

# Electrostatic interactions in slabs of polarizable particles

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# Electrostatic interactions in slabs of polarizable particles

H. J. H. Clercx<sup>a)</sup> and G. Bossis

Laboratoire de Physique de la Matière Condensée, Université de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice Cédex 2, France

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We present results of a study of electrostatic interactions in slabs consisting of  $L$  layers with polarizable spheres on a two-dimensional Bravais lattice in an externally applied electric field. A multipole expansion to describe  $N$ -particle electrostatic interactions, introduced by the authors in a simultaneously published paper, has been used to calculate the induced dipoles on particles in the respective layers of the slab. The conclusion is that the induced dipoles differ from their bulk values if situated near the surface, and these differences depend strongly on the internal structure of the slabs. With these results the surface energy has been calculated. Moreover, the local electric field has been studied as a function of the distance from the surface of the slab. These results are compared with a mean field approximation where each particle is considered to be surrounded by a homogeneous polarization. The differences between both models are striking.

## I. INTRODUCTION

In recent years several papers appeared concerning studies of electrorheological (ER) fluids, or magnetorheological (MR) fluids (see Ref. 1 for a recent review on ER fluids). In the past few years more insight has been gained into the structure of these fluids.<sup>2-10</sup> ER fluids consist of polarizable particles, with a high dielectric constant, immersed in a fluid with a low dielectric constant. If an electric field is applied to these fluids, induced dipoles arise on the particles which will attract each other if their interparticle axis is parallel to the applied field and repel each other if their interparticle axis is perpendicular to the applied field. It is not surprising that in electrorheological suspensions, with a high volume fraction of dispersed particles, structures will arise if a large external electric field is applied. The process of structure formation in ER fluids is described in a paper by Halsey and Toor.<sup>2</sup> They considered two parallel electrodes with a fixed potential difference; in the first instance chains and columns arise between the electrodes. In that paper they have made an estimation of the column width using the idea of a competition between the bulk energy and the surface energy. After a relaxation process the columns drift together to complete a phase separation process. It is interesting to note that differences exist between ER and MR fluids. An important reason is the difference of the boundary conditions, a constant potential on the parallel plates in an ER fluid (thus, existence of image dipoles) and a constant magnetic field in the case of a MR fluid. In an article of Lemaire *et al.*,<sup>5</sup> a simple model has been used where the structures in MR fluids are approximated by ellipsoidal aggregates of particles which are well separated of each other at low volume fractions ( $\phi < 10\%$ ). Their experiments seem to confirm

this model. The average diameter of these structures can be predicted by taking into account the repulsive interactions between these elongated aggregates.<sup>6</sup> In the electrorheological case ellipsoidal aggregates can also arise, but on a short time scale they will connect the plates and, due to image forces on the plates, they are quickly pulled into a cylinder.<sup>2</sup>

Besides this mesoscopic structure in the ER fluid itself, a study of the internal structure, or microscopic structure, of the columns is worthwhile. Recently Tao and Sun proposed a theoretical model for the structure of these columns<sup>9</sup> which has been supported with experimental evidence by a study of Chen *et al.*<sup>10</sup> They have studied the electric field induced columns using a light scattering technique. It should be emphasized that the theoretical calculations of Tao and Sun are based on a so-called dipole approximation (a lowest order calculation of dipolar interaction energies between the particles in an ER fluid). Accurate calculations of dipolar interaction energies of different structures, including the so-called multipole moments, give, in general, values which differ by approximately 10% with results obtained from a dipolar approximation (see this paper which provides a method to determine dipolar interaction energies very accurately). The dipolar interaction energies for different structures, calculated by Tao and Sun using a dipole approximation, differ by less than 10%; therefore, one should be careful in drawing conclusions (see, in this context, the discussion of this point in a recently published paper by Davis<sup>11</sup>). Nevertheless, experiments suggest that their claim, that the internal structure of the columns can be described by a body-centered tetragonal lattice, is correct.

We already pointed out that ER fluids are concentrated suspensions. In these suspensions not only electrostatic interactions play a role, but also hydrodynamic interactions. Actually, it is the balance between

<sup>a)</sup>Present address: Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

hydrodynamic and electrostatic forces (represented by the Mason number) which will determine the rheological properties of these fluids. To handle hydrodynamic interactions in concentrated suspensions is an extremely difficult task because these interactions are long ranged and nonadditive. The same remarks can be made about electrostatic interactions although this problem seems mathematically and numerically easier to tackle. Of course, a combination of both interactions in, e.g., sheared ER fluids is difficult to treat theoretically. In recent years another method has been developed to study these systems. It is a molecular-dynamics-like method to simulate systems of Brownian particles where hydrodynamic interactions play an important role.<sup>12</sup> This method has also been used by Bonnecaze and Brady to simulate sheared electrorheological suspensions.<sup>13</sup> In that study it was possible to take into account both electrostatic and hydrodynamic interactions.

In this paper we present the results of a theoretical study about surface effects on the induced dipoles of particles near the surface of a slab with some prescribed internal structure. For the calculation of the induced dipole moments we use a method to study  $N$ -particle electrostatic interactions which has been presented by the authors in a simultaneously published paper.<sup>14</sup> These slabs consist of a small number of layers composed of spherical, polarizable particles on a two-dimensional square or hexagonal Bravais lattice. In this paper results are presented concerning the cubic case only. In the cubic case the repetition of the layers is such that, after infinite extension in the third dimension, a sc lattice or a bcc lattice is obtained. Slabs with this property will be denoted in this paper to have a local sc lattice structure or a local bcc lattice structure. We shall show that striking differences between the different lattice structures exist for the induced dipoles on the particles near the surface, or for the local electric field near the surface. Recently, Toor and Halsey have treated the surface energies of a variety of lattices within the constant dipole approximation.<sup>15</sup> Their results also show a strong structure dependency of the surface energy. There are also striking differences when we compare our results obtained with the discrete structure to those obtained with a mean field theory. These differences arise already in the dipole approximation and are not a result of the incorporation of higher order multipole moments (see also Ref. 15 in the case of the constant dipole approximation). These multipole moments are necessary if accuracy is needed in the calculation of physical quantities related with the properties of concentrated electrorheological suspensions. They are indeed important as has been shown by McPhedran and McKenzie,<sup>16</sup> and by Sangani and Acrivos,<sup>17</sup> who have studied cubic lattices of conducting spheres. In particular, we shall show that the use of a mean field theory to calculate the surface energy (and then the size of the ellipsoidal aggregates in ER or MR fluids<sup>2,6</sup>) overestimates the surface energy relative to the discrete cubic or hexagonal arrangement. It is obvious that we have considered a very pure case, a flat boundary, and high internal symmetry in the slab, which cannot directly be compared with ellipsoids. Furthermore, it may be expected that the particles

are more or less randomly positioned in the ellipsoidal aggregates. However, we expect that our results will give a good qualitative understanding of surface effects for non-flat boundaries which are large in comparison with the particle diameter.

This paper is generally concerned with results and discussions. We have kept the detailed theoretical calculations to a minimum. A summary of the theoretical method, used to determine the induced dipole moments for the problem under consideration, is presented in Sec. II. Results are presented in Secs. III–V where we have focused on two aspects. First, the study of the local electric field at the boundaries of a slab (Sec. III) and, secondly, the change of the induced dipoles from the bulk to the boundary (Sec. IV). In Sec. V results are presented for the change of the local electric field when we approach the surface of the slab. In this case an exact calculation has been performed. Furthermore, some exact results for the surface energy are presented. We then end with some conclusions.

## II. THEORETICAL METHOD TO STUDY ELECTROSTATIC INTERACTIONS IN SLABS

In a simultaneously published paper (hereafter referred to as paper I) we have presented a method to study many-particle electrostatic interactions.<sup>14</sup> In this paper we use that method to study electrostatic interactions in slabs of polarizable particles. We consider the problem of slabs consisting of  $L$  layers, each layer having an infinite number of spherical particles disposed on the lattice sites, in an unbounded fluid. The dielectric constant of the particles is  $\epsilon_p$  and the one of the fluid is  $\epsilon_f$ . Each particle inside one of the specified layers is translationally equivalent. All the particles have the same radius  $a$  and they have position vectors  $\mathbf{R}_i$  with respect to an arbitrary chosen origin. A constant external electric field is applied to the slab.

In paper I we have determined a set of linear algebraic equations appropriate to describe the problem of spherical polarizable particles in an externally applied electric field. This set of equations has the form

$$\begin{aligned} & \beta_1 a^3 \delta_{p,1} [n_{10} E_{0x} \delta_{q,0} - \frac{1}{2} n_{11} (E_{0x} - iE_{0y}) \delta_{q,1} \\ & \quad + \frac{1}{2} n_{11} (E_{0x} + iE_{0y}) \delta_{q,-1}] \\ & = \frac{4\pi}{2p+1} Q_{pq}^j + \beta_p a^{2p+1} \frac{n_{pq}}{(p+q)!} \\ & \quad \times \sum_{j \neq i} \left( \sum_{l \geq 0} \frac{4\pi}{2l+1} Q_{lm}^j M_{lm,pq}^j(\mathbf{R}_{ij}) \right), \end{aligned} \quad (2.1)$$

with  $E_{0x}$ ,  $E_{0y}$ , and  $E_{0z}$  the components of the externally applied electric field, the constants  $n_{pq}$  (and  $n_{10}$  and  $n_{11}$ ) are a shorthand notation for

$$n_{pq} = \left( \frac{4\pi}{(2p+1)} \frac{(p+q)!}{(p-q)!} \right)^{1/2}. \quad (2.2)$$

The function  $M_{lm,pq}^j(\mathbf{R}_{ij})$  is obtained from the general form of the Hobson formula expressing a solid spherical harmonic, defined with respect to an origin  $O_j$ , in terms of

solid spherical harmonics defined with respect to the origin  $O_i$  (see, for a discussion, Refs. 18 and 19) and has the form

$$M_{lm;pq}^{ji}(\mathbf{R}_{ij}) = (-1)^{p+q} \frac{(l+p-m+q)!}{n_{lm}(l-m)!} n_{l+p,m-q} \times \frac{Y_{l+p,m-q}(\xi_{ij}, \eta_{ij})}{R_{ij}^{l+p+1}}, \quad (2.3)$$

with  $\xi_{ij}$  and  $\eta_{ij}$  being the polar and azimuthal angles of the vector  $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ . The coefficients  $\beta_p$  and  $\beta_1$  are shorthand notations for

$$\beta_p = \frac{p(\alpha-1)}{[p(\alpha+1)+1]}. \quad (2.4)$$

Finally, the multipole moments  $Q_{pq}^i$  are defined as<sup>20</sup>

$$Q_{pq}^i = \int_{V_i} Y_{pq}^*(\theta, \varphi) r^p \rho(\mathbf{r}) dV, \quad (2.5)$$

with  $V_i$  the volume of particle  $i$  and  $\rho(\mathbf{r})$  the charge density inside particle  $i$ . The electrostatic interactions are uniquely determined by the configuration of the particles, i.e., only depend on the geometry. Consequently, the induced dipole moments  $\mathbf{M}_i$  depend on the relative particle positions. This means that all the induced dipole moments on the particles in a particular layer are equal. Keeping this in mind we are able to simplify the infinite particle problem into an  $L$ -particle problem, with  $L$  the number of layers in the slab. Furthermore, the layers whose position is symmetric relative to the center of the slab will also have the same induced polarization. We denote the layers with the Greek letters  $\nu$  and  $\mu$ ,  $\nu, \mu \in \{1, \dots, L\}$  and introduce the generalized multipole moments  $\{A_{\nu,lm}^{\pm}\}$  via the transformations,

$$Q_{lm}^i \pm (-1)^m Q_{l,-m}^i = \frac{2l+1}{4\pi} n_{lm} a^{l+2} (-1)^{l+m} A_{\nu,lm}^{\pm},$$

$$A_{\nu,l,-m}^{\pm} = \pm (-1)^m \frac{(l+m)!}{(l-m)!} A_{\nu,lm}^{\pm}, \quad (2.6)$$

where we emphasize that particle  $i$  is situated on layer  $\nu$ . We see from the relations, for the generalized multipole moments  $\{A_{\nu,lm}^{\pm}\}$ , that it is sufficient to use the plus coefficients,  $A_{\nu,lm}^+$  etc., with  $m \geq 0$  and the minus ones,  $A_{\nu,lm}^-$  etc., with  $m > 0$  only. We do not present the total derivation of the rewritten set of linear equations but the final result only. For each layer  $\nu$  we obtain the following set of equations:

$$-\beta_1 \delta_{p,1} (2E_{0z} \delta_{q,0} + E_{0x} \delta_{q,1})$$

$$= A_{\nu,pq}^+ + \beta_p \sum_{\mu} \sum_{\substack{l \geq 0 \\ m \geq 0}} X_{lm;pq}^{\mu,R+} A_{\mu,lm}^+$$

$$+ i\beta_p \sum_{\mu} \sum_{\substack{l \geq 1 \\ m \geq 1}} X_{lm;pq}^{\mu,I-} A_{\mu,lm}^- \quad (2.7)$$

$$i\beta_1 \delta_{p,1} E_{0y} \delta_{q,1} = A_{\nu,pq}^- + \beta_p \sum_{\mu} \sum_{\substack{l \geq 1 \\ m \geq 1}} X_{lm;pq}^{\mu,R-} A_{\mu,lm}^-$$

$$+ i\beta_p \sum_{\mu} \sum_{\substack{l \geq 0 \\ m \geq 0}} X_{lm;pq}^{\mu,I+} A_{\mu,lm}^+ \quad (2.8)$$

In these equations we have introduced the shorthand notations

$$X_{lm;pq}^{\mu\{\pm\}} = \sum_{j \in \mu} \{r_{lm}^{\text{Re}}\} [P_{lm;pq}^{\pm j0}] x_{0j}^{l+p+1}, \quad (2.9)$$

with  $x_{0j} = a/R_j$ . These sums are modified two-dimensional lattice sums. We distinguish between two kinds of lattice sums. The first one is a lattice sum with the reference point in the plane of summation; the second one is a lattice sum with the reference point in another plane than the plane of summation. Furthermore, we have introduced the following shorthand notations which have already been introduced in several other papers, e.g., for the study of three particle hydrodynamic interactions in random suspensions:<sup>18</sup>

$$P_{lm;pq}^{\pm ji} = (1 - \frac{1}{2} \delta_{m,0}) \frac{(-1)^{l+p+m+q}}{(p+q)!} n_{lm} R_{ij}^{l+p+1}$$

$$\times (M_{lm;pq}^{ji}(\mathbf{R}_{ij}) \pm (-1)^m M_{l,-m;pq}^{ji}(\mathbf{R}_{ij})). \quad (2.10)$$

It is noteworthy to emphasize that the special functions  $P_{lm;pq}^{\pm ji}$  are functions of the polar and azimuthal angles  $\xi_{ij}$  and  $\eta_{ij}$  only.

The set of linear equations presented earlier has a form suitable for computations, but is not very transparent. However, our set of linear equations (2.1) is, after a suitable reformulation, equivalent to the following matrix equation, which is comparable to the matrix notation introduced in paper I (Secs. II and III):

$$\begin{pmatrix} \mathbf{E}_1 \\ \vdots \\ \mathbf{E}_\nu \\ \vdots \\ \mathbf{E}_L \end{pmatrix} = \begin{pmatrix} Z_{11} & \cdots & Z_{1L} \\ \vdots & Z_{\nu\mu} & \vdots \\ Z_{L1} & \cdots & Z_{LL} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{Q}_1 \\ \vdots \\ \mathbf{Q}_\mu \\ \vdots \\ \mathbf{Q}_L \end{pmatrix}, \quad (2.11)$$

with  $\mathbf{Q}_\mu$  the vector of multipole moments of one of the particles in layer  $\mu$ ,  $\mathbf{Q}_\mu = (Q_{\mu,00}, Q_{\mu,1m}, Q_{\mu,2m}, \dots)$ ,  $\mathbf{E}_\nu$  the vector of the moments of the applied electric field,  $\mathbf{E}_\nu = (0, E_{1m}, 0, \dots)$ . The index  $\nu$  is superfluous because the externally applied electric field is assumed to be constant, i.e., independent of particle position. A given submatrix  $Z_{\nu\mu}$  contains the infinite sum of the interactions between all the particles of the plane  $\mu$  with a representative one of the plane  $\nu$ .

In principle, it is possible to partially solve the set of linear algebraic equations if we express all generalized multipole moments  $A_{\mu,lm}^{\pm}$  with  $l \geq 2$ ,  $|m| \leq l$  and all  $\mu$ , in terms of the moments  $\{A_{\mu,10}^+, A_{\mu,11}^+, A_{\mu,11}^-\}$ . These remaining generalized multipole moments are related with the components of the induced dipole moments on a particle situated on layer  $\mu$  via the relations

$$A_{\mu;10}^+ = -\frac{2}{a^3} M_{\mu,z} \quad A_{\mu;11}^+ = -\frac{1}{a^3} M_{\mu,x}$$

$$A_{\mu;11}^- = \frac{i}{a^3} M_{\mu,y}, \quad (2.12)$$

where we have used Eq. (3.13) of paper I and Eq. (2.6). We use the notation  $M_\mu$  to denote the induced dipole moment on a particle in layer  $\mu$ . We are now able to calculate (numerically) the components of the grand potential matrix [Eq. (2.7) of paper I].

The presented set of linear algebraic equations can be simplified considerably by implementing the additional symmetries of the two-dimensional lattice. One of the lattices we have studied is the square lattice. It is not difficult to show that the two-dimensional lattice sums [Eq. (2.9)] are nonzero only if the following relation exists between the azimuthal indices  $m$  and  $q$ , namely,  $m = q + 4n$ , with  $n$  an integer. Furthermore, it can be shown that these lattice sums are real. If we use these properties of this lattice sum we can rewrite the set of linear equations (2.7) and (2.8), and it can be shown that three independent sets of linear equations are obtained. Each set is related with one of the components of the externally applied electric field. Consequently, it is possible to study separately the two cases where an applied electric field is imposed parallel to and perpendicular to the planes of the slab respectively.

Finally, we want to make some remarks concerning the lattice sums. We have used the technique of Nijboer and de Wette to calculate the two-dimensional lattice sums.<sup>21</sup> We have to distinguish two separate cases. First we have to determine the lattice sum with a reference lattice point in the plane itself. In this summation we have to exclude that reference lattice point. These lattice sums can be calculated very accurately with the Nijboer and de Wette method. The second kind of summation is more difficult to handle. The reference lattice point is in another layer of the slab (thus no exclusion of lattice points in the summation). We expect that a proper mathematical formulation like that of the Nijboer and de Wette's exists to accelerate convergence of the lattice sums. Nevertheless it is possible to use an approximate method to accelerate the convergence of the sums. With this method we obtain very accurate values of the lattice sums if the origin is not too far from the layer in which the sums are done. In three-dimensional lattice sums it is generally known how to use the Nijboer and de Wette method and the results of these sums for the sc and the bcc lattice are used to check our two-dimensional lattice sum calculations. We find that they are indeed in excellent agreement with these three-dimensional sums. Furthermore, it is interesting to emphasize that the electrostatic interactions between layers  $\nu$  and  $\kappa \neq \nu$ , with  $\kappa \geq 4$ , are negligible (which is partially reflected in the lattice sums themselves). Consequently, we only have to incorporate the lattice sums with  $\kappa \in \{0, 1, 2, 3\}$ ; thus we may use our approximate method.

### III. LOCAL ELECTRIC FIELD AT THE SURFACE: A CONSTANT DIPOLE APPROXIMATION

As a first approach to estimate the change of the local field at the surface of a dielectric medium, we can assume that the polarization does not vary when we approach the surface. In that case we have the same dipole on each particle and we can calculate the local field inside the slab or at its surface. Of course, this is not a self-consistent approximation, but it is helpful to understand what happens in the real case which is treated in Sec. IV.

Consider a slab with thickness  $(L-1)d$ , with  $L$  the number of layers in the slabs consisting of spherical particles and  $d$  the layer thickness. For convenience we assume that  $L$  is odd. The  $xy$  plane is defined to be parallel to the layers. First we have studied the case of a slab consisting of homogeneous material of thickness  $(L-1)d$ . Suppose we apply an external electric field parallel to the  $xy$  plane. The material will be polarized. The local electric field inside a spherical cavity in the slab can be determined easily.<sup>20</sup> The result is (using Gaussian units)

$$\mathbf{E}_{v,\text{loc}} = \mathbf{E}_0 + \frac{4\pi}{3} \mathbf{P}, \quad (3.1)$$

with  $\mathbf{E}_0$  the external electric field and  $\mathbf{P}$  the polarization per unit volume of the material under consideration. The local electric field inside a half spherical cavity on the surface of the slab is

$$\mathbf{E}_{s,\text{loc}} = \mathbf{E}_0 + \frac{2\pi}{3} \mathbf{P}. \quad (3.2)$$

From this simple analysis it is assumed that the local field exerted on particles situated on the surface of a slab should be a factor  $(2\pi/3)\mathbf{P}$  lower than the bulk local electric field. An analogous conclusion can be made if we consider an electric field perpendicular to the slab.

Suppose we have the same slab, but now with spherical, polarizable particles on the lattice sites. We apply an external electric field parallel to the  $x$  axis. Assume that all the induced dipoles have the same value,  $\mathbf{M}_i = R^3 \mathbf{P}$  for the sc lattice (with  $R^3$  the volume of the sc unit cell) and  $\mathbf{M}_i = \frac{1}{2} R^3 \mathbf{P}$  for the bcc lattice (with  $\frac{1}{2} R^3$  the volume of the bcc unit cell). These dipoles are also parallel to the applied field. The polarization  $\mathbf{P}$  is in both cases consistent with its definition as dipole moment per unit volume. At a lattice site we have a local electric field which is composed of the external field and the field of all induced dipoles. The electric field of a dipole, oriented in the  $x$  direction is

$$\mathbf{E}(\mathbf{r}) = \frac{4\pi}{3n_{11}} \frac{M_x}{r^3} [\mathbf{B}_{1,1}(\theta, \varphi) - \mathbf{B}_{1,-1}(\theta, \varphi)], \quad (3.3)$$

with  $\mathbf{B}_{1,1}(\theta, \varphi)$  and  $\mathbf{B}_{1,-1}(\theta, \varphi)$  special cases of the vector spherical harmonics  $\mathbf{B}_{lm}(\theta, \varphi)$ :

$$\mathbf{B}_{lm}(\theta, \varphi) = -(l+1) Y_{lm}(\theta, \varphi) \hat{\delta}_r + \frac{\partial Y_{lm}(\theta, \varphi)}{\partial \theta} \hat{\delta}_\theta$$

$$+ \frac{1}{\sin \theta} \frac{\partial Y_{lm}(\theta, \varphi)}{\partial \varphi} \hat{\delta}_\varphi. \quad (3.4)$$

TABLE I. The values of  $\langle E(\mathbf{r}) \rangle_{\nu+\kappa}$ , normalized by  $4\pi P_x/3$ , for the sc and the bcc lattice. The reference point is situated in layer  $\nu$ . In the case  $\kappa=0$ , one should expect the same value for both lattices (the same lattice sum), however, due to normalization all values for the bcc lattice are a factor of 2 smaller.

$\kappa$	sc	bcc
0	+1.078 309 2	+0.539 154 6
1	-0.039 088 2	+0.249 259 8
2	-0.000 066 2	-0.019 544 1
3	-0.000 000 1	+0.000 738 8
4	-0.000 000 0	-0.000 033 1
5	-0.000 000 0	+0.000 001 4
6	-0.000 000 0	-0.000 000 1

The  $\hat{\delta}_r$ ,  $\hat{\delta}_\theta$ , and  $\hat{\delta}_\varphi$  are unit vectors in a spherical coordinate system. More details and references about these vector functions can be found in Ref. 19. Due to the isotropy of square or hexagonal lattice sites, the field resulting from a sum of the local fields coming from the dipoles located in the  $\mu$  plane will be parallel to the external field (assumed to be the  $x$  direction):

$$\langle E(\mathbf{r}) \rangle_{x,\mu} = -M_x \left\langle \frac{n_{20} Y_{20}(\theta, \varphi)}{r^3} \right\rangle_{\mu}, \quad (3.5)$$

where  $\langle \rangle_{\mu}$  denotes a lattice summation in plane  $\mu$ . Suppose we want to know the local field in layer  $\nu$ . The result is

$$E_{loc,\nu} = E_{0x} + \langle E(\mathbf{r}) \rangle_{x,\nu} + \sum_{\mu \neq \nu} \langle E(\mathbf{r}) \rangle_{x,\mu}. \quad (3.6)$$

We have calculated the two-dimensional lattice sums for different layers  $\mu$  and for several lattice structures, i.e., the local simple cubic and local hexagonal structure. Furthermore we considered a slab with a local bcc structure. In that case the respective layers are shifted over a half lattice parameter in the  $x$  and  $y$  direction. In Table I we present the results for the local simple cubic lattice structure and of the local body centered cubic lattice structure. The results for the local hexagonal lattice structure are comparable to those for the simple cubic structure and are not presented here. The contribution of the layers,  $\langle E(\mathbf{r}) \rangle_{x,\mu}$ , is normalized by the factor  $(4\pi/3)P_x$ . The inversion symmetry of the spherical harmonic  $Y_{20}(\theta, \varphi)$  causes the equality of the lattice sums for the layers  $\nu-\kappa$  and  $\nu+\kappa$ . If the number of layers  $L$  is large and if we are far from the boundaries (more than three layers from the boundary) we see from Table I that the sum of the field coming from the layer  $\nu$  itself plus the field of the immediate surrounding layers gives back the mean field result

$$E_{u,loc}^{sc} = E_{0x} + \frac{4\pi}{3} P_x, \quad E_{v,loc}^{bcc} = E_{0x} + \frac{4\pi}{3} P_x, \quad (3.7)$$

the values expected from studies of three-dimensional cubic lattices. On the other hand, we have for the local field at the boundaries (a sum of the values in Table I),

$$E_{s,loc}^{sc} = E_{0x} + \frac{4\pi}{3} P_x + 0.164 P_x, \quad (3.8)$$

$$E_{s,loc}^{bcc} = E_{0x} + \frac{4\pi}{3} P_x - 0.965 P_x, \quad (3.9)$$

$$E_{s,loc}^{hom} = E_{0x} + \frac{4\pi}{3} P_x - 2.094 P_x. \quad (3.10)$$

Equation (3.10) is a rewritten version of Eq. (3.2) for the homogeneous case. We see large differences if we compare the homogeneous slab with the sc slab, the local field at the boundary of the sc slab is even larger than the bulk value. This anomalous behavior has recently also been pointed out by Toor and Halsey.<sup>15</sup> Comparable results can be obtained for the hexagonal lattice. The local field at the boundary of the bcc slab is lower than the bulk field as in the homogeneous case, but the difference between the volume and the surface fields is still two times smaller than for the homogeneous case.

In this section we used the assumption of constant induced dipoles on the particles independent of the position of the particles with respect to the boundary. The same assumption is used by Toor and Halsey concerning the calculation of the surface energy.<sup>15</sup> It is not difficult to reproduce these results with the method used in this section. We can calculate the local field in a particular layer  $\nu$  and express it in a way showing explicitly the difference with the bulk value of the local field,  $E_{loc,\nu} = E_{u,loc} + \chi_\nu P_x$ . The summation of  $\chi_\nu$  over all layers (in practice only the first few layers from the boundary), and further using the procedure of Toor and Halsey for close packed structures, easily give the final results for the surface energy. For the sc lattice we obtain  $-2.567 02 \times 10^{-3}$  and for the bcc structure  $1.353 51 \times 10^{-2}$  (both in units of  $\epsilon_f M_x^2/a^5$ ), in perfect agreement with the results presented in Ref. 15 (see column 1 in Table II).

In Sec. V we shall return to this problem and present exact results of a study of the local electric field at the boundary of slabs and of the surface energy in slabs.

#### IV. RESULTS FOR DIPOLE VARIATION IN SLABS

The results presented in Sec. III are, of course, approximations but we see that the local field at the boundary depends strongly on the internal structure. We may expect the same behavior for the induced dipoles if we consider them more carefully because these dipoles are not *a priori* equal, but depend on the layer in which the particle is situated. Two important modifications should be incorporated in the calculations. The first one, as already pointed out, is the fact that the dipoles induced on different layers are not equal, but can be determined by the solution of Eqs. (2.7) and (2.8). The second one is the inclusion of higher order multipole moments in the calculation of the grand potential matrix  $\Pi$  [Eq. (2.7) of paper I], and related with the potential matrix the calculation of the induced dipoles (via the capacitance matrix<sup>13</sup>).

In this section we present results about calculations of the induced dipoles for two internal structures, several lattice parameters (or volume fractions  $\varphi$ , which is only defined inside the slabs), and several values of  $\alpha$ , the ratio between the particle and fluid dielectric constant. With

TABLE II. The normalized induced dipoles on particles at the boundary layer of a sc slab for several values of  $\alpha$  and  $\varphi$ . The external field is in the  $x$  and  $z$  direction, respectively. The bulk value of the induced dipole moment, normalized with the one particle induced dipole moment in the same external field, is given in the last column (external field in the  $x$  direction).

$\alpha$	$\varphi$	$\tilde{M}_{1x}$	$\tilde{M}_{1z}$	$M_\rho$
$\infty$	0.30	1.0129	0.9808	1.4810
	0.40	1.0147	0.9701	1.8855
	0.45	1.0141	0.9611	2.2836
	0.50	1.0113	0.9442	3.2609
10.0	0.30	1.0092	0.9850	1.3152
	0.40	1.0106	0.9774	1.5160
	0.45	1.0105	0.9718	1.6688
	0.50	1.0095	0.9630	1.9063
5.0	0.30	1.0068	0.9882	1.2199
	0.40	1.0081	0.9827	1.3380
	0.45	1.0083	0.9789	1.4168
	0.50	1.0080	0.9737	1.5201
0.2	0.30	0.9956	1.0095	0.9053
	0.40	0.9935	1.0120	0.8821
	0.45	0.9922	1.0129	0.8726
	0.50	0.9906	1.0135	0.8649
0.1	0.30	0.9947	1.0114	0.8911
	0.40	0.9921	1.0144	0.8660
	0.45	0.9904	1.0154	0.8563
	0.50	0.9882	1.0160	0.8492
0.0	0.30	0.9938	1.0137	0.8763
	0.40	0.9905	1.0172	0.8498
	0.45	0.9882	1.0184	0.8404
	0.50	0.9850	1.0189	0.8350

these exactly determined values of the induced dipoles we have studied the local field at the boundaries of the slabs. The values of the local electric field, obtained in this way, are the exact values which should be used in theories determining the shape of large clusters of polarizable particles. The calculated induced dipoles may also be used to study the difference between the electrostatic energy of a particle in the bulk and one on the surface of the slab. Using Eq. (4.1) for the total electrostatic energy if the medium is linear,<sup>20</sup>

$$W = \frac{1}{8\pi} \int_{R_3} \mathbf{E}(\mathbf{r}) \cdot \mathbf{D}(\mathbf{r}) dV, \quad (4.1)$$

we obtain the following exact expression for the change in electrostatic energy of particle  $i$  in a cluster of polarizable particles with arbitrary geometry:

$$\Delta W_i = -\frac{1}{2} \epsilon_f \mathbf{M}_i \cdot \mathbf{E}_0. \quad (4.2)$$

The derivation is analogous to the one used in Sec. V for the local electric field.

The grand potential matrix is determined using a Fortran-77 computer program. From this grand potential matrix it is possible to calculate the induced dipole moments on the particles. We normalize the calculated values of the induced dipole moments with the induced dipole moment  $M_\rho$  of the central layer

$$\tilde{M}_\nu = \frac{M_\nu}{M_\rho}, \quad (4.3)$$

with  $\rho = (L+1)/2$ . Of course, we have assumed that  $L$  is odd. If the number of layers of the slab is large enough, and the externally applied electric field is parallel to the surface of the slab, then the induced dipole moment of the central layer is equivalent to the three-dimensional bulk value  $M_{\text{bulk}}$  of the induced dipole moment. If, on the other hand, the external field is perpendicular to the surface of the slab we have  $M_\rho = M_{\text{bulk}}/\epsilon_{\text{eff}}$ , with  $\epsilon_{\text{eff}} = 1 + 3\beta_1\varphi(M_{\text{bulk}}/M_0)$  the relative dielectric constant of the bulk material ( $M_0$  is the induced dipole moment of one particle in the same externally applied electric field). The calculations to obtain numerical results for these induced dipoles are performed for slabs with several numbers of layers,  $L \in \{1, 3, 5, 9\}$ . We restrict ourselves in this paper to the results obtained for the slabs with  $L=5$  (local sc structure) and  $L=9$  (local bcc structure). The reason for this choice is the fact that a slab with five layers for a sc or nine for a bcc slab show the same surface effects concerning induced dipoles as a semi-infinite lattice with the same symmetry.

In our calculations we have restricted the number of multipole moments by performing calculations with  $L \leq 14$ . However, the obtained results for the normalized induced dipoles are accurate with five significant figures except in the case of close packing structures. In the latter case it is not very difficult to increase the accuracy of the calculations. If we change the computer program a little bit to perform matrix inversion of larger matrices, and if we use a larger set of data representing the lattice sums, we may perform these calculations without an excessive use of computation time. However, the most important features of the behavior of the dipoles in going from the center to the surface of the slab can be shown using intermediate and near close packing samples. This is also the case when we are studying the local electric field at the boundaries.

We have checked our calculations in several ways. The most important one is a comparison of results of induced dipoles on particles on the central layer of slabs with  $L=5$  or 9, which are assumed to be bulk values (see the prior discussion concerning  $M_\rho$ ), with results from the literature. We used, for this comparison, results of McPhedran and McKenzie<sup>16</sup> and results of Sangani and Acrivos.<sup>17</sup> We may conclude that the results of our calculations agree with those from the literature. Furthermore, we have used symmetry properties to check the calculations.

The calculations are performed for the simple cubic, the body centered cubic, and the simple hexagonal lattice. The results for the simple hexagonal structure are not presented because the behavior of the induced dipoles as function of the layer is comparable to those of the simple cubic structure. Results are presented in the Tables II–IV for four values of the volume fraction (sc,  $\varphi=0.5, 0.45, 0.4, 0.3$ ; bcc,  $\varphi=0.65, 0.6, 0.5, 0.4$ ) and six values of the ratio of particle to fluid dielectric constant,  $\alpha \in \{0, 0.1, 0.2, 5, 10, \infty\}$ . Because of symmetry we have to consider the induced dipoles from surface layer to the central layer, i.e.,  $\tilde{M}_1, \tilde{M}_2$ , and so on. We consider only those layers with  $\tilde{M}_\mu \neq 1$ . We make a distinction between two different situations; in the first the applied external field is



TABLE III. The normalized induced dipoles on particles of the first three layers of a bcc slab for several values of  $\alpha$  and  $\varphi$ . The external field is in the  $x$  direction. The bulk value of the induced dipole moment, normalized with the one particle induced dipole moment in the same external field, is given in the last column.

$\alpha$	$\varphi$	$\tilde{M}_{1x}$	$\tilde{M}_{2x}$	$\tilde{M}_{3x}$	$M_p$
$\infty$	0.40	0.8792	1.0034	1.0000	1.6959
	0.50	0.8303	1.0033	1.0000	2.1105
	0.60	0.7578	1.0028	1.0000	2.9675
	0.65	0.6969	1.0024	1.0000	4.1163
10.0	0.40	0.9162	1.0040	0.9999	1.4411
	0.50	0.8868	1.0050	0.9999	1.6398
	0.60	0.8488	1.0068	0.9998	1.9406
	0.65	0.8229	1.0085	0.9997	2.1800
5.0	0.40	0.9393	1.0035	0.9999	1.3025
	0.50	0.9199	1.0046	0.9999	1.4179
	0.60	0.8964	1.0060	0.9998	1.5695
	0.65	0.8820	1.0070	0.9997	1.6697
0.2	0.40	1.0310	0.9971	1.0001	0.8744
	0.50	1.0377	0.9964	1.0001	0.8493
	0.60	1.0435	0.9957	1.0001	0.8272
	0.65	1.0459	0.9953	1.0001	0.8175
0.1	0.40	1.0361	0.9966	1.0001	0.8556
	0.50	1.0437	0.9957	1.0001	0.8278
	0.60	1.0500	0.9948	1.0001	0.8040
	0.65	1.0524	0.9944	1.0001	0.7940
0.0	0.40	1.0415	0.9960	1.0001	0.8359
	0.50	1.0500	0.9949	1.0001	0.8057
	0.60	1.0567	0.9938	1.0001	0.7805
	0.65	1.0587	0.9932	1.0001	0.7709

TABLE IV. The normalized induced dipoles on particles of the first three layers of a bcc slab for several values of  $\alpha$  and  $\varphi$ . The external field is in the  $z$  direction. The bulk values can be derived from those in Table III.

$\alpha$	$\varphi$	$\tilde{M}_{1z}$	$\tilde{M}_{2z}$	$\tilde{M}_{3z}$
$\infty$	0.40	1.1323	0.9840	1.0012
	0.50	1.1519	0.9833	1.0011
	0.60	1.1621	0.9855	1.0007
	0.65	1.1576	0.9895	1.0004
10.0	0.40	1.1065	0.9880	1.0008
	0.50	1.1245	0.9870	1.0007
	0.60	1.1372	0.9874	1.0006
	0.65	1.1398	0.9887	1.0005
5.0	0.40	1.0857	0.9909	1.0005
	0.50	1.1016	0.9898	1.0005
	0.60	1.1143	0.9896	1.0005
	0.65	1.1187	0.9899	1.0004
0.2	0.40	0.9207	1.0046	0.9999
	0.50	0.8956	1.0061	0.9999
	0.60	0.8671	1.0082	0.9998
	0.65	0.8512	1.0095	0.9998
0.1	0.40	0.9033	1.0050	1.0000
	0.50	0.8710	1.0067	0.9999
	0.60	0.8332	1.0090	0.9999
	0.65	0.8114	1.0106	0.9999
0.0	0.40	0.8825	1.0052	1.0000
	0.50	0.8407	1.0068	1.0000
	0.60	0.7897	1.0090	1.0000
	0.65	0.7587	1.0106	1.0000

parallel to the slab ( $E_0 \parallel \hat{\delta}_x$ ) and in the second case this external field is perpendicular to the slab.

The induced dipoles on the particles in the slab with the simple cubic structure (Table II) do not depend very much on the layer. The induced dipole on the surface is only slightly different from bulk value. The difference depends, of course, on the value of  $\alpha$ .  $\tilde{M}_{1x}$  is between 0% and 2% of the bulk value and  $\tilde{M}_{1z}$  is between 0% and 6%. In both cases the bulk values are related to the three-dimensional value of the induced dipole moment as discussed earlier. It is surprising that the difference of the relative induced dipole between the boundary and the bulk is, for  $\alpha \gg 1$ , not largest when the volume fraction is near the close packing value.

The induced dipoles on the particles in the slab with the local bcc structure are much more influenced by the presence of a boundary than for the simple cubic structure. The values of the induced dipoles on the particles belonging to the first three layers at the surface of the slab are different from the bulk value. It is obvious that  $\tilde{M}_{3x}$  and  $\tilde{M}_{3z}$  do not differ much from unity, but the values of the relative difference of the induced dipoles on the second layer is already of the same order as the differences in the surface layer of the slab with the local simple cubic structure. The induced dipole on the surface of the slab is between 10% and 30% lower than in the bulk. We see that the sign of the change in the induced dipoles alternates from layer to layer.

From Eq. (4.2) we see that the presence of the surfaces in the sc slab lowers the energy per particle relative to the three-dimensional sc lattice (see also Ref. 15). On the other hand, the presence of the surfaces in the bcc slab increases the energy per particle relative to the three-dimensional bcc lattice, i.e., a surface tension exists. For (nearly) close packed slabs of two or three layers it can be shown that, for  $\alpha \gg 1$ , the local sc structure is energetically more favorable than the local bcc structure. For more than three layers the bcc structure is more favorable than the sc structure as is the case for three-dimensional lattices. For the comparison of the electrostatic energy of slabs it is necessary to incorporate many multipoles in the calculation. A dipolar approach does not always lead to correct results. We hope to present results of a study of these aspects of thin slabs in a future communication.

We can draw three important conclusions from this section. First we see that the values of the induced dipoles are not independent of the layers in which the particle under consideration is situated, even if many multipole moments are included. This effect was expected, but as far as we know it was not calculated explicitly. A second conclusion is that the calculated relative induced dipoles are very sensitive to the structure under consideration. We have shown the results for two different structures only but the third structure which we have studied, the local simple hexagonal (sh) lattice, also shows the same kind of behaviour. Some structures of slabs lead to a surface tension (bcc) and others favor a boundary (sc and sh). A final conclusion is more indirect. The values in the tables are correct values from the numerical calculations except, of

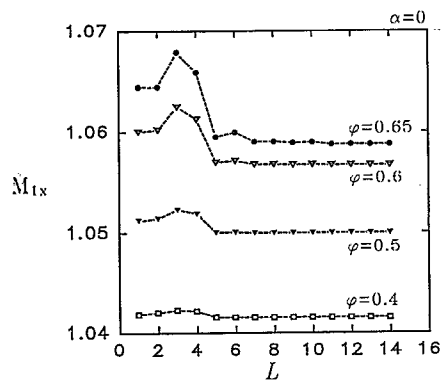


FIG. 1. The normalized induced dipole  $\tilde{M}_{1x}$  of the bcc slab ( $\alpha=0$ ) as a function of the order  $L$ , the number of multipoles used in its calculation.

course, rounding off errors in the last figure. The presented method is thus a convenient one to study the effects of higher order multipole moments on, e.g., induced dipoles. As we shall show, the final values differ considerably from the lowest order values ( $L=1$ ). For this reason it is important to have a good method to do calculations for these kind of problems. In Figs. 1–4 we present some examples for the two extreme cases,  $\alpha=0$  and  $\alpha=\infty$ . Note that the  $L=1$  solution is not equivalent to the constant dipole result. Several years ago Miller and Jones presented some results on the dielectric constant of columns or layers of dielectric spheres.<sup>22</sup> They made the assumption that the different layers do not interact with each other. However, we have shown that we do not need this assumption to perform the calculations and this method can as well be used to deduce the permittivity of different kinds of structured media.

## V. LOCAL ELECTRIC FIELD AT THE THE SURFACE: AN EXACT CALCULATION

In Sec. III we have presented some approximate results about the local electric field in the slab and near the surface. These results were based on the hypothesis of a constant polarization throughout the slab. In Sec. IV we

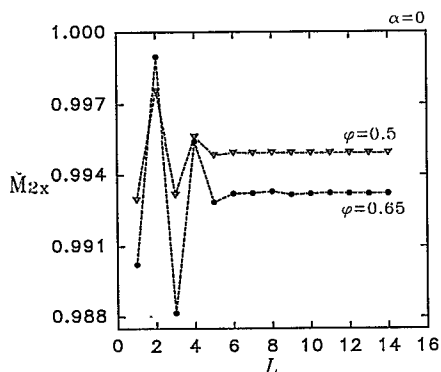


FIG. 2. The normalized induced dipole  $\tilde{M}_{2x}$  of the bcc slab ( $\alpha=0$ ) as a function of the order  $L$ , the number of multipoles used in its calculation.

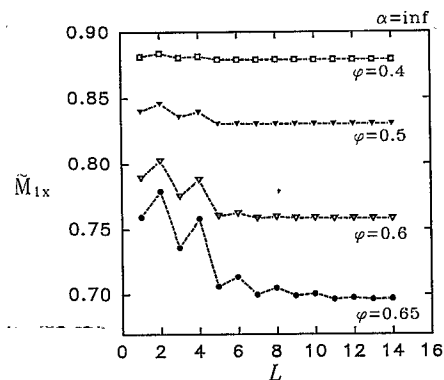


FIG. 3. The normalized induced dipole  $\tilde{M}_{1x}$  of the bcc slab ( $\alpha=\infty$ ) as a function of the order  $L$ , the number of multipoles used in its calculation.

have shown that this is not the case (even in lowest order calculations with  $L=1$ ). Furthermore, higher order multipole moments are neglected in these calculations. Here we present some exact results for the local electric field. We may expect that the variation of the local electric field on the lattice sites depend strongly on the sphere density. We expect this behavior because the induced dipoles also depend on the volume fraction, especially for the slab with a local bcc structure (see Tables III and IV).

Let us consider a system of  $N$  polarizable particles at arbitrary positions in the fluid acted upon by an external electric field. We are interested in the local electric field near the center of particle  $i$ . This field is a sum of the external electric field and of the scattered electric fields by the  $N-1$  other particles. The local electric field near the center of particle  $i$  is [using Eq. (3.5) of Ref. 14]

$$\mathbf{E}_{i,\text{loc}}(\mathbf{r}_i) = -\nabla_i \varphi_{\text{out}}(\mathbf{r}_i) = \mathbf{E}_0 - \sum_{\substack{l>0 \\ m}} r_i^{l-1} \mathbf{A}_{lm}(\theta_i, \varphi_i) \frac{n_{lm}}{(l+m)!} \times \sum_{j \neq i} \left( \sum_{\substack{p>0 \\ q}} \frac{4\pi}{2p+1} Q_{pq}^j M_{pg,lm}^{ji}(\mathbf{R}_{ij}) \right). \quad (5.1)$$

This relation can be simplified by using Eq. (2.1):

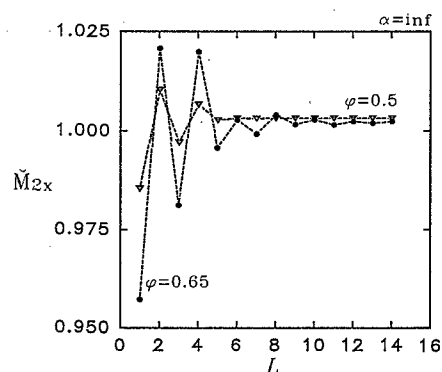


FIG. 4. The normalized induced dipole  $\tilde{M}_{2x}$  of the bcc slab ( $\alpha=\infty$ ) as a function of the order  $L$ , the number of multipoles used in its calculation.

$$\mathbf{E}_{i,\text{loc}}(\mathbf{r}_i) = \sum_{\substack{l>1 \\ m}} \frac{1}{\beta_1 \alpha^{2l+1}} \frac{4\pi}{2l+1} Q_{lm}^i r_i^{l-1} A_{lm}(\theta_i, \varphi_i). \quad (5.2)$$

For the local electric field at the center of particle  $i$ , we obtain, by using Eq. (3.13) of Ref. 14,

$$\mathbf{E}_{i,\text{loc}}(|\mathbf{r}_i|=0) = \frac{1}{\beta_1 \alpha^3} \mathbf{M}_i. \quad (5.3)$$

Although this relation for the local electric field has the simple form, which relates the dipole of a spherical particle to the local field through the polarizability  $\beta_1 \alpha^3$ , it should be emphasized that all higher order multipoles are implicitly included. The set of linear algebraic equations for the  $N$ -particle problem has to be solved to obtain accurate values for  $\mathbf{M}_i$  and thus for  $\mathbf{E}_{i,\text{loc}}$ . For a slab, a special case of the  $N$ -particle problem described earlier, we can use Eq. (5.3), and the local electric field in layer  $\mu$  (at the center of one of the particles in that layer) is then

$$\mathbf{E}_{\mu,\text{loc}} = \frac{1}{\beta_1 \alpha^3} \mathbf{M}_\mu. \quad (5.4)$$

After normalization of the respective components of Eq. (5.4) with those of the bulk local electric field, we obtain  $\tilde{\mathbf{E}}_{\mu,\text{loc}} = \tilde{\mathbf{M}}_\mu$ . Results for the local electric field near the surface can be found in Tables II–IV. For a discussion of the data we refer to Sec. IV.

In order to compare with the approximate results represented by Eqs. (3.8)–(3.10), we write the local field, Eq. (5.4), as

$$E_{\mu,\text{loc}} = E_0 + \frac{4\pi}{3} P + \chi P, \quad (5.5)$$

where  $P$  is the bulk polarization given by  $M_\rho/V$  for  $\rho$  corresponding to an internal layer and  $V$  is the volume of the unit cell. The quantity  $\chi$  expresses the difference of field between the homogeneous situation (Lorentz field) and the discrete one. This quantity is practically zero inside the slab, but can become important on the surface. Its exact value obtained with our method is given in Table V together with the homogeneous result [Eq. (3.10)] and the results from the constant dipole approximation [Eqs. (3.8) and (3.9)]. These results for the surface layer are presented for three values of  $\alpha$  and several values of  $\varphi$ . It appears that for the simple cubic case  $\chi_{\text{sc}}$  is positive as in the constant dipole approximation instead of tending to  $\chi_{\text{hom}} = -2\pi/3$ , the value obtained for a slab of homogeneous material. All the values of  $\chi_{\text{sc}}$  are of the same order as the one given by the constant dipole approximation. For the bcc slab the values of  $\chi_{\text{bcc}}$  are generally intermediate between the constant dipole approximation and the homogeneous case. Furthermore, we see a strong dependence relative to the volume fraction  $\varphi$  of particles in the slab. Another interesting point is that, for the bcc slab, the local electric field in the second and third layer from the surface also differ from the bulk value. This is not shown explicitly, but can be seen by inspection of Table III.

Finally, we compare our results for the surface energy with those of Toor and Halsey<sup>15</sup> which is a result of the

constant dipole approximation. The relation expressing the electrostatic energy per particle is  $\Delta W = -\frac{1}{2} \epsilon_f \mathbf{M} \cdot \mathbf{E}_0$  (see Sec. IV). We are interested in numerical results of the following expression, the relative surface energy,

$$\Delta W_s = \frac{\sum_v (\Delta W_v - \Delta W_\rho)}{|\Delta W_\rho|} = \sum_v (1 - \tilde{M}_v), \quad (5.6)$$

where the summation includes all layers (in practice only the first few layers from the boundary). The results of Toor and Halsey (TH) can also be rewritten in a similar form. We then obtain

$$\Delta W_{\text{TH}} = \sum_v (1 - \tilde{E}_{\text{loc},v}), \quad (5.7)$$

with  $\tilde{E}_{\text{loc},v}$  the local field in layer  $v$  normalized by the bulk local field [the local field is always determined on a lattice site, see Eq. (5.3)]. Both expressions give the sum over the layers of the slab of the difference between the actual energy per particle and the three-dimensional bulk energy per particle normalized by this latter bulk energy. Equation (5.7) is only valid in the point dipole approximation. A positive value for  $\Delta W_s$  means that the existence of the surface leads to a surface tension. In the case of a negative value of this quantity the structure favors a surface. We have indirectly shown in Sec. III that, in the constant dipole approximation,  $\Delta W_s = \Delta W_{\text{TH}}$ . The numerical values for the two lattices under consideration are  $\Delta W_{\text{TH,sc}} = -0.03922$  and  $\Delta W_{\text{TH,bcc}} = 0.21226$ . In Table VI we present some results for  $\Delta W_s$  for the sc and bcc slab obtained with the multipolar approach. We restrict ourselves to a few examples because the results are directly related to the normalized induced dipole moments presented in Tables II and III. We can conclude that the exact results are of the same order as the results of Toor and Halsey. The results depend on volume fraction and the value of  $\alpha = \epsilon_p/\epsilon_f$  which may be expected by considering the data presented in Sec. IV. We have also determined the relative surface energy of the close packed configurations. To obtain these results we have performed calculations up to

TABLE V. The coefficients  $\chi$  for a sc and bcc lattice for several values of  $\alpha$  and  $\varphi$  compared with the values for the homogeneous slab,  $\chi_{\text{hom}} = -2.094$  [Eq. (3.10)], and the so-called constant dipole results for the respective slabs,  $\chi_{\text{sc}}^{\text{cd}} = 0.164$  and  $\chi_{\text{bcc}}^{\text{cd}} = -0.965$  [Eqs. (3.8) and (3.9)]. The external electric field is in the  $x$  direction.

$\alpha$	$\varphi$	$\chi_{\text{sc}}$	$\varphi$	$\chi_{\text{bcc}}$
$\infty$	0.30	0.166	0.40	-1.233
	0.40	0.131	0.50	-1.351
	0.45	0.105	0.60	-1.530
10	0.50	0.068	0.65	-1.679
	0.30	0.161	0.40	-1.147
	0.40	0.130	0.50	-1.215
0	0.45	0.110	0.60	-1.307
	0.50	0.084	0.65	-1.371
	0.30	0.184	0.40	-0.885
	0.40	0.225	0.50	-0.868
	0.45	0.260	0.60	-0.845
	0.50	0.318	0.65	-0.827

TABLE VI. The relative surface energies  $\Delta W_s$  for a sc and bcc lattice for several values of  $\alpha$  and  $\varphi$  compared with the values obtained by Toor and Halsey (Ref. 15) using the so-called constant dipole approximation. These results are  $\Delta W_{\text{TH,sc}} = -0.0392$  and  $\Delta W_{\text{TH,bcc}} = 0.2123$ . The external electric field is in the  $x$  direction.

$\alpha$	$\varphi$	$\Delta W_{s,\text{sc}}$	$\varphi$	$\Delta W_{s,\text{bcc}}$
$\infty$	0.40	-0.0147	0.50	0.1664
	0.50	-0.0113	0.65	0.3007
	0.5236	-0.008	0.6802	0.37
10	0.40	-0.0106	0.50	0.1083
	0.50	-0.0095	0.65	0.1689
	0.5236	-0.0085	0.6802	0.188

$L=14$  only. Consequently, there is an uncertainty in the last figure, but we may get an idea of the value of  $\Delta W_s$  for dense structures.

From this section we may conclude that the local electric field near the surface of a slab of spherical particles does not behave as predicted for a homogeneous material, and strongly depends on the local structure. In contrast we see that another approximation method, the constant dipole approximation, gives good qualitative results.

## VI. CONCLUSION

From the results presented in this paper we may conclude that it is possible to perform exact calculations of the induced dipole moments of polarizable particles in slabs and also of the local electric field. Of course, these calculations can be performed as well for slabs with other internal structures. For instance, we can use this method to calculate the electrostatic forces on particles in slabs with a sheared cubic structure. This gives us the possibility to study more exactly rupture effects in these systems. For these kind of problems it is necessary to use the multipolar approach, a dipolar approach does not give satisfactory results, even qualitatively. We hope to present a future communication concerning these problems. Furthermore, a confirmation is given about the large influence of the structure on induced dipole moments, on the local electric field, and on the surface energy, especially in the neighborhood of boundaries. Moreover, the incorporation of higher order multipole moments is shown to give significant changes. Furthermore, it is shown that one should be careful by replacing a slab consisting of spherical, polarizable

particles by a slab of homogeneous material even if only qualitative results are required. In the case of a local bcc structure, differences with a homogeneous slab are not too big, thus this approximation can be used if we are only interested in qualitative results. This is not true for a sc structure since in that case the presence of the surface lowers the total energy of the system instead of increasing it. On the other hand, good qualitative results may already be obtained using the constant dipole approach as has been used in Sec. III (see also Toor and Halsey<sup>15</sup>). Finally, we may conclude that it is possible to study electrostatic interactions among polarizable, spherical particles in slabs with some prescribed local structure without the need to introduce additional simplifications like the separation of interactions into column or layer interactions.

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- <sup>1</sup>T. C. Halsey, *Science* **258**, 761 (1992).
- <sup>2</sup>T. C. Halsey and W. Toor, *Phys. Rev. Lett.* **65**, 2820 (1990).
- <sup>3</sup>T. C. Halsey, J. E. Martin, and D. Adolf, *Phys. Rev. Lett.* **68**, 1519 (1992).
- <sup>4</sup>G. Bossis, Y. Grasselli, E. Lemaire, L. Petit, and J. Persello, *Proceedings of the International Conference on Electrorheological Fluids, 1991, Carbondale*, edited by R. Tao (World Scientific, Singapore, 1992).
- <sup>5</sup>E. Lemaire, Y. Grasselli, and G. Bossis, *J. Phys. II France* **2**, 359 (1992).
- <sup>6</sup>Y. Grasselli, G. Bossis, and E. Lemaire, *J. Phys. II France* (submitted).
- <sup>7</sup>T. C. Halsey and W. Toor, *J. Stat. Phys.* **61**, 1257 (1990).
- <sup>8</sup>J. E. Martin, J. Odinek, and T. C. Halsey, *Phys. Rev. Lett.* **69**, 1524 (1992).
- <sup>9</sup>R. Tao and J. M. Sun, *Phys. Rev. Lett.* **67**, 398 (1991).
- <sup>10</sup>T. Chen, R. N. Zitter, and R. Tao, *Phys. Rev. Lett.* **68**, 2555 (1992).
- <sup>11</sup>L. C. Davis, *Phys. Rev. A* **46**, R719 (1992).
- <sup>12</sup>J. F. Brady and G. Bossis, *Annu. Rev. Fluid Mech.* **20**, 111 (1988).
- <sup>13</sup>R. T. Bonnecaze and J. F. Brady, *J. Chem. Phys.* **96**, 2183 (1992).
- <sup>14</sup>H. J. H. Clercx and G. Bossis, *Phys. Rev. E* (submitted) (to be referred to as I).
- <sup>15</sup>W. R. Toor and T. C. Halsey, *Phys. Rev. A* **45**, 8617 (1992).
- <sup>16</sup>R. C. McPhedran and D. R. McKenzie, *Proc. R. Soc. London, Ser. A* **359**, 45 (1978).
- <sup>17</sup>A. S. Sangani and A. Acrivos, *Proc. R. Soc. London, Ser. A* **386**, 263 (1983).
- <sup>18</sup>H. J. H. Clercx and P. P. J. M. Schram, *J. Chem. Phys.* **96**, 3137 (1992).
- <sup>19</sup>H. J. H. Clercx and P. P. J. M. Schram, *Physica A* **174**, 293 (1991).
- <sup>20</sup>J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975), Chaps. 3 and 6.
- <sup>21</sup>B. R. A. Nijboer and F. W. de Wette, *Physica* **23**, 309 (1957).
- <sup>22</sup>R. D. Miller and T. B. Jones, *J. Phys. D* **21**, 527 (1988).