Microscopic versus Macroscopic Calculation of Dielectric Nanospheres

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Abstract. The issue of nanodielectrics has recently become an important field of interest. The term describes nanometric dielectrics, i.e. dielectric materials with structural dimensions typically smaller than 100 nm. In contrast to the behaviour of a bulk material the nanodielectrics can behave completely different. With shrinking dimensions the surface or rather boundary effects outweigh the volume effects. This leads to a different observable physics at the nanoscale. A crucial point is the question whether a continuum model for the calculation of dielectric properties is still applicable for these nanomaterials. In order to answer this question we simulated dielectric nanospheres with a microscopic local field method and compared the results to the macroscopic mean field theory.

1. Introduction
In the last 10 years, more and more experiments have been performed using dielectrics with nanometric dimensions. Nanoparticles for example can be embedded in a matrix having different dielectric properties. This raises the question whether for a material, which has got a permittivity \( \varepsilon \) on a macroscopic scale, the same permittivity is preserved if the material has nanoscale dimensions, presumed that the lattice structure is not altered. Since the dielectric properties are strongly influenced by dipole-dipole interactions it seems to be obvious that in a small finite particle the magnitude of these interactions is different from those in a large extended material. Moreover, if the dielectric is placed between coplanar electrodes the lattice can virtually be extended to infinity by the image charges in the electrodes [1, 2]. In order to concentrate on the essential effects we consider in the following a dielectric sphere.

From the standpoint of the macroscopic continuum theory the sphere has a homogeneous permittivity \( \varepsilon \) and in an external field that was homogeneous before the sphere was brought in the field inside the material is also homogeneous, but reduced by the depolarisation field. Therefore, the polarisation of the sphere is homogeneous.

From the standpoint of a microscopic approach the whole sphere consists of discrete atoms with a positive nucleus and a negative electron shell which form point dipoles if a local electric field acts on them. The local field evokes a dipole moment at the atom proportional to the field itself. The local field comprises the applied field and the sum of the dipole fields of all other atomic point dipoles. Thus intuitively the local fields close to the centre of the sphere can not be the same as in the regions close to the surface, since the surroundings are different.
In our model we calculate the local field at each atom in an iterative procedure. The sum over all dipole moments yields the polarisation of the sphere which in this model turns out to be inhomogeneous.

2. Theoretical Considerations

It shall be worked out now more rigorously why there is a need for a microscopic local approach. For the macroscopic calculation the applied field $E_a$ causes a macroscopic polarisation $P$. This polarisation with its surface charges is the origin of the depolarisation field. The superposition of the applied field $E_a$ and the depolarisation field $E_{dep}$ results in the macroscopic electric field $E$ of the dielectric which feeds back on the polarisation $P$ (see figure 1). $E$ is the field which appears in Maxwell’s equations.

\[
E = E_a - \frac{P}{3\varepsilon_0}
\]  

(1)

This field $E$ is an average field which clearly deviates from the local field at the atoms. As the field $E$ is homogeneous, the same is also valid for the polarisation $P$. Thus the dipole moments have to be uniform inside the sphere. In this approach, all local fields at each atom have the same value. They evoke identical dipoles and a homogeneous polarisation.

If we apply a discrete microscopic model we come to a different conclusion. The dielectric sphere consists of atoms with positive nuclei and negative electron shells. When exposed to a local field $E_{loc}$, the atoms form point dipoles and the dipole moments $p$ become proportional to $E_{loc}$. The local field is the superposition of the applied field $E_a$ and the field $E_D$ of all other dipoles:

\[
E_{loc} = E_a + E_D
\]  

(2)

The microscopic local field approach inherently comprises all depolarisation effects. Due to reasons of symmetry, this last contribution $E_D$ cancels out in the centre of the sphere if all dipoles are identical [3]. This was already deduced by Lorentz [4]:

\[
E_D = p \cdot \sum_i \frac{2z_i^2 - x_i^2 - y_i^2}{r_i^5} = 0
\]

(3)

Using equation (3) we obtain $E_{loc}(0) = E_a$ in the centre of the sphere with $E_D = 0$. Outside the centre of the sphere, this symmetry no longer persists and the dipole fields can’t compensate each other any more. Hence, the local field in the centre of the sphere deviates from those outside the centre. The macroscopic assumption of a uniform dipole moment is wrong, as the local field varies inside the dielectric sphere. Except for the centre of the sphere we find $E_D \neq 0$ and therefore $E_{loc} \neq E_a$. Since the dipole moments are proportional to $E_{loc}$ their magnitude must vary in space and the polarisation is no longer homogeneous, which is a contradiction to the assumption. This effect may be the more
pronounced the smaller the particle is. Therefore we suggest, especially for nanosized particles, a model which inherently takes into account the local field variations.

### 3. Model Considerations

The local electric field at dipole $j$ is the linear superposition of the contributions $E_{ij}$ of all other dipoles and the applied electric field $E_a$.

$$ E_{loc}(r_j) = E_a + E_{D}(r_j) = E_a + \sum_{i=1,i\neq j}^{n} E_{ij}(r_j) $$

In this formula, the dipole fields are calculated using the far-field approximation for the dipole field. The electric field of the induced electric dipole placed at the position $r_i$ with its dipole moment $p_i$ can be approximated for the position $r_j$ by the following formula which is applied in our simulations:

$$ E_{ij}(r_j) \approx \frac{1}{4\pi\epsilon_0} \left[ \frac{3(r_j - r_i)\cdot p_i}{|r_j - r_i|^3} (r_j - r_i) - \frac{1}{|r_j - r_i|^3} p_i \right] $$

In the case of electronic polarisation the dipole moment is proportional to the local field at that dipole:

$$ p = \alpha \cdot E_{loc} $$

We use an iterative procedure to calculate the local fields and the polarisation [5]. Initially, the dipole moments equal zero. The dipoles are labelled from 1 to $N$. For an applied electric field $E_a$ a number $k$ is generated randomly and the local field at dipole $k$ is calculated from the sum of the field contributions of all other dipoles and the applied external field. The calculated local field induces a new dipole moment for dipole $k$ according to equation (6). Then a new random number is generated to pick the next dipole from the remaining $N-1$ dipoles. For this dipole the local field is calculated again, but now considering the new dipole moment of the previous dipole $k$. All dipoles are processed in this way. The polarisation $P_1$ of the whole system is calculated from the sum of all $N$ dipole moments divided by the volume $V$ of the system. This procedure is repeated 10 times yielding the 10 polarisation values $P_1 \ldots P_{10}$ of the iteration process. The iterations finally converge to a stationary polarisation $P$.

With this model we can simulate local fields at the sites of the dipoles, compute the polarisation of the whole system, and calculate the effective susceptibility for a given system.

![Figure 2](image-url)  
**Figure 2.** Discrete realisation of a dielectric nanosphere. The applied electric field has got a z-component only. The origin of the coordinate system is at the centre of the sphere. Dipoles at the surface visibly exhibit x-components in addition to their z-components.
4. Results
The identical atoms with polarizability $\alpha = 0.2$ eÅ$^2$/V are arranged on cubic lattice sites with a lattice constant of $L_C = 3$ Å. For a bulk material with $\alpha = 0.2$ eÅ$^2$/V and $L_C = 3$ Å we find the corresponding susceptibility $\chi = 2.4$ from the Clausius-Mossotti equation. The system size can become up to $N = 5000$ dipoles which corresponds to a sphere diameter $\Theta$ of 21 dipoles or rather 63 Å. The external field $E_a = 5 \cdot 10^5$ V/cm which corresponds to a macroscopic internal field $E = 2.7 \cdot 10^5$ V/cm is applied in z-direction.

Simulations for different sphere diameters clearly show that the local field and thus the dipole moments are not uniform. Figure 3 shows the z-component of the local electric field along the z-axis for $E_a = 5 \cdot 10^5$ V/cm. Figure 4 shows the z-component of the local electric field along the x-axis for $E_a = 5 \cdot 10^5$ V/cm.

The fields at the sphere boundaries vary noticeably from the electric field inside the sphere. For small spheres this effect can be very pronounced.

**Figure 3.** Local electric field $E_z$ along the z-axis. The applied field is $E_a = 5 \cdot 10^5$ V/cm. The sphere diameter $\Theta$ varies between 27 Å and 63 Å.

**Figure 4.** Local electric field $E_z$ along the x-axis. The applied field is $E_a = 5 \cdot 10^5$ V/cm. The sphere diameter $\Theta$ varies between 27 Å and 63 Å.
With increasing sphere diameter \( \varnothing \) the local field at the centre dipole becomes smaller and obviously converges towards the value of the applied external field as shown in figure 5. We fitted a first order exponential decay function with offset \( y_0 \), prefactor \( A \) and decay constant \( L \) using a least squares fitter. The extrapolation yields that for \( \varnothing > 75 \) Å the relative deviation of the field at the centre dipole from the external field is less than 1%. Figure 6 also shows the local fields outside the sphere along the \( z \)- and \( x \)-axis. Along the \( z \)-axis we find a strong amplification of \( E_z \) in front of the dielectric nanosphere in contrast to a pronounced attenuation of \( E_z \) on the sides of the sphere. Outside the sphere our calculations converge with the classical macroscopic results.

The microscopic calculation of the polarisation \( P \) yields \( P_{\text{micro}} = 5.969 \times 10^{-8} \text{ C/cm}^2 \) for \( \varnothing = 63 \) Å and \( P_{\text{micro}} = 6.024 \times 10^{-8} \text{ C/cm}^2 \) for \( \varnothing = 27 \) Å. The macroscopic calculation according to equation (7) yields \( P_{\text{macro}} = 5.933 \times 10^{-8} \text{ C/cm}^2 \) which is independent of the sphere diameter \( \varnothing \).

In addition, we find that the microstructure is significantly responsible for the increased local fields at the sphere surface. Figure 8 shows that different realisations for the shape of the sphere (see figure 7) yield extensively increased local fields at the surface. In this case the polarisation of the dielectric sphere also shows slightly higher values. It is worth mentioning that the local fields close to the centre of the sphere are not affected by these geometrical variations but depend on the sphere diameter.

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Figure 5. Local electric field \( E_z \) at the centre dipole. The applied field is \( E_a = 5 \times 10^5 \text{ V/cm} \). The sphere diameter \( \varnothing \) varies between 33 Å and 63 Å.

Figure 6. Local electric field \( E_z \) along the \( z \)- and \( x \)-axis. The applied electric field is \( E_a = 5 \times 10^5 \text{ V/cm} \). The sphere diameter \( \varnothing \) is 27 Å.
5. Conclusion

The polarisation calculated from the local field simulations show slightly higher values than the results of the macroscopic field calculations but the difference is small. On the other hand, the local electric fields noticeably differ from the macroscopic values. In fact, the local fields and thus the dipole moments aren’t uniform inside the sphere. The local field at the centre dipole isn’t equal to the applied electric field due to varying local fields and varying moments. The local field at the centre is higher than the applied field but converges to E_a for increasing sphere diameters.

Furthermore, we have to take boundary effects into consideration: The local fields at boundaries strongly depend on the microstructure of the dielectric.

With regard to dielectric nanospheres or other geometrical shapes which are used for dielectric nanocomposites the application of the microscopic local field method can calculate the actual local fields whereas a macroscopic mean field calculation yields misleading results. The macroscopic calculation of the polarisation using $E_{loc} = E_a$ yields

$$\mathbf{P} = \mathbf{n} \cdot \mathbf{E}_a$$

which actually has to be replaced by

$$\mathbf{P} = \frac{1}{V} \sum_{i=1}^{N} \mathbf{p}_i = \frac{1}{V} \sum_{i=1}^{N} \alpha \cdot E_{loc,i}$$

References

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