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LETTER TO THE EDITOR

Effective field of a dipole in a lattice of polarisable spheres

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Abstract. The effective electric field in a simple cubic lattice (of spacing L) with polarisable sphere of polarisability α at each vertex, due to a permanent dipole μ_1 of polarisability α_1 at one vertex deep within the lattice is evaluated. The dielectric constant of the lattice is: $\varepsilon(\alpha, \alpha_1, L) = (1-4\pi\alpha/3L^3)(1+8\pi\alpha/3L^3) - 2(4\pi\alpha/3L^3)^2(\alpha_1/\alpha - 1)$.

The unbalanced source of the electric field within the lattice of polarisable particles produces a collective response of the system. Part of this response is due to the N-particle induced-dipole–induced-dipole interaction. In earlier papers (Wielopolski 1973a, b, Stecki and Wielopolski 1973) we have developed the formalism for calculating the polarisability contribution to the energy of the various point defects in crystal lattices and various examples were studied. Alder and Pollock (1977) calculated numerically the electric field due to a permanent dipole in a medium of 108 polarisable atoms by molecular dynamics. Smith (1980) has calculated the dielectric constant of the lattice of polarisable particles with a permanent dipole as a source of the electric field by a method similar to that reported in Wielopolski (1973a, b) and Stecki and Wielopolski (1973).

In this letter we point out the effect of the polarisability of the permanent dipole itself upon the electric field in the lattice. Alder and Pollock (1977) put the polarisability of the permanent dipole equal to zero, whereas in Smith (1980) it was taken to be equal to that of the surrounding particles; this effect for any polarisability is calculated below.

Consider the simple cubic lattice, of spacing L, with atoms of polarisability α at the vertices. Deep within the lattice on the vertex labelled 1 the permanent dipole μ_1, of polarisability α_1, is situated. The response of the system to the electric field is purely via polarisation. The effective electric field at particle i is expressed in the following way:

$$\boldsymbol{E}_i = -\mathbf{T}_{i1}(\boldsymbol{\mu}_1 + \boldsymbol{p}_1) - \sum_{j\neq 1} \mathbf{T}_{ij}\boldsymbol{p}_j = -\mathbf{T}_{i1}\boldsymbol{\mu}_1 - \sum_j \mathbf{T}_{ij}\boldsymbol{p}_j \tag{1}$$

where $\mathbf{T}_{ij} = -\boldsymbol{\nabla}_j\boldsymbol{\nabla}_j|\boldsymbol{r}_{ij}|^{-1}$ is the dipole–dipole tensor, $\mathbf{T}_{ii} \equiv 0$, and $\boldsymbol{p}_i = \alpha_i\boldsymbol{E}_i$ is the induced dipole moment.

The first part of equation (1) represents the direct contribution from the permanent dipole, the second part is the contribution from all induced dipoles. The solution of

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equation (1) is of the following form:

$$\begin{aligned}\boldsymbol{E}_i &= -\sum_j(\mathbf{U}\delta_{ij} - \mathbf{T}_{ij}\alpha_j + \sum_k \mathbf{T}_{ik}\alpha_k\mathbf{T}_{kj}\alpha_j - \ldots)\mathbf{T}_{j1}\boldsymbol{\mu}_1 \\ &= -\sum_j \mathbf{A}_{ij}\mathbf{T}_{j1}\boldsymbol{\mu}_1.\end{aligned} \tag{2}$$

Expression (2) is easy to calculate in terms of the finite Fourier transform (Wielopolski 1973a, Bellemans and Stecki 1961). Making use of the integral representation of the Kronecker delta:

$$\delta_{ij} = \int_\Gamma \mathrm{d}k \exp[2\pi \mathrm{i}\boldsymbol{k}(\boldsymbol{n}_i - \boldsymbol{n}_j)] \tag{3}$$

where Γ is the cube $(-\frac{1}{2}, \frac{1}{2})^3$ in the case of the simple cubic lattice and $\boldsymbol{n}_i$, $\boldsymbol{n}_j$ are the non-dimensional lattice vectors, we obtain

$$\boldsymbol{E}_i = -\int_\Gamma \mathrm{d}\boldsymbol{k} \exp[-2\pi \mathrm{i}\boldsymbol{k}(\boldsymbol{n}_1 - \boldsymbol{n}_i)][\mathbf{U} + \boldsymbol{\tau}(\boldsymbol{k})\alpha]^{-1}\tau(\boldsymbol{k})\boldsymbol{\mu}_1 \tag{4}$$

where $\boldsymbol{\tau}(\boldsymbol{k})$ is defined as follows:

$$\boldsymbol{\tau}(\boldsymbol{k}) = \sum_L \mathbf{T}_{il} \exp[2\pi \mathrm{i}\boldsymbol{k}(\boldsymbol{n}_1 - \boldsymbol{n}_i)]. \tag{5}$$

Expression (5) can be evaluated numerically with the aid of the method described by Nijboer and De Wette (1957) for a number of $\boldsymbol{k}$ values; then, the numerical integration of expression (4) gives the electric field in an arbitrary vertex of the lattice.

In this letter we approximate $\boldsymbol{\tau}(\boldsymbol{k})$ by its asymptotic form (Wielopolski 1973b):

$$\lim_{k\to 0} \boldsymbol{\tau}(\boldsymbol{k}) = -\frac{4\pi}{3L^3}\left(\mathbf{U} - 3\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right). \tag{6}$$

The use of this form of the tensor $\boldsymbol{\tau}(\boldsymbol{k})$ is equivalent to a continuum approximation ; the results are also correct for the electric field in the lattice far away from the vertex 1.

Expression (4) is correct provided that all polarisabilities are equal to each other. Then (see also Wielopolski 1973b)

$$\mathbf{a}^0(\boldsymbol{k}, \alpha) = [\mathbf{U} + \boldsymbol{\tau}(\boldsymbol{k})\alpha]^{-1} = \frac{1+\beta}{(1-\beta)(1+2\beta)} - \frac{\alpha'}{(1-\beta)(1+2\beta)}\boldsymbol{\tau}'(\boldsymbol{k}) \tag{7}$$

where

$$\alpha' = \alpha/L^3 \qquad \boldsymbol{\tau}'(\boldsymbol{k}) = L^3\boldsymbol{\tau}(\boldsymbol{k}) \qquad \beta = 4\pi\alpha/L^3$$

and

$$\mathbf{A}^0_{ij} = \int_\Gamma \mathrm{d}k \exp[-2\pi \mathrm{i}\boldsymbol{k}(\boldsymbol{n}_j - \boldsymbol{n}_i)]\mathbf{a}^0(\boldsymbol{k}, \alpha). \tag{8}$$

In the case when $\alpha \neq \alpha_1$ the function $\mathbf{A}_{ij}$ may be expressed in terms of the combinations of $\mathbf{A}^0_{ij}$ (Wielopolski 1973b and Stecki and Wielopolski 1973) in the following form:

$$\mathbf{A}_{ij} = \mathbf{A}^0_{ij} - (\mathbf{U}\delta_{ij} - \mathbf{A}^0_{i1})\frac{\omega}{\mathbf{U} + (\mathbf{U} - \mathbf{A}^0_{11})\omega}\mathbf{A}^0_{1j} \tag{9}$$

where $\omega = (\alpha_1 - \alpha)/\alpha$.

Introduction of this expression into equation (2) leads to

$$\boldsymbol{E}_i = -\Big(\sum_j \mathbf{A}^0_{ij}\mathbf{T}_{j1}\boldsymbol{\mu}_1 - (\mathbf{U}\delta_{i1} - \mathbf{A}^0_{i1})\frac{\omega}{\mathbf{U}+(\mathbf{U}-\mathbf{A}^0_{11})\omega}\sum_j \mathbf{A}^0_{1j}\mathbf{T}_{j1}\boldsymbol{\mu}_1\Big)$$

$$= -\alpha^{-1}(\mathbf{U}\delta_{i1} - \mathbf{A}^0_{i1})\Big(\mathbf{U} - \frac{\omega}{\mathbf{U}+(\mathbf{U}-\mathbf{A}^0_{11})\omega}(\mathbf{U}-\mathbf{A}^0_{11})\Big)\boldsymbol{\mu}_1. \tag{10}$$

Making use of equations (7) and (8) we obtain

$$\mathbf{A}^0_{ij} = \int_\Gamma \mathrm{d}\boldsymbol{k}\, \exp[-2\pi \mathrm{i}\boldsymbol{k}(\boldsymbol{n}_j - \boldsymbol{n}_i)]\mathbf{a}^0(\boldsymbol{k},\alpha) = \frac{1+\beta}{(1-\beta)(1+2\beta)}\delta_{ij} - \frac{\alpha}{(1-\beta)(1+2\beta)}\mathbf{T}_{ij} \tag{11}$$

and

$$\boldsymbol{E}_i = \frac{1}{(1-\beta)(1+2\beta)-2\beta^2\omega}\mathbf{T}_{i1}\boldsymbol{\mu}_1. \tag{12}$$

The electric field at point i due to a dipole $\boldsymbol{\mu}_1$ in a continuum with dielectric constant ε is

$$\boldsymbol{E}_i = -\varepsilon^{-1}\mathbf{T}_{i1}\boldsymbol{\mu}_1.$$

Thus, in this case, for long-range interactions the lattice can be regarded as a continuum medium with dielectric constant

$$\varepsilon(\alpha, L) = (1-4\pi\alpha/3L^3)(1+8\pi\alpha/3L^3) - 2(4\pi\alpha/3L^3)^2\omega. \tag{13}$$

The expansion of expression (12) in powers of α/L^3 leads to an agreement with the results of Alder and Pollock (1977) and Smith (1980)

$$\boldsymbol{E}_i = -(1-4\pi\alpha/3L^3)\mathbf{T}_{i1}\boldsymbol{\mu}_1 + \mathrm{O}(\alpha^2). \tag{14}$$

The dependence on the polarisability α_1 of the permanent dipole appears in higher-order terms.

For the reaction field of the dipole $\boldsymbol{\mu}_1$ we obtain

$$\boldsymbol{E}_1 = \alpha^{-1}\frac{2\beta^2}{(1-\beta)(1+2\beta)-2\beta^2\omega}\boldsymbol{\mu}_1 \tag{15}$$

or after the expansion in powers of α/L^3

$$\boldsymbol{E}_1 = (4\pi/3)(8\pi\alpha\boldsymbol{\mu}_1/3L^6)(1-4\pi\alpha/3L^3) + \mathrm{O}(\alpha^3). \tag{16}$$

This result differs in the factor $(4\pi/3)$ from the results of the continuum theory (Frohlich 1949) and from the results of Alder and Pollock (1977), which in this notation is

$$\boldsymbol{E}_1 = (8\pi\alpha\boldsymbol{\mu}_1/3L^6)(1-5\pi\alpha/8L^3) + \mathrm{O}(\alpha^3).$$

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