A new method for determining dipole-dipole energy in 1D and 2D systems

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An alternative method for computing dipole-dipole interaction energy in systems of 1D and 2D periodicity like nanowires, nanotubes and thin films is presented. The approach is based on the use of periodic Green’s functions that satisfy Laplace’s equation and are analytically determined. The method, when combined with short-ranged interaction as in effective Hamiltonian, is suitable for studying finite-temperature properties of low-dimensional ferroelectric systems.

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I. INTRODUCTION

In the past decade it was shown that the finite-temperature behaviour of ferroelectric systems like BaTiO$_3$ can be successfully simulated by using the statistical mechanics of an Effective Hamiltonian, which, in its turn, is based on the first-principles calculations of total energies for small distortions of the high-temperature cubic structure. Such an approach predicts sequence of phase transformations, electromechanical responses and statistical energies for small distortions of the high-temperature cubic structure. An alternative method for computing dipole-dipole interaction energy in systems of 1D and 2D periodicity like nanowires, nanotubes and thin films is presented. The approach is based on the use of periodic Green’s functions that satisfy Laplace’s equation and are analytically determined. The method, when combined with short-ranged interaction as in effective Hamiltonian, is suitable for studying finite-temperature properties of low-dimensional ferroelectric systems.

The conventional effective first-principles Hamiltonian approach is developed for the bulk systems infinitely repeated in all three Cartesian directions (3D case) [1]. Formally it can also be applied to the systems which are effectively infinite only in one or two dimensions simply repeating them many times in finite direction(s) (in this case sufficiently thick vacuum gap(s) must be created between periodic replicas). Such a procedure, however, inevitably leads to errors in depolarizing electric fields and in corresponding shape-dependent electrostatic energy [2, 3]. Consequently, in passing from the systems with three- to that with two- and one-dimensional periodicity the part of the effective Hamiltonian connected with long-range dipole-dipole interactions should be modified.

The existing methods for rapid evaluation of dipole-dipole interactions in 1D [4, 5] and 2D [6, 7, 8] systems are based on Ewald type summation technique exploiting the integral representation of the Gamma function (or Euler’s integral) and Poisson summation formula. This technique leads to fast convergent sums in real and reciprocal spaces, which, however, are rather bulky.

Here, we present a new elegant method for the treatment of dipole-dipole interaction in partially periodic systems which leads to much simpler final expressions than the Ewald technique. The method is based on using the analytically determined periodic Green’s functions of the Laplace’s equation $G(r', r)$. The simplicity of our final expressions is partly due to the fact that we do not use Ewald type transformations in 1D case at all, whereas in 2D case we use it only for the special case when the interacting dipoles lay in the same plane. The other reason comes from the fact that we perform the summation of dipole-dipole interactions (from dipoles located in different unit cells) entirely in reciprocal space— with the only exception for the 1D case when the dipoles lay along the line parallel to the periodicity direction.

II. DIPOLE-DIPOLE INTERACTIONS IN SYSTEMS WITH 1D AND 2D PERIODICITY

We regard the systems with 1D and 2D periodicity as infinite in one and two of the three Cartesian directions correspondingly. They can be obtained by replicating a “unit cell” an infinite number of times along that directions. The dipole-dipole interaction energy can be written as

$$
\mathcal{E}_{\text{dip}} = \frac{1}{2} \sum_{i \neq j} \left\{ \frac{\mathbf{d}(\mathbf{R}_i) \cdot \mathbf{d}(\mathbf{R}_j)}{R_{ij}^3} - \frac{3 |\mathbf{d}(\mathbf{R}_i) \cdot \mathbf{R}_{ij}| |\mathbf{d}(\mathbf{R}_j) \cdot \mathbf{R}_{ij}|}{R_{ij}^5} \right\}
$$

where $R_{ij} = |\mathbf{R}_{ij}|$ is the distance between dipoles, $d_{\alpha}(\mathbf{R}_i)$ is the $\alpha$-component ($\alpha = x, y, z$) of the dipole moment at the site $i$ and

$$
D_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) = - \lim_{r \to 0} \frac{\partial}{\partial r_{\alpha}} \frac{\partial}{\partial r_{\beta}} \left( \frac{1}{|\mathbf{r} - \mathbf{R}_i + \mathbf{R}_j|} \right).
$$

Due to periodicity each vector $\mathbf{R}_i$ is represented as $\mathbf{r}_i - \mathbf{R}_i$ where $\mathbf{r}_i$ is the dipole position inside the 0-th unit cell and $\mathbf{R}_i$ is an appropriate vector from the infinite number of vectors forming 1D or 2D lattice. Accordingly, we may rewrite Eq. (1) as

$$
\mathcal{E}_{\text{dip}} = \frac{N}{2} \sum_{\alpha\beta, \mathbf{R}_i} \sum_{ij} D_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j + \mathbf{R}_i) d_{\alpha}(\mathbf{r}_i) d_{\beta}(\mathbf{r}_j),
$$

where the summation over $i, j$ runs only inside the 0-th unit cell, the prime means that the term with $\mathbf{r}_i = \mathbf{r}_j$ in the case of $\mathbf{R}_i = 0$ must be omitted, $N$ is the number of unit cells allowed to tend to infinity. We are interested in $\mathcal{E}$ per unit cell, so $N$ in Eq. (3) can be omitted. Using
Now our task is to evaluate the vectors $k$ where $\Delta$.

Inserting (8), (9), and (10) into Eq.(6) we obtain

$$\left\{ \begin{array}{l} 12, 13 \\ \end{array} \right.$$

is nothing but the periodic Green’s function of Laplace’s equation satisfying the point source equation

$$\nabla^2 \mathcal{G}(\mathbf{r}, \mathbf{r}') = -4\pi \sum_{\mathbf{R}_i} \delta(\mathbf{r} - \mathbf{r}' + \mathbf{R}_i),$$

and the translation symmetry

$$\mathcal{G}(\mathbf{r}, \mathbf{r}') = \mathcal{G}(\mathbf{r} + \mathbf{R}_\parallel, \mathbf{r}' + \mathbf{R}_\parallel).$$

Now our task is to evaluate $\mathcal{G}(\mathbf{r}, \mathbf{r}')$ and then $E_{\text{dip}}$ for 1D and 2D cases according to (11).

### A. 1D case

Let $z$-axis to be along the infinite dimension, then all the vectors $\mathbf{R}_i$ lay in it. We represent each vector $\mathbf{r}$ as decomposed into two components $\{\rho, z\}$, where $\rho$ is the projection of the $\mathbf{r}$ on the $(x, y)$ plane. Accordingly, the Dirac functions $\delta(\mathbf{r} - \mathbf{r}' + \mathbf{R}_\parallel)$ in the right-hand side of Eq.(11) become $\delta(\rho - \rho') \delta(z - z' + \mathbf{R}_\parallel)$. The 2D and the sum of 1D Dirac functions can be expressed as Fourier integral and sum correspondingly:

$$\delta(\rho - \rho') = \frac{1}{(2\pi)^2} \int e^{i\mathbf{k}_\perp \cdot (\rho - \rho')} d\mathbf{k}_\perp,$$

$$\sum_{\mathbf{R}_\parallel} \delta(z - z' + \mathbf{R}_\parallel) = \frac{1}{a} \sum_{\mathbf{G}_\parallel} e^{i\mathbf{G}_\parallel \cdot (z - z'}),$$

where $\mathbf{k}_\perp$ is the 2D wave-vector perpendicular to the $z$-direction, $a$ is the period along this direction, and $\mathbf{G}_\parallel$ are the reciprocal lattice vectors corresponding to the 1D lattice of repeated cells. We shall look for the Green’s function in the form

$$\mathcal{G}(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{G}_\parallel} \int g(\mathbf{k}_\perp, \mathbf{G}_\parallel) e^{i(\mathbf{k}_\perp + \mathbf{G}_\parallel) \cdot (\mathbf{r} - \mathbf{r}')} d\mathbf{k}_\perp$$

Inserting (8), (9), and (10) into Eq.(11) we obtain

$$\left\{ \begin{array}{l} 12, 13, 11 \\ \end{array} \right.$$

where $K_0(x)$ is the 0-th order modified Bessel’s function of the imaginary argument. Since the Bessel function $K_0(x)$ decays exponentially for large argument $x$, the series over $\mathbf{G}_\parallel$ converge much faster than the direct lattice sum (11). This is valid only for the contributions to $E_{\text{dip}}$ with $\rho_i \neq \rho_j$. As to contributions coming from the dipole-dipole interactions with $\rho_i = \rho_j$ or, in other words, from the chains of dipoles parallel to the $x$-axis, they can be easily calculated in the real space; the corresponding 1D sums are rapidly convergent like $1/n^3$.

Moreover, doing so one can automatically solve the problem of excluding of the “self-interaction” term from the sum (3).

Substituting (11) into Eq.(4) and taking into account that $K_0(x) = -K_1(x)$ and $K_0''(x) = K_2(x) - K_1(x)/x$ one can easily obtain

$$E_{\text{dip}} = \frac{1}{a} \sum_{\mathbf{G}_\parallel} \sum_{ij} \left( \begin{array}{l} 1 \\ \end{array} \right.$$

$$\times \left\{ \begin{array}{l} K_0(G_{\parallel} | \rho_{ij}) d_z(r_i) d_z(r_j) \\ + \frac{1}{\rho_{ij}} K_1(G_{\parallel} | \rho_{ij}) [d_z(r_i) d_z(r_j) + d_y(r_i) d_y(r_j)] \\ - \frac{1}{\rho_{ij}^2} K_2(G_{\parallel} | \rho_{ij}) \left[ \rho_{ij} \cdot d(r_i) \right] \left[ \rho_{ij} \cdot d(r_j) \right] \right\}$$

$$\times f(\rho_{ij}) \right\}$$

$$\left. \times \sin(\mathbf{G}_\parallel \cdot \mathbf{z}_{ij}) \right\} K_1(G_{\parallel} | \rho_{ij}) \rho_{ij}^{-1}$$

$$\times \left\{ \begin{array}{l} [G_{\parallel} \cdot d(r_i)] [\rho_{ij} \cdot d(r_j)] + [G_{\parallel} \cdot d(r_j)] [\rho_{ij} \cdot d(r_i)] \\ + \frac{1}{a} \sum_{ij} [d_z(r_i) d_y(r_i) + d_y(r_i) d_y(r_j)] - 2d_z(r_i) d_z(r_j) \right\}$$

$$\times f(\rho_{ij}) \right\}$$

$$\times f(\rho_{ij}) \right\}$$

Here, $G_{\parallel} = |G_{\parallel}|$, $\mathbf{z}_{ij} = z_i - z_j$, $\rho_{ij} = \rho_i - \rho_j$, $\rho_{ij} = |\rho_{ij}|$, and

$$f(\rho_{ij}) = \sum_{n=-\infty}^{\infty} \left( \begin{array}{l} n \\ \end{array} \right.$$

$$\frac{\rho_{ij}}{a} \right\} ^3,$$

where the prime at the sum means that the term $n = 0$ is to be excluded for the case $i = j$. The last sum in (12) describes the contribution to the energy associated with the chains parallel to the $z$-axis; this contribution is separated from the first two sums marked by the primes. Note that the function $f(\rho_{ij})$ is periodic in real space with period $a$. It is also worth noticing that the term $G_{\parallel} = 0$ does contribute to the sum (12). Taking into consideration that as $x \to 0$ $K_0(x) \to -\ln(x)$, $K_1(x) \to 1/x$, and $K_2(x) \to 2/x^2$, we find

$$E_{\text{dip}}(G_{\parallel} = 0) = \frac{1}{a} \sum_{ij} \rho_{ij}^{-2} \left( \begin{array}{l} d_z(r_i) d_z(r_j) + d_y(r_i) d_y(r_j) \\ -2\rho_{ij}^{-2} [\rho_{ij} \cdot d(r_i)] [\rho_{ij} \cdot d(r_j)] \right\}.$$
If all \( d(r_i) \parallel z \), this contribution turns to zero. In the macroscopic limit it describes the energy connected with the depolarizing field.

### B. 2D case

Consider a slab or thin film with normal along the \( z \)-direction, each layer of which representing an infinite array of electric dipoles in the \((x, y)\) plane. For this geometry the vectors \( R_\parallel \) form a 2D lattice parallel to this plane. The corresponding Green’s function, as easily to show acting similar to the previous case and using the methods\[13, 14\], is

\[
G(r, r') = \frac{2\pi}{S} \sum_{G_\parallel} \int e^{ik_z\cdot(z-z')} \frac{e^{iG_\parallel\cdot(\rho-\rho')}}{G_\parallel + k_z^2} dk_z = \frac{2\pi}{S} \sum_{G_\parallel} \frac{e^{-G_\parallel\cdot|z-z'|} e^{iG_\parallel\cdot(\rho-\rho')}}{G_\parallel^2} ,
\]

(15)

where \( S \) is the primitive unit cell area \[13\], parallel to the slab plane, \( G_\parallel \) are the reciprocal lattice vectors corresponding to the 2D lattice and \( \rho = \{x, y\} \). By inserting (15) into (14) it can be shown that only the contributions to \( \mathcal{E}_{dip} \) with \( z_i \neq z_j \) exponentially converge as \( G_\parallel \) increases (compare with the 1D case). The terms with \( z_i = z_j \) describing the dipole-dipole interactions in the \( z \)-layers need additional care; we separate these terms and denote them as \( A \). Now instead of Eq. (12) we have

\[
\mathcal{E}_{dip} = A + \frac{\pi}{S} \sum_{G_\parallel} \sum_{i,j} G_\parallel \exp(-G_\parallel \cdot |z_{ij}|)
\]

\[
\times \left[ B \cos(G_\parallel \cdot \rho_{ij}) + C \sin(G_\parallel \cdot \rho_{ij}) \right] \frac{z_{ij}}{|z_{ij}|} ,
\]

(16)

where

\[
B = -d_z(r_i)d_z(r_j) + \frac{1}{G_\parallel} [G_\parallel \cdot d(r_i)] [G_\parallel \cdot d(r_j)] ,
\]

(17)

\[
C = -\frac{1}{G_\parallel} \left\{ [G_\parallel \cdot d(r_i)] d_z(r_j) + [G_\parallel \cdot d(r_j)] d_z(r_i) \right\} .
\]

(18)

The prime at the second sum in (16) indicates the terms with \( z_{ij} = 0 \) to be dropped. To evaluate these terms (collected together in \( A \)) we apply the Ewald type transformation to the Green’s function \[13\] representing it in both coordinate and reciprocal spaces:

\[
G(r, r') = \sum_{R_\parallel} \frac{\text{erfc}(\eta |r-r' + R_\parallel|)}{|r-r' + R_\parallel|} + \frac{2\sqrt{\pi}}{S}
\]

\[
\times \sum_{G_\parallel} e^{iG_\parallel\cdot(\rho-\rho')} \int_0^\eta e^{-|z-z'|^2/2t^2} e^{-G_\parallel^2/4t^2} t^{-2} dt.\]

(19)

Here \( \eta \) is the Ewald parameter, and \( \text{erfc} \) is the complementary error function

\[
\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) dt .
\]

(20)

Using (19) and excluding the self-interaction term corresponding to \( r_i = r_j \) when \( R_\parallel = 0 \), one obtains

\[
A = \frac{\pi}{S} \sum_{G_\parallel} \sum_{i,j} G_\parallel \cos(G_\parallel \cdot \rho_{ij}) \times \left\{ \frac{1}{\sqrt{4\pi}} \Gamma \left(-\frac{1}{2}, \frac{G_\parallel^2}{4\eta^2} \right) d_z(r_i)d_z(r_j) \right. \\
\left. + \frac{1}{G_\parallel^2} \text{erfc} \left( \frac{G_\parallel}{2\eta} \right) [G_\parallel \cdot d(r_i)] [G_\parallel \cdot d(r_j)] \right\} - \sum_i \frac{2\eta^3 |d(r_i)|^2}{3\sqrt{\pi}} ,
\]

(21)

where the summation over \( i, j \) is constrained by the condition \( z_{ij} = 0 \), \( \Gamma \) is the incomplete Gamma function \[14\]

\[
\Gamma(\alpha, x) = \int_x^\infty e^{-t} t^{\alpha-1} dt ,
\]

(22)

and the Ewald parameter \( \eta \) is presumed to be large enough, so that the real space summation can be entirely neglected. It is interesting that the first sum in (21) contains the term \( G_\parallel = 0 \). Indeed, since

\[
\lim_{G_\parallel \to 0} \Gamma \left(-\frac{1}{2}, \frac{G_\parallel^2}{4\eta^2} \right) = 4\eta/G_\parallel ,
\]

(23)

we have

\[
A(G_\parallel = 0) = \frac{2\sqrt{\pi} \eta}{S} \sum_{i,j} d_z(r_i)d_z(r_j) \]

\[
= \frac{2\sqrt{\pi} \eta}{S} \sum_n (D^n_z)^2 ,
\]

(24)

where \( D^n_z \) is the \( z \)-component of the total dipole moment in the \( n \)-th layer parallel to the \((x, y)\) plane.

Finally we note that in both 1D and 2D cases the dipole energy \[14\] can be rewritten as

\[
\mathcal{E}_{dip} = \frac{1}{2} \sum_{\alpha, \beta, ij} Q_{\alpha\beta, ij} d_\alpha(r_i)d_\beta(r_j) ,
\]

(25)

where \( Q_{\alpha\beta, ij} \) is the structure constant matrix; the latter can be calculated once and for all similar to the case of 3D periodicity \[11\]. Explicitly, the matrices are
\[ Q^{(1D)}_{\alpha\beta,ij} = \frac{2}{a} \sum G^2 \cos(G \cdot z_{ij}) \left\{ K_0(G\rho_{ij}) \delta_{\alpha z} \delta_{\beta z} + \frac{\delta_{\alpha x} \delta_{\beta x} + \delta_{\alpha y} \delta_{\beta y}}{G\rho_{ij}} K_1(G\rho_{ij}) \right\} \]

\[ -\frac{1}{\rho_{ij}^2} K_2(G\rho_{ij}) \rho_{\alpha,ij} \rho_{\beta,ij} \right\} - \frac{2}{a} \sum G \sin(G \cdot z_{ij}) K_1(G\rho_{ij}) \rho_{ij}^{-1} \times G_{\alpha \rho_{\beta,ij}} + \]

\[ \frac{1}{a^3} \left( \delta_{\alpha x} \delta_{\beta x} + \delta_{\alpha y} \delta_{\beta y} - 2\delta_{\alpha z} \delta_{\beta z} \right) \sum_{n=-\infty}^{\infty} \left| n + \frac{z_{ij}}{a} \right|^{-3}, \]

\[ Q^{(2D)}_{\alpha\beta,ij} = \frac{2\pi}{S} \sum G \left\{ G \cos(G \cdot \rho_{ij}) \left[ \frac{1}{\sqrt{4\pi}} \frac{1}{\frac{1}{2} G^2 + \frac{1}{4\eta^2}} \delta_{\alpha z} \delta_{\beta z} + \frac{1}{G^2} \text{erfc} \left( \frac{G}{2\eta} \right) G_{\alpha} G_{\beta} \right] \right\} + G \exp(-G |z_{ij}|) \left[ \frac{G_{\alpha} G_{\beta}}{G^2} - \delta_{\alpha z} \delta_{\beta z} \right] \cos(G \cdot \rho_{ij}) - \frac{G_{\alpha} \delta_{\beta z}}{G} \sin(G \cdot \rho_{ij}) \left| z_{ij} \right| \right\} ^{\frac{3}{3\sqrt{\pi}}}. \]

(26)

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