(\varepsilon')$ and $RF(\varepsilon', R_c)$ (with **MM** or $\mathbf{M}_\Omega\mathbf{M}$) produce reasonable estimates for the dielectric constant (within 10%) provided $N \geqslant 10$ for $PBC(\varepsilon')$, or R_c is greater than half the system size and lattice side $L \simeq 30$–35 in the case of $RF(\varepsilon', R_c)$.

With $PBC(\varepsilon')$ we can ask which choice of ε' gives the most rapid convergence to the thermodynamic limit as N increases. The evidence of this model suggest that $\varepsilon' = 0$ gives most rapid convergence to the thermodynamic limit. We presume that this is because $\varepsilon' = 0$ supresses dipole moment fluctuations. We might expect this to generalize to

continuous systems, where the problem has apparently been to ensure adequate sampling of the fluctuations. This needs exploration with actual simulations of continuous systems in $PBC(\varepsilon')$.

With $RF(\varepsilon', R_c)$ we can ask which choice of ε' gives most rapid convergence to the limit as $R_c \to \infty$. This is important for large molecular systems. It seems that $\varepsilon' = 1$ gives the electrostatic response of the cutoff sphere most accurately, at least in this model.

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