

## Concept of dielectric constant for nanosized systems

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(Received 30 June 2003; published 12 September 2003)

The screening properties of dielectric nanocrystals are analyzed. General arguments confirmed by detailed numerical calculations are presented. It is shown how macroscopic components of the electric field can still be defined for sizes larger than a few Fermi wavelengths and can still be obtained from the bulk dielectric function. The decrease of the average dielectric response with decreasing size is found to be due to the breaking of polarizable bonds at the surface and is not due to the opening of the band gap induced by the confinement.

DOI: 10.1103/PhysRevB.68.115411

PACS number(s): 73.22.-f, 77.22.-d

There is not yet a coherent understanding of dielectric screening in semiconductor nanostructures. Several calculations<sup>1-3</sup> of the average dielectric constant  $\epsilon_{\text{in}}(R)$  have been performed for nanocrystals which all conclude that it decreases with radius  $R$  of the spherical cluster. However, the origin of this decrease is not understood. It is often attributed to the opening of the gap which should lower the polarizability but it could as well be explained by a local reduction of the polarizability in the surface region. The relation between  $\epsilon_{\text{in}}(R)$  and the bulk wave-vector-dependent dielectric function  $\epsilon_0(\mathbf{q})$  also remains unclear. Finally, nobody knows when the macroscopic approach of such problems really breaks down. It is desirable to answer these fundamental questions for a variety of reasons: to obtain a simplified version of *ab initio* approaches like the GW approximation for quasiparticles<sup>4</sup> or the Bethe-Salpeter equations for excitons<sup>5</sup> and to calculate the quasiparticle and optical gap of quantum dots using semiempirical methods.<sup>6,7</sup> We thus present results concerning these problems. We combine two approaches: (i) general arguments based on von Laue's theorem<sup>8</sup> showing that the macroscopic response is the bulk one a few Fermi wavelengths away from the boundary and (ii) numerical calculations on Si nanostructures using the tight binding (TB) method which fully confirm the general conclusions. We show that the decrease of  $\epsilon_{\text{in}}(R)$  is not due to the opening of the gap but to a breaking of polarizable bonds at the surface. We also show that the bulk response function  $\epsilon_0(\mathbf{q})$  provides most of the needed information even for very small nanostructures.

Let us start with the formalism of dielectric screening applied to nanosized systems in view of relating it to a macroscopic formulation. We thus apply a bare perturbation  $w_b(\mathbf{r})$  which induces a change  $\delta n(\mathbf{r})$  in the electron density so that the final (screened) potential energy is

$$w(\mathbf{r}) = w_b(\mathbf{r}) + \int v(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') d\mathbf{r}', \quad (1)$$

where  $v = e^2/|\mathbf{r} - \mathbf{r}'|$ . Equation (1) can be formally condensed as  $w = w_b + v \delta n$ . To first order  $\delta n$  can be expressed as

$$\delta n(\mathbf{r}) = \int p(\mathbf{r}, \mathbf{r}') w(\mathbf{r}') d\mathbf{r}' \quad (\delta n = pw), \quad (2)$$

where  $p$  is the polarizability function. Combining Eqs. (2) and (1) one gets  $w = (1 - vp)^{-1} w_b$ . Usually  $(1 - vp)^{-1}$  is then identified with the inverse dielectric function  $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$  but it is not the correct approach in nanostructures in view of the surface polarization charges. We now follow, for instance, Ref. 9 in defining macroscopic quantities (written in capital letters) as suitable averages of the microscopic quantities defined above. More specifically we write here

$$F(\mathbf{r}) = \int g(\mathbf{r} - \mathbf{r}') f(\mathbf{r}') d\mathbf{r}', \quad (3)$$

where  $g$  is a weighting function which suppresses the short-period oscillations contained in the microscopic quantity  $f(\mathbf{r})$ . For a bulk periodic crystal, for instance, one could take the Fourier transform  $g(\mathbf{q})$  as constant within the first Brillouin zone, zero outside. We now consider that the bare perturbation is macroscopic (i.e.,  $W_b = w_b$ , corresponding to an electric field  $\mathbf{E}_b$ ) and want to express the macroscopic component of the screened field. Using the fact that Maxwell's equations remain invariant under the averaging procedure (3) we can write

$$\nabla(\mathbf{E} - \mathbf{E}_b) = -4\pi e \delta N, \quad (4)$$

where  $\delta N$  is the macroscopic average of  $\delta n$ . The main point is now to relate  $\delta n$  and thus  $\delta N$  to the macroscopic potential or field. For this we combine Eqs. (1) and (2) to get

$$w = W_b + vpw, \quad (5)$$

which can be averaged via Eq. (3) to give

$$W = W_b + \bar{v}pw, \quad (6)$$

where  $\bar{v}$  is the average of  $v(\mathbf{r}, \mathbf{r}')$  over  $\mathbf{r}$  given by Eq. (3). From the difference between Eqs. (5) and (6) we can write

$$w = W + \delta vpw, \quad (7)$$

where  $\delta v = v - \bar{v}$  is the short-range part of the Coulomb interaction. Equation (7) combined with Eq. (2) gives the desired relation between  $\delta n$  and  $W$ :

$$\delta n = p(1 - \delta v p)^{-1} W. \quad (8)$$

Equations (4) and (8) lead to a complete macroscopic formulation of the problem, the influence of the microscopic fields being taken into account in Eq. (8). To achieve the connection with the macroscopic bulk equations we make use of an important theorem due to von Laue.<sup>8</sup> This one states that the electron density recovers its bulk value at distances from boundaries of the order of a few Fermi wavelengths  $\lambda_F$ —i.e., typically the interatomic distance. In our case this means that the response function given by Eq. (8) is the bulk one inside a nanocrystal as long as its characteristic size exceeds a few  $\lambda_F$ . This seems to contradict the general belief that screening becomes less effective in nanocrystals due to the opening of the gap which increases the denominator in the polarization function  $p$ . We shall see in the following that this conclusion is confirmed by numerical calculations and how it is possible to get an overall consistent picture of dielectric screening in these systems. However, before doing this it will prove of interest to solve Eqs. (4) and (8) deep inside the nanocrystal where the response function is the bulk one. In this region we can thus find a solution as a linear combination of the bulk solutions. Considering a bare perturbation of the form  $\mathbf{E}_{bq} \exp(i\mathbf{q} \cdot \mathbf{r})$  the macroscopic field is also of this form with amplitude given by

$$\mathbf{q} \cdot \mathbf{E}_q = \epsilon_0^{-1}(\mathbf{q}) \mathbf{q} \cdot \mathbf{E}_{bq}. \quad (9)$$

Here  $\epsilon_0^{-1}(\mathbf{q})$  is the bulk inverse dielectric function given by

$$\epsilon_0^{-1}(\mathbf{q}) = 1 - \frac{4\pi e^2}{q^2 V} \int_V e^{-i\mathbf{q} \cdot \mathbf{r}} p_0 (1 - \delta v p_0)_{\mathbf{r}\mathbf{r}'}^{-1} e^{i\mathbf{q} \cdot \mathbf{r}'}. \quad (10)$$

The expression corresponds to the standard bulk formula in reciprocal space but we shall see that Eq. (9) keeps its validity even for small nanosystems.

Let us now present our numerical TB calculations. As discussed in Refs. 10 and 11 screening can be described in a simple way from the following procedure: (i) calculate the net atomic charges  $N_k$  by summing the electron population of the various orbitals on a given atom  $k$ , (ii) by considering only the diagonal on-site matrix elements of the electrostatic potential, and (iii) by taking the electrostatic potential on site  $l$  due to an electron on site  $k$  to be  $e^2/R_{kl}$  if  $k \neq l$  where  $R_{kl}$  is the interatomic distance and to the Coulomb intra-atomic term  $U$  if  $k = l$ . This leads to a formalism fully similar to Eqs. (1) and (2) except that one deals with matrix equations of size  $N \times N$  ( $N$  being the number of atoms) instead of complex integral equations. The advantage is that they can be solved for fairly large nanostructures. The TB electronic structure itself is calculated using an atomic basis composed of one  $s$  and three  $p$  orbitals for each silicon atom and one  $s$  orbital for each hydrogen saturating the surface dangling bonds. We use the TB parametrization of Ref. 12 which includes interactions up to third nearest neighbors and three

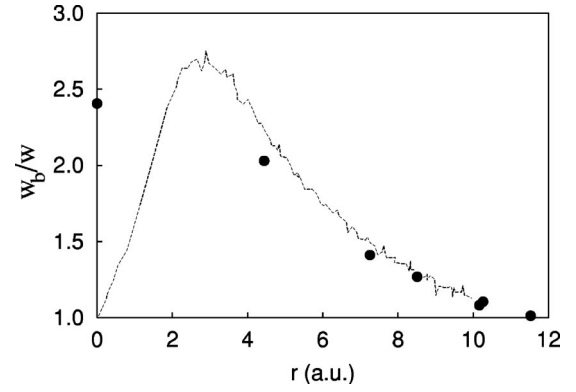


FIG. 1. Ratio between the bare ( $w_b$ ) and the screened ( $w$ ) electrostatic potentials induced by a point charge placed at the center of a  $\text{Si}_{35}\text{H}_{36}$  cluster as a function of the distance to this charge (line, *ab initio* calculations of Ref. 13; dots, present tight binding results).

center terms. It gives for bulk silicon a fairly accurate band structure and also leads to a fairly good value of the bulk dielectric constant  $\epsilon_0(\mathbf{q} \rightarrow 0) = 10.62$ .<sup>11</sup> We have also verified that TB calculations describe very well the screening in small silicon clusters by comparing our results to recent *ab initio* calculations.<sup>13</sup> For example, Fig. 1 shows that there is an excellent agreement between the two methods to predict the screened potential induced by a point charge at the center of a  $\text{Si}_{35}\text{H}_{36}$  cluster. We see that the TB procedure provides averages (over atomic volumes) which are close to the microscopic quantities. Note that we have also performed calculations for InAs nanostructures with the TB parameters of Ref. 14: they lead to the same conclusions as for Si.

We first consider the simplest case of Si thin layers with (001)-oriented planes submitted to a bare electric field  $\mathbf{E}_b$  constant in the direction parallel to the (100) planes and which can be either constant or vary as  $\sin(n\pi z/d)$  in the perpendicular direction  $z$  if  $d$  is the film thickness. In the TB procedure we treat electric fields from the finite differences between neighboring potentials. Figure 2 gives the electric field along the layer for a constant bare field  $E_b$  inside but vanishing abruptly between the terminating Si-H planes. The most striking feature of these curves is that the local dielectric constant defined as  $E_b/E$  keeps its bulk value to a high accuracy except between the last two planes. This confirms the general analysis developed before. Furthermore, on the same figure we have plotted what one would obtain by screening each Fourier component of  $E_b$  (Heaviside function) by the bulk  $\epsilon_0(\mathbf{q})$ . The agreement with the full calculation is striking even near surfaces where, however, the oscillatory behavior depends on the nature of the boundary conditions. Again this is a proof that bulk screening appropriately describes the situation even for very small thicknesses (five silicon planes).

A second interesting view of the problem is provided by Fig. 3 which gives an average of the dielectric constant over the layer thickness. For a constant field one observes an overall decrease with decreasing thickness. This is due to the surface contribution as can be judged from Fig. 2, the major effect being a decrease of the local dielectric constant from the bulk value to 1 over the last two planes. In the same

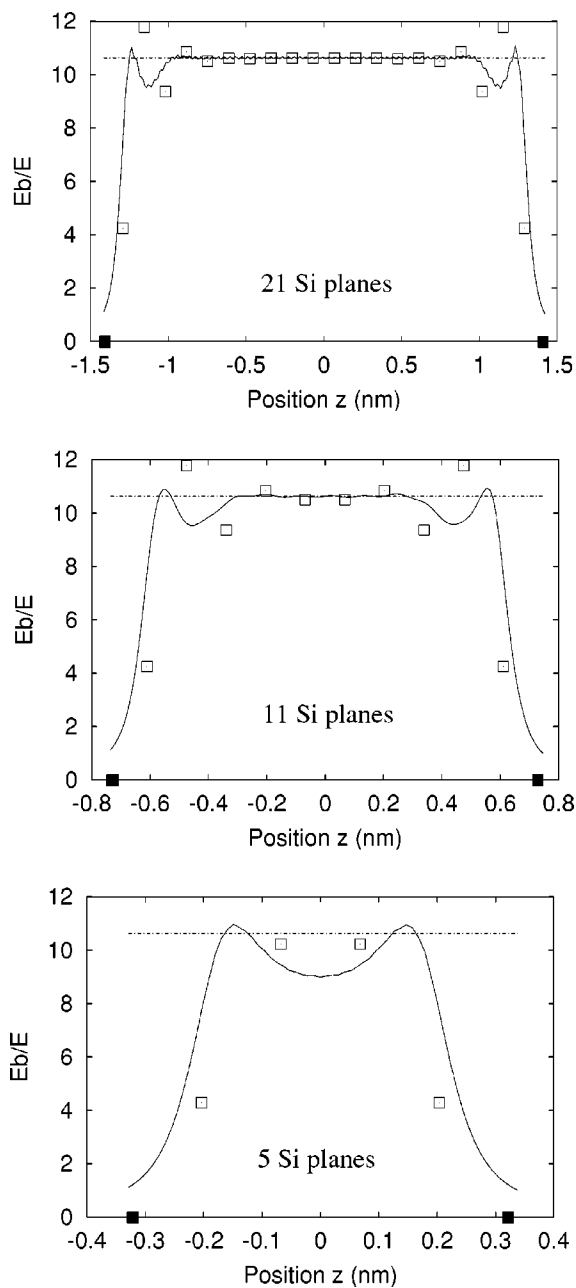


FIG. 2. Ratio between the bare electric field  $E_b$  and the screened one  $E$  in Si layers submitted to a constant electric field [ $\square$ ,  $\blacksquare$ , TB results; lines, continuous model using the bulk dielectric constant  $\epsilon_0(\mathbf{q})$ ]. In the TB procedure, the field is calculated at the middle of atomic neighboring planes by the finite difference of the potential. The results between the terminating Si-H planes ( $\blacksquare$ ) vanish because we considered a situation where  $E_b=0$  in these regions.

figure 3 we have also drawn the average dielectric constant for two sinusoidal bare electric fields  $\sin(n\pi z/d)$  with  $n=1$  and  $n=2$ . Comparison with the corresponding bulk  $\epsilon_0(\mathbf{q})$  with  $\mathbf{q}=(0,0,\pi/d)$  or  $(0,0,2\pi/d)$  leads to exact agreement since for such perturbations the surface contribution almost exactly cancels because the  $E_b$  is zero on the Si surface planes. This again represents a strong confirmation of our general analysis.

We now discuss briefly the dielectric response of spheri-

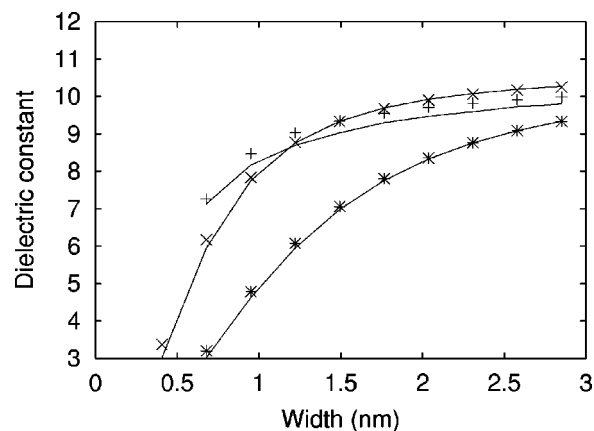


FIG. 3. Average dielectric constant calculated in TB vs layer thickness  $d$  for a bare electric field  $E_b$  which is either constant (+) or is sinusoidal [ $\times$ ,  $\sin(\pi z/d)$ ;  $*$ ,  $\sin(2\pi z/d)$ ]. Lines: model using the bulk dielectric constant  $\epsilon_0(\mathbf{q})$ .

cal crystallites which we had already treated before but not in the same context.<sup>3,11,15</sup> The situation is more difficult to analyze than the case of thin layers. However, it is possible to define a bare perturbation which can be used in common for the isolated cluster and for the bulk crystal. This consists in a charge  $+q$  on the central atom of the sphere and a neutralizing charge uniformly spread on the outer shell of silicon atoms. Figure 4 again compares the local dielectric constants obtained from the direct calculation and from the use of the bulk  $\epsilon_0(\mathbf{q})$ . Apart from some differences near the boundaries (center and surface) the results are again in close agreement. Figure 5 gives the average dielectric constant versus size calculated from different TB approaches. All of them give comparable results close to those obtained from the bulk dielectric function  $\epsilon_0(\mathbf{q})$ .

As mentioned above the basic reason for the predominance of bulk properties even at very small sizes comes from von Laue's theorem.<sup>8</sup> To check this further we have calcu-

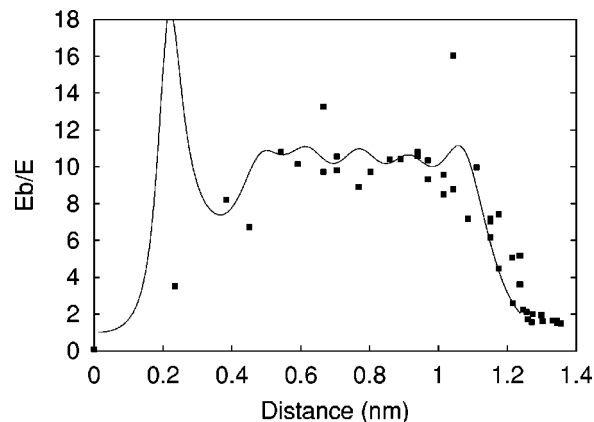


FIG. 4. Ratio between the bare electric field  $E_b$  and the screened one  $E$  vs the distance to the center in a 2.5-nm Si spherical nanocrystal. The bare field is due to a charge  $+q$  at the center and a charge  $-q$  uniformly spread on the surface of the sphere [ $\blacksquare$ , TB results; lines, continuous model using the bulk dielectric constant  $\epsilon_0(\mathbf{q})$ ].

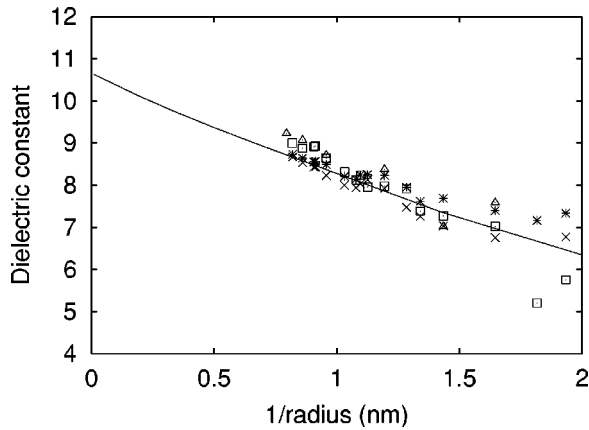


FIG. 5. Dielectric constant of Si spheres defined in different situations: average of  $E_b/E$  with a constant bare electric field  $E_b$  ( $\times$ ) or with  $E_b$  due to a charge  $+q$  at the center and  $-q$  at the surface [triangles, TB calculations; line, continuous model using the bulk dielectric constant  $\epsilon_0(\mathbf{q})$ ]; fit of the potential induced by charge  $+q$  at the center, the radius  $R$  considered as a parameter (squares).

lated the ratio of the TB nearest-neighbor interatomic polarization  $p(0,1)$  with respect to the bulk value at the center of nanostructures. We have done this for Si layers and for Si and InAs spherical nanocrystals that we have compared to the evolution of the gap  $E_g$  since it is generally believed that  $p(0,1)$  should scale roughly like  $1/E_g$ . Figure 6 strikingly shows that  $p(0,1)/p_{\text{bulk}}(0,1)$  does not deviate at all from 1 while over the same range of sizes  $E_g$  varies up to one order of magnitude. This is clear evidence of the validity of von Laue's theorem and of the fact that bulk parameters are still pertinent even for very small nanocrystals. Interestingly, the nature of the gap—direct for InAs or indirect for Si—plays no role in the evolution of the polarization with size.

At this point it is interesting to comment on Fig. 5 again. A quite similar trend was obtained in Ref. 2 from a semi-empirical pseudopotential calculation and use of the formula  $\epsilon_{\text{in}}(R) = 1 + (2/\pi) \int_0^\infty \epsilon_2(E)/E dE$  where  $\epsilon_2$  is the imaginary part corresponding to the absorption spectrum. For the bulk

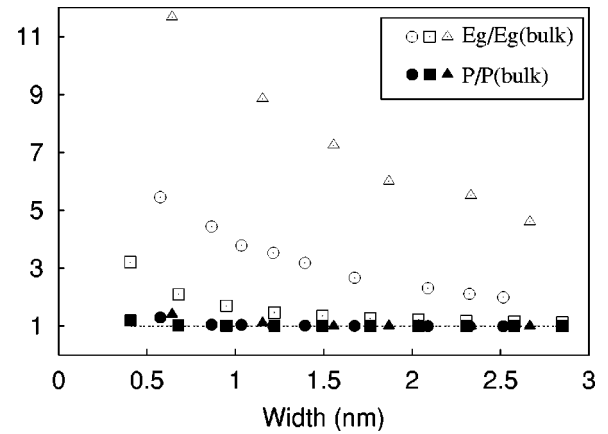


FIG. 6. Ratio of the nearest-neighbor interatomic polarization  $p(0,1)$  and of the bulk value  $p_{\text{bulk}}(0,1)$  at the center of Si layers (squares), Si spheres (circles), and InAs spheres (triangles) vs size compared to the ratio of the nanostructure gap and the bulk value.

it is a standard result that this is equivalent to Eq. (10) in the limit  $\mathbf{q} \rightarrow 0$  when neglecting local field effects [i.e., taking  $\epsilon^{-1}(\mathbf{q}, \mathbf{q}) = 1/\epsilon(\mathbf{q}, \mathbf{q})$ ] which is known to introduce an error of order 15%. In our case it is then reasonable that it gives results similar to Fig. 5 to within 15% as for the bulk. Another interesting point is that the size dependence of  $\epsilon_{\text{in}}(R)$  can be reproduced directly from the use of the bulk response function. Finally, a good representation of  $\epsilon_{\text{in}}(R)$  is obtained by assuming that one recovers the bulk dielectric constant within a sphere of radius  $R$  with a linear decrease from  $\epsilon_0$  to 1 between spheres of radius  $R$  and  $R + \Delta$ .

In conclusion we have analyzed local dielectric screening in nanostructures. General arguments as well as numerical TB calculations show that irrespective of the size one recovers locally the bulk dielectric function for the macroscopic component of the field except in a thin surface layer of the order of a few Fermi wavelengths. This provides a consistent interpretation of all their dielectric properties and shows that the decrease of the average dielectric constant with size is due to a breaking of the polarizable bonds at the surface.

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<sup>15</sup>The average dielectric constants of Si spheres given in Ref. 3 have been obtained from the fit of the electrostatic potential which actually depends on the definition of the macroscopic radius  $R$  of the spheres. Here the dielectric constant is calculated from the ratio of the bare electric field and of the screened one and thus does not depend on  $R$ , explaining why we obtain larger values than in Ref. 3.