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Response of a lattice of polarisable points to imposed electric fields

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Abstract. A simple cubic lattice Λ of unit spacing with a point of polarisability α at each lattice vertex is considered. The response of the lattice to an applied constant electric field and to the electric field due to a charged or dipolar impurity is calculated and asymptotic representations for the polarisation at lattice points far from the surface of the lattice sample and far from the impurities are obtained. Polarisation due to a constant applied external field is shown to depend on the shape of the lattice sample and the dielectric constant of the medium exterior to the lattice sample. Polarisation due to charged or dipolar impurities is shown to be independent of shape and external dielectric constant. The asymptotic representations obtained for the polarisation are compared with model calculations treating the lattice sample as a continuum dielectric of dielectric constant ε. This dielectric constant is found to be $\varepsilon = (1+8\pi\alpha/3)/(1-4\pi\alpha/3)$ so that the standard Lorentz relation between macroscopic and microscopic electric fields is confirmed for all the cases considered. For the dipolar impurity case the continuum picture must use a rescaled dipole moment which is calculated explicitly. The reaction fields giving this rescaled dipole moment are discussed.

1. Introduction

The response of dense matter composed of polarisable particles to an external field and to the field of a charged or dipolar impurity has been considered by several authors. Recently Lehnen and Bruch (1980) have studied the response of a lattice of polarisable spheres to a static point charge near a plane surface of the lattice, while Smith (1980a) and Wielopolski (1981) have considered the response of such a lattice system to a dipole embedded deep within the lattice. These papers considered a fixed lattice, ignoring the considerations of statistical mechanics. This approach is of interest because the system is a simple model of the response of a static ionic crystal to external fields and impurities (Bellemans and Plaitin 1975). Pollock and Alder (1977, 1978) and Pollock *et al* (1980) carried out molecular dynamics studies of a dipolar or charged impurity in a fluid of spherical Lennard-Jones particles with a point polarisability. They were able to predict local fields at large distances from the impurity in terms of a continuum picture of the fluid with a dielectric constant. They then used the simulation data to consider the way the fluid system responds to the field of an impurity by screening that field at short distances from the impurity. Pollock *et al* (1980) pointed out that particular care had to be taken with the continuum picture of the fluid to be able to predict the local electric field at a point far from the impurity correctly. For the polarisable lattice system, Smith (1980a) and Wielopolski (1981) gave expressions for the polarisation density far from a dipolar impurity, but calculated a dielectric constant for their system using an incorrect continuum picture of the system, thus obtaining an incorrect value for the dielectric constant. This paper is a correction and extension of the results of Smith (1980a) and Wielopolski (1981).

Consider a simple cubic lattice Λ of unit spacing with a point of polarisability α at each lattice vertex with a microscopic electric field $\boldsymbol{f}(\boldsymbol{m})$ imposed at each lattice site $\boldsymbol{m}$. The polarisation $\boldsymbol{\mu}(\boldsymbol{m})$ at site $\boldsymbol{m}$ then satisfies the equation

$$\boldsymbol{\mu}(\boldsymbol{m})=\alpha\boldsymbol{f}(\boldsymbol{m})-\alpha\sum_{\boldsymbol{n}\in\Lambda} t(\boldsymbol{m}-\boldsymbol{n})\cdot\boldsymbol{\mu}(\boldsymbol{n}) \tag{1.1}$$

where

$$t(\boldsymbol{m})=\begin{cases}|\boldsymbol{m}|^{-3}(I-3\boldsymbol{mm}/|\boldsymbol{m}|^2) & \boldsymbol{m}\neq\boldsymbol{0}\\ 0 & \boldsymbol{m}=\boldsymbol{0}.\end{cases} \tag{1.2}$$

The second term on the right-hand side of equation (1.1) is the electric field at $\boldsymbol{m}$ due to the dipoles $\boldsymbol{\mu}(\boldsymbol{n})$ at all the other sites of the lattice. Widom (1965) has considered general techniques for the solution of equations of the form of equation (1.1) for one-dimensional lattices. His considerations imply that because the function

$$T(\boldsymbol{\xi})=\sum_{\boldsymbol{n}\in\Lambda} t(\boldsymbol{n})\exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}) \tag{1.3}$$

is bounded for $\boldsymbol{\xi}\in V=[-\pi,\pi]^3$, then if

$$\sum_{\boldsymbol{m}\in\Lambda}|\boldsymbol{f}(\boldsymbol{m})|^2<\infty \tag{1.4}$$

standard Fourier transform methods will give the solution

$$\boldsymbol{\mu}(\boldsymbol{m})=\frac{\alpha}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\xi}[I+\alpha T(\boldsymbol{\xi})]^{-1}\cdot\boldsymbol{F}(\boldsymbol{\xi})\exp(-\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{m}) \tag{1.5}$$

to equation (1.1) where

$$\boldsymbol{F}(\boldsymbol{\xi})=\sum_{\boldsymbol{n}\in\Lambda}\boldsymbol{f}(\boldsymbol{n})\exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}) \tag{1.6}$$

provided that α is small enough to ensure that $[I+\alpha T(\boldsymbol{\xi})]$ has a finite inverse for all $\boldsymbol{\xi}\in V$. The constraint on α is not surprising, since the lattice system may be expected to show a polarisation catastrophe for α large enough. While the fields due to a charged or dipolar impurity obey the inequality (1.4), a constant external electric field will not. In that case, $\boldsymbol{F}(\boldsymbol{\xi})$ is a generalised function proportional to $\delta(\boldsymbol{\xi})$. The solution (1.5) will still apply, but care must be taken with $T(\boldsymbol{\xi})$ since the lattice sum for it (equation (1.3)) is conditionally convergent at $\boldsymbol{\xi}=\boldsymbol{0}$. Thus the solution of equation (1.1) for an applied field not obeying (1.4) will reflect the shape of the macroscopic sample of the lattice concerned, since this shape defines a summation order, and thus a value, for $T(\boldsymbol{0})$.

It is necessary then to consider a large sample of the lattice, $\Omega_N(\Lambda)$ of shape Ω defined in the following way. Let Ω_0 be the interior and surface of the closed region of $\boldsymbol{R}^3$ containing the origin and with the surface given by

$$\Omega_0(\boldsymbol{r})=\boldsymbol{0}. \tag{1.7}$$

The region Ω_0 has volume $\|\Omega_0\|$. The large Ω-shaped sample is then given by

$$\Omega_N(\Lambda) = \{\boldsymbol{n} \in \Lambda : \boldsymbol{n}/N \in \Omega_0\} \tag{1.8}$$

with N chosen to be large. The sample $\Omega_N(\Lambda)$ contains $N^3\|\Omega_0\|$ lattice sites. In this paper, two sample shapes are considered, a plane slab $P_N(\Lambda)$, of width $2N$ and a sphere $S_N(\Lambda)$ of radius N. The region exterior to the sample is considered to be a dielectric continuum of dielectric constant ε', the external dielectric constant.

In setting up the equations for $\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon')$ in a sample $\Omega_N(\Lambda)$, care must be taken to include any reaction field effects. These effects and the appropriate equations (analogous to equation (1.1)) are established in § 2 of this paper. Section 3 contains a discussion of continuum pictures of the systems discussed, in which the lattice sample is replaced by a continuum sample of dielectric constant ε. Section 4 derives solutions to the equations of § 2 and the paper concludes with a discussion of these solutions in § 5.

2. Equations for the polarisation

The polarisation $\boldsymbol{\mu}(\boldsymbol{m})$ obeys the equation

$$\boldsymbol{\mu}(\boldsymbol{m}) = \alpha(\boldsymbol{m})\boldsymbol{E}(\boldsymbol{m}) \tag{2.1}$$

where $\alpha(\boldsymbol{m})$ is the polarisability of the point at $\boldsymbol{m}$ ($\alpha(\boldsymbol{m}) = \alpha$ unless $\boldsymbol{m}$ is the site at which an impurity is placed) and $\boldsymbol{E}(\boldsymbol{m})$ is the electric field at $\boldsymbol{m}$.

2.1. *Plane slab sample $P_N(\Lambda)$ with constant electric field applied normal to the surface*

The slab occupies the region $-N \leq x \leq N$ and the external field is $\boldsymbol{E}_{\mathrm{A}} = (E_{\mathrm{A}}, 0, 0)$ as $x \to \pm\infty$. The applied field in the slab is then

$$\boldsymbol{E}(\boldsymbol{m}) = \varepsilon' \boldsymbol{E}_{\mathrm{A}}. \tag{2.2}$$

The field set up at $\boldsymbol{m}$ due to a dipole $\boldsymbol{\mu}(\boldsymbol{n})$ at $\boldsymbol{n}$ may now be calculated using the method of images and the result expanded for large N. As $N \to \infty$ this field is

$$\boldsymbol{E}(\boldsymbol{m}, \boldsymbol{n}) = -t(\boldsymbol{m} - \boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}) \tag{2.3}$$

so that for this case

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \alpha\varepsilon' \boldsymbol{E}_{\mathrm{A}} - \alpha \sum_{\boldsymbol{n} \in P_N(\Lambda)} t(\boldsymbol{m} - \boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}, \varepsilon'). \tag{2.4}$$

There is a reaction field term in equation (2.3) which is $O(N^{-3})$, but even for constant solutions to equation (2.5) this reaction field makes a contribution to equation (2.5) which is $O(N^{-1})$ and thus may be ignored.

2.2. *Spherical sample $S_N(\Lambda)$ with constant electric field applied*

The sphere occupies the region $|\boldsymbol{r}| \leq N$ and the external field is $\boldsymbol{E}_{\mathrm{A}}$ as $|\boldsymbol{r}| \to \infty$. The field applied to sites inside the sample is then

$$\boldsymbol{E}(\boldsymbol{m}) = \frac{3\varepsilon'}{2\varepsilon' + 1} \boldsymbol{E}_{\mathrm{A}}. \tag{2.5}$$

The field at $\boldsymbol{m}$ due to a dipole $\boldsymbol{\mu}(\boldsymbol{n})$ at $\boldsymbol{n}$ contains a reaction field part which is also $O(N^{-3})$, but this must be included in the equation for $\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon')$ for this case since, as will be shown in § 4, it can contribute to the solution. The net field at $\boldsymbol{m}$ due to $\boldsymbol{\mu}(\boldsymbol{n})$ is then

$$\boldsymbol{E}(\boldsymbol{m}, \boldsymbol{n}) = -t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}) + \frac{2(\varepsilon'-1)}{(2\varepsilon'+1)N^3} \boldsymbol{\mu}(\boldsymbol{n}). \tag{2.6}$$

Thus the polarisation equation is

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \frac{3\alpha\varepsilon'}{2\varepsilon'+1} \boldsymbol{E}_{\mathrm{A}} - \alpha \sum_{\boldsymbol{n} \in S_N(\Lambda)} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}, \varepsilon') + \frac{2\alpha(\varepsilon'-1)}{(2\varepsilon'+1)N^3} \sum_{\boldsymbol{n} \in S_N(\Lambda)} \boldsymbol{\mu}(\boldsymbol{n}, \varepsilon'). \tag{2.7}$$

Since $S_N(\Lambda)$ contains $4\pi N^3/3$ lattice sites, it can be seen that for a solution $\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \bar{\boldsymbol{\mu}}(\varepsilon')$, a constant, the reaction field term will contribute.

2.3. *Sample with the point at $\boldsymbol{m} = \boldsymbol{0}$ replaced by a point of polarisability $\alpha' = \alpha(1+\omega)$ and bearing a charge Q*

The direct field due to the charge Q is

$$\boldsymbol{E}(\boldsymbol{m}) = Q\boldsymbol{m}|\boldsymbol{m}|^{-3}(1-\delta_{\boldsymbol{m},0}). \tag{2.8}$$

This gives a square summable (i.e. obeying inequality (1.4)) inhomogeneous term in the equation for $\boldsymbol{\mu}(\boldsymbol{m})$. Widom's analysis shows that the solutions to equations of the form (1.1) are also square summable so that reaction fields do not contribute to the solution as $N \to \infty$ for any shape Ω of sample. Thus the equation for $\boldsymbol{\mu}(\boldsymbol{m})$ is

$$\boldsymbol{\mu}(\boldsymbol{m}) = \alpha \frac{Q\boldsymbol{m}(1-\delta_{\boldsymbol{m},0})}{|\boldsymbol{m}|^3} - \alpha \sum_{\boldsymbol{n} \in \Lambda} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}) - \alpha\omega\delta_{\boldsymbol{m},0} \sum_{\boldsymbol{n} \in \Lambda} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}). \tag{2.9}$$

Notice that this is not as simple as equation (1.1) whenever $\omega \neq 0$. Nonetheless, the method of Fourier transform together with a method used by Wielopolski (1981) can be used to give solutions for $\boldsymbol{\mu}(\boldsymbol{m})$.

2.4. *Sample with the point at $\boldsymbol{m} = \boldsymbol{0}$ replaced by a point of polarisability $\alpha' = \alpha(1+\omega)$ and bearing a dipole moment $\boldsymbol{\nu}$*

The direct field due to the dipole $\boldsymbol{\nu}$ is

$$\boldsymbol{E}(\boldsymbol{m}) = -t(\boldsymbol{m}) \cdot \boldsymbol{\nu} \tag{2.10}$$

and so the polarisation satisfies

$$\boldsymbol{\mu}(\boldsymbol{m}) = -\alpha t(\boldsymbol{m}) \cdot \boldsymbol{\nu} - \alpha \sum_{\boldsymbol{n} \in \Lambda} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}) - \alpha\omega\delta_{\boldsymbol{m},0} \sum_{\boldsymbol{n} \in \Lambda} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}) \tag{2.11}$$

with reaction fields being ignored as in the charged impurity case and for the same reasons.

3. Continuum pictures of lattice polarisation

In this section the lattice sample is supposed to be a continuous medium of dielectric constant ε.

3.1. Plane slab sample with constant field applied normal to the slab surface

The field at $\boldsymbol{r}$ inside the sample is

$$\boldsymbol{E}(\boldsymbol{r})=\frac{\varepsilon'}{\varepsilon}\boldsymbol{E}_{\mathrm{A}} \tag{3.1}$$

and the polarisation density is

$$\boldsymbol{p}(\boldsymbol{r})=\frac{\varepsilon-1}{4\pi\varepsilon}\,\varepsilon'\boldsymbol{E}_{\mathrm{A}}. \tag{3.2}$$

3.2. Spherical sample with constant field applied

Here standard methods using spherical harmonics (Bottcher 1973) give for the field at $\boldsymbol{r}$ inside the sample

$$\boldsymbol{E}(\boldsymbol{r})=\frac{3\varepsilon'}{2\varepsilon'+\varepsilon}E_{\mathrm{A}} \tag{3.3}$$

with polarisation density

$$\boldsymbol{p}(\boldsymbol{r})=\frac{3(\varepsilon-1)\varepsilon'}{4\pi(2\varepsilon'+\varepsilon)}\boldsymbol{E}_{\mathrm{A}}. \tag{3.4}$$

Notice that from these results it can be seen that the polarisation density depends on sample shape and external dielectric constant. The solutions to equations (2.4) and (2.7) may then be expected to show similar dependence. This shape and external dielectric constant dependence of $\boldsymbol{p}(\boldsymbol{r})$ does not occur for a charged or dipolar impurity in the limit as the sample becomes large, as may be checked by constructing explicit solutions by the method of images for the plane slab case or spherical harmonic expansions for the spherical case.

3.3. Sample with charge Q^* at centre

The electric field at $\boldsymbol{r}$ is

$$\boldsymbol{E}(\boldsymbol{r})=Q^*\boldsymbol{r}/\varepsilon|\boldsymbol{r}|^3 \tag{3.5}$$

with polarisation density

$$\boldsymbol{p}(\boldsymbol{r})=(\varepsilon-1)Q^*\boldsymbol{r}/4\pi\varepsilon|\boldsymbol{r}|^3. \tag{3.6}$$

3.4. Sample with dipole $\boldsymbol{\nu}^*$ at centre

The electric field at $\boldsymbol{r}$ is

$$\boldsymbol{E}(\boldsymbol{r})=-\varepsilon^{-1}t(\boldsymbol{r})\cdot\boldsymbol{\nu}^* \tag{3.7}$$

with polarisation density

$$\boldsymbol{p}(\boldsymbol{r})=-\frac{\varepsilon-1}{4\pi\varepsilon}\,t(\boldsymbol{r})\cdot\boldsymbol{\nu}^*. \tag{3.8}$$

These results for polarisation density may be compared with solutions to the equations for $\boldsymbol{\mu}(\boldsymbol{m})$ in the lattice, since the unit cell of the lattice has unit volume, so that $\boldsymbol{\mu}(\boldsymbol{m})$

is a polarisation density. Such a comparison for the constant field case will enable the dielectric constant ε' to be evaluated. It may be expected that the symmetry of the charged impurity case will allow an interpretation with $Q^* = Q$, since there should be no electric field on the polarisable point at $\boldsymbol{m} = \boldsymbol{0}$. On the other hand, for the dipolar impurity case there will be an electric field on the polarisable point at $\boldsymbol{m} = \boldsymbol{0}$, so that a continuum picture of this case is not expected to use $\boldsymbol{\nu}^* = \boldsymbol{\nu}$. This is indeed the case, as is discussed in § 5.

4. Solution of polarisation equations

These equations are solved by taking Fourier transforms, with

$$\boldsymbol{M}(\boldsymbol{\xi}) = \sum_{\boldsymbol{n}\in\Lambda} \boldsymbol{\mu}(\boldsymbol{n}) \exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}) \tag{4.1}$$

with inverse

$$\boldsymbol{\mu}(\boldsymbol{n}) = \frac{1}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\xi}\, \boldsymbol{M}(\boldsymbol{\xi}) \exp(-\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}). \tag{4.2}$$

A useful function is

$$\boldsymbol{Y}(\boldsymbol{\xi}) = \boldsymbol{T}(\boldsymbol{\xi}) \cdot \boldsymbol{M}(\boldsymbol{\xi}) \tag{4.3}$$

with inverse $\boldsymbol{y}(\boldsymbol{n})$. The Fourier transform of $f(\boldsymbol{m}) = 1$ is $(2\pi)^3\delta(\boldsymbol{\xi})$. The Fourier transform of $t(\boldsymbol{n})$ is shape dependent if $N\boldsymbol{\xi} = \mathrm{O}(1)$. For $N\boldsymbol{\xi} = \mathrm{O}(N)$ the Fourier transform

$$T_\Omega(\boldsymbol{\xi}) = \sum_{\boldsymbol{n}\in\Omega_N(\Lambda)} t(\boldsymbol{n}) \exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}) \tag{4.4}$$

is (De Leeuw *et al* 1980, Smith 1981)

$$T_\Omega(\boldsymbol{\xi}) = -\nabla\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{\xi})|_{\boldsymbol{r}=\boldsymbol{0}} + 4\pi\, \boldsymbol{\xi}\boldsymbol{\xi}/\xi^2 \tag{4.5}$$

where

$$\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{\xi}) = \sum_{\substack{\boldsymbol{n}\in\Lambda \\ \boldsymbol{n}\neq\boldsymbol{0}}} \frac{\operatorname{erfc}(\eta|\boldsymbol{r}+\boldsymbol{n}|)}{|\boldsymbol{r}+\boldsymbol{n}|} \exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{n}) - |\boldsymbol{r}|^{-1} \operatorname{erf}(\eta|\boldsymbol{r}|)$$
$$+ \sum_{\substack{\boldsymbol{m}\in R \\ \boldsymbol{m}\neq\boldsymbol{0}}} \frac{\pi}{(\pi\boldsymbol{m} - \frac{1}{2}\boldsymbol{\xi})^2} \exp[-\eta^{-2}(\pi\boldsymbol{m} - \tfrac{1}{2}\boldsymbol{\xi})^2 + 2\mathrm{i}\boldsymbol{r}\cdot(\pi\boldsymbol{m} - \tfrac{1}{2}\boldsymbol{\xi})]. \tag{4.6}$$

Here $\operatorname{erf}(x)$ is the error function, $\operatorname{erfc}(x)$ the complementary error function, R is the lattice reciprocal to Λ (and equal to Λ for this simple cubic case) and η is an arbitrary parameter. This representation of $T_\Omega(\boldsymbol{\xi})$ is used since the lattice sums are absolutely and rapidly convergent so that $T_\Omega(\boldsymbol{\xi})$ may be computed without much difficulty. Note that the lattice sums are analytic in the components of $\boldsymbol{\xi}$ and that since $t(-\boldsymbol{n}) = t(\boldsymbol{n})$, $T_\Omega(\boldsymbol{\xi})$ is an even function of $\boldsymbol{\xi}$. Thus for small $\boldsymbol{\xi}$

$$T_\Omega(\boldsymbol{\xi}) = -\nabla\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{0})|_{\boldsymbol{r}=\boldsymbol{0}} + 4\pi\, \boldsymbol{\xi}\boldsymbol{\xi}/\xi^2 + \mathrm{O}(\xi^2) \tag{4.7}$$

and this is shape independent.

On the other hand, for $N\boldsymbol{\xi} = \mathrm{O}(1)$, $T_\Omega(\boldsymbol{\xi})$ is shape dependent. De Leeuw *et al* (1980) give for the spherical case

$$T_{\mathrm{S}}(\boldsymbol{\xi}) = -\nabla\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{0})|_{\boldsymbol{r}=\boldsymbol{0}} + \tfrac{4}{3}\pi I + \mathrm{O}(\boldsymbol{\xi}^2) \tag{4.8}$$

while for the plane slab case, Smith (1981) gives

$$T_{\mathrm{P}}(\boldsymbol{\xi}) = -\nabla\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{0})|_{\boldsymbol{r}=\boldsymbol{0}} + 4\pi S + \mathrm{O}(\boldsymbol{\xi}^2) \tag{4.9}$$

where S is the matrix

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{4.10}$$

Further

$$T_{\mathrm{S}}(\boldsymbol{0}) = \sum_{\substack{\boldsymbol{n}\in S_N(\Lambda) \\ \boldsymbol{n}\neq\boldsymbol{0}}} (n_x^2 + n_y^2 + n_z^2)^{-5/2} \begin{pmatrix} n_y^2 + n_z^2 - 2n_x^2 & -3n_x n_y & -3n_x n_z \\ -3n_x n_y & n_x^2 + n_z^2 - 2x_y^2 & -3n_y n_z \\ -3n_x n_z & -3n_y n_z & n_x^2 + n_y^2 - 2x_z^2 \end{pmatrix}. \tag{4.11}$$

The region $S_N(\Lambda)$ is symmetric in each of the components of $\boldsymbol{n}$ and so

$$T_{\mathrm{S}}(\boldsymbol{0}) = 0. \tag{4.12}$$

Thus

$$-\nabla\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{0})|_{\boldsymbol{r}=\boldsymbol{0}} = -\tfrac{4}{3}\pi I \tag{4.13}$$

so that for $N\boldsymbol{\xi} = \mathrm{O}(1)$,

$$T_{\mathrm{S}}(\boldsymbol{\xi}) = \mathrm{O}(\boldsymbol{\xi}^2) \tag{4.14}$$

while

$$T_{\mathrm{P}}(\boldsymbol{\xi}) = -\tfrac{4}{3}\pi I + 4\pi S + \mathrm{O}(\boldsymbol{\xi}^2). \tag{4.15}$$

Finally consider

$$\boldsymbol{C}(\boldsymbol{\xi}) = \sum_{\boldsymbol{m}\in\Lambda} \frac{\boldsymbol{m}}{|\boldsymbol{m}|^3} \exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{m}). \tag{4.16}$$

There is no difficulty at $\boldsymbol{\xi} = 0$ for this case since the oddness of the summand ensures $\boldsymbol{C}(\boldsymbol{0}) = \boldsymbol{0}$. Note that $\boldsymbol{C}(\boldsymbol{\xi})$ is an odd function of $\boldsymbol{\xi}$. Further Smith (1980b) gives

$$\boldsymbol{C}(\boldsymbol{\xi}) = -\nabla\Psi_{\mathrm{E}}(\boldsymbol{r}, \boldsymbol{\xi})|_{\boldsymbol{r}=\boldsymbol{0}} + 4\pi\mathrm{i}\boldsymbol{\xi}/\boldsymbol{\xi}^2 \tag{4.17}$$

for $N\boldsymbol{\xi} = \mathrm{O}(N)$ and thus

$$\boldsymbol{C}(\boldsymbol{\xi}) = 4\pi\mathrm{i}(\boldsymbol{\xi}/\boldsymbol{\xi}^2)(1 + \mathrm{O}(\boldsymbol{\xi}^2)). \tag{4.18}$$

It is now possible to proceed to the solution of the polarisation equations by using the convolution formula

$$\sum_{\boldsymbol{m}\in\Omega_N(\Lambda)} \exp(\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{m}) \sum_{\boldsymbol{n}\in\Omega_N(\Lambda)} t(\boldsymbol{m}-\boldsymbol{n})\cdot\boldsymbol{\mu}(\boldsymbol{n}) = T_\Omega(\boldsymbol{\xi})\cdot\boldsymbol{M}(\boldsymbol{\xi}). \tag{4.19}$$

4.1. Plane slab with external field $\boldsymbol{E}_{\mathrm{A}} = (E_{\mathrm{A}}, 0, 0)$ applied

For this case the polarisation equation is given by equation (2.4) which has the Fourier transform

$$\boldsymbol{M}(\boldsymbol{\xi}, \varepsilon') = \alpha\varepsilon' \boldsymbol{E}_{\mathrm{A}} \cdot (2\pi)^3 \delta(\boldsymbol{\xi}) - \alpha T_{\mathrm{P}}(\boldsymbol{\xi}) \cdot \boldsymbol{M}(\boldsymbol{\xi}, \varepsilon'). \tag{4.20}$$

This equation may be solved for $\boldsymbol{M}(\boldsymbol{\xi})$ and the inverse taken to give

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \alpha\varepsilon' \int_V \mathrm{d}^3\boldsymbol{\xi} [I + \alpha T_{\mathrm{P}}(\boldsymbol{\xi})]^{-1} \cdot \boldsymbol{E}_{\mathrm{A}} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{m}) \delta(\boldsymbol{\xi}). \tag{4.21}$$

It can be seen that the delta function in the integrand probes the nature of $T_{\mathrm{P}}(\boldsymbol{\xi})$ for $N\boldsymbol{\xi} = \mathrm{O}(1)$. Thus the form of equation (4.15) applies. The matrix $[I + \alpha T_{\mathrm{P}}(\boldsymbol{\xi})]$ is diagonal for $\boldsymbol{\xi} = \boldsymbol{0}$ so that it may be easily inverted to give

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \frac{\alpha\varepsilon'}{1 + 2x} \boldsymbol{E}_{\mathrm{A}} \tag{4.22}$$

where $x = 4\pi\alpha/3$. This solution will break down for $\boldsymbol{m}$ close to the edge of $P_N(\Lambda)$ because in fact the delta function used here should be

$$(2\pi)^2 \frac{\sin(N + \frac{1}{2})\xi_x}{\sin \frac{1}{2}\xi_x} \delta(\xi_y)\delta(\xi_z). \tag{4.23}$$

While this acts as a delta function $(2\pi)^3\delta(\boldsymbol{\xi})$ for large N in the integrand in equation (4.21) when $\boldsymbol{m} = \mathrm{O}(1)$, if $\boldsymbol{m} = \mathrm{O}(N)$ (i.e. near the edge of $P_N(\Lambda)$) it will not act as $(2\pi)^3\delta(\boldsymbol{\xi})$. Details of the polarisation near the edge of the slab may be found in Smith (1980b).

4.2. Spherical sample in an applied field

Equation (2.7) for the polarisation in this case may be written

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \boldsymbol{F} - \alpha \sum_{\boldsymbol{n} \in S_N(\Lambda)} t(\boldsymbol{m} - \boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}, \varepsilon') \tag{4.24}$$

with

$$\boldsymbol{F} = \frac{3\alpha\varepsilon'}{2\varepsilon' + 1} \boldsymbol{E}_{\mathrm{A}} + \frac{2\alpha(\varepsilon' - 1)}{(2\varepsilon' + 1)N^3} \sum_{\boldsymbol{n} \in S_N(\Lambda)} \boldsymbol{\mu}(\boldsymbol{n}, \varepsilon') \tag{4.25}$$

and solution

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \int_V \mathrm{d}^3\boldsymbol{\xi} [I + \alpha T_{\mathrm{S}}(\boldsymbol{\xi})]^{-1} \cdot \boldsymbol{F} \delta(\boldsymbol{\xi}) \exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{m}). \tag{4.26}$$

The appropriate form for $T_{\mathrm{S}}(\boldsymbol{\xi})$ is given by equation (4.14) so that

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \bar{\boldsymbol{\mu}}(\varepsilon') = \boldsymbol{F}. \tag{4.27}$$

Substituting this result into equation (4.25) for $\boldsymbol{F}$ gives

$$\bar{\boldsymbol{\mu}}(\varepsilon') = \frac{3\alpha\varepsilon'}{2\varepsilon' + 1} \boldsymbol{E}_{\mathrm{A}} + \frac{2x(\varepsilon' - 1)}{2\varepsilon' + 1} \bar{\boldsymbol{\mu}}(\varepsilon'). \tag{4.28}$$

Hence

$$\boldsymbol{\mu}(\boldsymbol{m}, \varepsilon') = \bar{\boldsymbol{\mu}}(\varepsilon') = \frac{3\alpha\varepsilon'}{2\varepsilon'(1-x)+(1+2x)} \boldsymbol{E}_{\mathrm{A}} \tag{4.29}$$

except close to the boundary of $S_N(\Lambda)$

4.3. Sample with charge Q at $\boldsymbol{m} = \boldsymbol{0}$

The Fourier transform of equation (2.9) is

$$\boldsymbol{M}(\boldsymbol{\xi}) = \alpha Q \boldsymbol{C}(\boldsymbol{\xi}) - \alpha T(\boldsymbol{\xi}) \cdot \boldsymbol{M}(\boldsymbol{\xi}) - \alpha\omega \cdot \frac{1}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\lambda}\, T(\boldsymbol{\lambda}) \cdot \boldsymbol{M}(\boldsymbol{\lambda}). \tag{4.30}$$

Note that

$$\boldsymbol{y}(\boldsymbol{0}) = \frac{1}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\lambda}\, T(\boldsymbol{\lambda}) \cdot \boldsymbol{M}(\lambda). \tag{4.31}$$

Thus, multiplying equation (4.30) by $T(\boldsymbol{\xi})$, solving for $\boldsymbol{Y}(\boldsymbol{\xi})$ and taking the inverse transform,

$$\boldsymbol{y}(\boldsymbol{0}) = \frac{1}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\xi} [I + \alpha T(\boldsymbol{\xi})]^{-1} [\alpha Q T(\boldsymbol{\xi}) \cdot \boldsymbol{C}(\boldsymbol{\xi}) - \alpha\omega T(\boldsymbol{\xi}) \cdot \boldsymbol{y}(\boldsymbol{0})]. \tag{4.32}$$

Since $T(\boldsymbol{\xi})$ is even in $\boldsymbol{\xi}$ while $\boldsymbol{C}(\boldsymbol{\xi})$ is odd in $\boldsymbol{\xi}$, equation (4.32) has the solution $\boldsymbol{y}(\boldsymbol{0}) = \boldsymbol{0}$ and so

$$\boldsymbol{\mu}(\boldsymbol{m}) = \frac{\alpha Q}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\xi} [I + \alpha T(\boldsymbol{\xi})]^{-1} \cdot \boldsymbol{C}(\boldsymbol{\xi}) \exp(\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{m}). \tag{4.33}$$

For $|\boldsymbol{m}|$ large, an estimate of $\boldsymbol{\mu}(\boldsymbol{m})$ with error $\mathrm{O}(|\boldsymbol{m}|^{-2})$ with respect to the estimate may be obtained by using the leading-order expansions of $T(\boldsymbol{\xi})$ and $\boldsymbol{C}(\boldsymbol{\xi})$ for small $\boldsymbol{\xi}$. Now

$$I + \alpha T(\boldsymbol{\xi}) = (1-x)I + 3x\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2 + \mathrm{O}(\xi^2) \tag{4.34}$$

so that

$$[I + \alpha T(\boldsymbol{\xi})]^{-1} = \frac{1}{1-x} I - \frac{3x}{(1-x)(1+2x)} \frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2} + \mathrm{O}(\xi^2) \tag{4.35}$$

while

$$\boldsymbol{C}(\boldsymbol{\xi}) = 4\pi\mathrm{i}(\boldsymbol{\xi}/\xi^2)(1 + \mathrm{O}(\xi^2)). \tag{4.36}$$

Further

$$\frac{1}{(2\pi)^3} \int_V \mathrm{d}^3\boldsymbol{\xi}\, 4\pi\mathrm{i} \frac{\boldsymbol{\xi}}{\xi^2} \exp(-\mathrm{i}\boldsymbol{\xi} \cdot \boldsymbol{m}) = \frac{\boldsymbol{m}}{|\boldsymbol{m}|^3} (1 + \mathrm{O}(|\boldsymbol{m}|^{-2})). \tag{4.37}$$

Thus for the charged impurity case

$$\boldsymbol{\mu}(\boldsymbol{m}) = \frac{\alpha Q}{1+2x} \frac{\boldsymbol{m}}{|\boldsymbol{m}|^3} (1 + \mathrm{O}(|\boldsymbol{m}|^{-2})). \tag{4.38}$$

4.4. Sample with dipole $\boldsymbol{\nu}$ at $\boldsymbol{m}=\mathbf{0}$

Equation (2.11) has Fourier transform

$$\boldsymbol{M}(\boldsymbol{\xi}) = -\alpha T(\boldsymbol{\xi})\cdot\boldsymbol{\nu} - \alpha T(\boldsymbol{\xi})\cdot\boldsymbol{M}(\boldsymbol{\xi}) - \alpha\omega\boldsymbol{y}(\mathbf{0}). \tag{4.39}$$

By the procedure used to find $\boldsymbol{y}(\mathbf{0})$ for the charged case, it can be shown that

$$\boldsymbol{y}(\mathbf{0}) = -\alpha P(\omega,\alpha)\cdot\boldsymbol{\nu} \tag{4.40}$$

where

$$P(\omega,\alpha) = \left((I+\omega)I - \frac{\omega}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\lambda}[I+\alpha T(\boldsymbol{\lambda})]^{-1}\right)^{-1} \frac{1}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\lambda}[I+\alpha T(\boldsymbol{\lambda})]^{-1}T^2(\boldsymbol{\lambda}). \tag{4.41}$$

Thus, the equation for $\boldsymbol{M}(\boldsymbol{\xi})$ may be solved to give

$$\boldsymbol{\mu}(\boldsymbol{m}) = -\boldsymbol{\nu}\delta_{\boldsymbol{m},\mathbf{0}} + \frac{1}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\xi}[I+\alpha T(\boldsymbol{\xi})]^{-1}\exp(-\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{m})\cdot[I+\alpha^2\omega P(\omega,\alpha)]\cdot\boldsymbol{\nu}. \tag{4.42}$$

Except at $\boldsymbol{m}=\mathbf{0}$, the only change introduced by setting $\omega\neq 0$ is that the dipole $\boldsymbol{\nu}$ is replaced by a dipole

$$\boldsymbol{\nu}(\omega,\alpha) = [I+\alpha^2\omega P(\omega,\alpha)]\cdot\boldsymbol{\nu}. \tag{4.43}$$

For $|\boldsymbol{m}|$ large, the solution may be expanded using

$$\frac{1}{2\pi^2}\int_V \mathrm{d}^3\boldsymbol{\xi}\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2}\exp(-\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{m}) = t(\boldsymbol{m})(1+\mathrm{O}(|\boldsymbol{m}|^{-2})) \tag{4.44}$$

so that for $|\boldsymbol{m}|$ large,

$$\boldsymbol{\mu}(\boldsymbol{m}) = -\frac{\alpha}{(1-x)(1+2x)}t(\boldsymbol{m})\cdot\boldsymbol{\nu}(\omega,\alpha). \tag{4.45}$$

It is also important to note that

$$\boldsymbol{\mu}(\mathbf{0}) = -\boldsymbol{\nu} + \frac{1}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\xi}[I+\alpha T(\boldsymbol{\xi})]^{-1}\cdot\boldsymbol{\nu}(\omega,\alpha). \tag{4.46}$$

5. Discussion

First it is of interest to compare the solutions of the polarisation equation in the applied external field case equation (4.23) (for a plane slab) and equation (4.29) (for a spherical sample) with the polarisation densities from the continuum picture given by equation (3.2) (for a plane slab) and equation (3.4) (for a spherical sample). Comparison of appropriate solutions shows that they are identical for all ε' with

$$\varepsilon = (1+2x)/(1-x) \tag{5.1}$$

the standard Clausius–Mossotti result. Note that this expression for ε gives

$$(\varepsilon-1)/4\pi = \tfrac{1}{3}\alpha(\varepsilon+2). \tag{5.2}$$

Thus, since the microscopic field is $\boldsymbol{\mu}(\boldsymbol{m})/\alpha$ while the macroscopic field is given by

$4\pi\boldsymbol{\mu}(\boldsymbol{m})/(\varepsilon-1)$, the microscopic and macroscopic electric fields are related in all cases by

$$\boldsymbol{E}_{\text{micro}}(\boldsymbol{m})=\tfrac{1}{3}(\varepsilon+2)\boldsymbol{E}_{\text{macro}}(\boldsymbol{m}) \tag{5.3}$$

the standard Lorentz relation linking the microscopic and macroscopic fields. This solution for ε will also ensure that equation (4.38) for the polarisation in the lattice responding to a charge Q agrees precisely at large $|\boldsymbol{m}|$ with the polarisation of a continuum dielectric responding to a charge Q, given in equation (4.38). Thus, under a wide range of circumstances, the large-scale response of the system (both the polarisation and the relation between macroscopic and microscopic fields) is given by a continuous medium picture using equation (5.1). It is useful to have some confidence in equation (5.1) because the relation between the continuous medium polarisation density of equation (3.8) and the lattice polarisation of equation (4.45) is not simple.

The two expressions are identical with

$$\boldsymbol{\nu}^*=\tfrac{1}{3}(\varepsilon+2)(1+\omega\alpha^2P(\omega,\alpha))\cdot\boldsymbol{\nu}. \tag{5.4}$$

It is useful to consider the net dipole at $\boldsymbol{m}=\boldsymbol{0}$, which is

$$\boldsymbol{\nu}(\boldsymbol{0})=\boldsymbol{\nu}+\boldsymbol{\mu}(\boldsymbol{0}) \tag{5.5}$$

and

$$\boldsymbol{\nu}(0)=\frac{1}{(2\pi)^3}\int_V \mathrm{d}^3\boldsymbol{\xi}[I+\alpha T(\boldsymbol{\xi})]^{-1}\cdot\boldsymbol{\nu}(\omega,\alpha). \tag{5.6}$$

The polarisation of the lattice by the original dipole $\boldsymbol{\nu}$ produces a lattice reaction field $\boldsymbol{R}$ at $\boldsymbol{m}=\boldsymbol{0}$ given by

$$\boldsymbol{R}=\alpha'^{-1}(\boldsymbol{\nu}(0)-\boldsymbol{\nu}). \tag{5.7}$$

This reaction field gives the net dipole $\boldsymbol{\nu}(\boldsymbol{0})$ at $\boldsymbol{m}=0$.

One method for investigating the lattice reaction field is to use the approximation

$$T(\boldsymbol{\xi})=-\tfrac{4}{3}\pi I+4\pi\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2 \tag{5.8}$$

in the expressions for $\boldsymbol{R}$. Some tedious algebra gives

$$\boldsymbol{R}=\frac{\tfrac{8}{3}\pi x\boldsymbol{\nu}}{1+x-2x^2(1+\omega)}. \tag{5.9}$$

On the other hand, a direct power series expansion (in powers of α) gives

$$\boldsymbol{R}=\alpha\sum_{\boldsymbol{n}\in\Lambda}t^2(\boldsymbol{n})\cdot\boldsymbol{\nu}+\mathrm{O}(\alpha^2). \tag{5.10}$$

Since the lattice sum here is a multiple of the unit matrix and

$$\sum_{\boldsymbol{n}\in\Lambda}\frac{1}{|\boldsymbol{n}|^6}=8.40063 \tag{5.11}$$

$$\boldsymbol{R}=16.80126\alpha\boldsymbol{\nu}+\mathrm{O}(\alpha^2) \tag{5.12}$$

and the approximate result (5.9) has a first term in its x expansion which is in error by a factor of approximately 2.

Perhaps the most important result here is not the precise details of the lattice reaction field, but equation (5.4) which gives the rescaled dipole moment $\boldsymbol{\nu}^*$ which must be used in a continuous medium picture to give the correct polarisation at distances far from the defect. Making a continuous system model without an exact microscopic picture of the system can be difficult as it will usually involve guesses at the properties of some polarisable sphere whose diameter must be chosen in an arbitrary fashion. The solution of the polarisation equations for a dipolar defect makes life somewhat simpler, since they give a precise prescription for evaluating $\boldsymbol{\nu}^*$ from $\boldsymbol{\nu}$ and hence the polarisation in the lattice far from a dipolar defect. Presumably, similar considerations apply in considering the response of an ionic crystal to a charged or dipolar defect. Work on these considerations is in progress.

References

Bellemans A and Plaitin M 1975 *Bull. Classe Sci. Acad. R. Belgique* **61** 324
Bottcher C J F 1973 *Theory of Electric Polarization* (Amsterdam: Elsevier)
De Leeuw S W, Perram J W and Smith E R 1980 *Proc. R. Soc.* A **373** 27
Lehnen A P and Bruch L W 1980 *Phys. Rev.* B **21** 3193
Pollock E L and Alder B U 1977 *Phys. Rev. Lett.* **39** 299
——1978 *Phys. Rev. Lett.* **41** 903
Pollock E L, Alder B H and Pratt L R 1980 *Proc. US Nat. Acad. Sci.* in press
Smith E R 1980a *J. Phys. A: Math. Gen.* **13** L107
——1980b *Lectures at NATO Summer School on Superionic Conductors, Odense, Denmark, August 1980* (New York: Plenum) to appear
——1981 *Proc. Soc.* A **375** 475
Widom H 1965 *Studies in Mathematics*: vol 3, *Studies in Real and Complex Analysis* ch 8, ed I I Hirschman Jr (The Mathematical Association of America)
Wielopolski P 1981 *J. Phys. A: Math. Gen.* **14** L263