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LETTER TO THE EDITOR

The dielectric constant of a lattice of polarisable spheres

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Abstract. The response of a simple cubic lattice of spacing L with a polarisable sphere of polarisability α at each vertex to a permanent dipole $\boldsymbol{\mu}$ at one vertex deep within the lattice is evaluated. This gives the dielectric constant of the lattice as $\epsilon(\alpha, L) = (1-4\pi\alpha/3L^3)(1+8\pi\alpha/3L^3)$.

The response of a many-body system in which part of the interaction is due to induced-dipole interaction is very difficult to calculate, since for N particles the induced-dipole–induced-dipole interaction becomes an N-particle interaction. Wertheim (1973) has developed a formalism for calculating polarisability contributions in statistical mechanics, and Alder and Pollock (1977) have recently published numerical studies on 108 particles which are polarisable. The work of Alder and Pollock shows that standard methods in treating polarisability effects to low order in powers of α can be incorrect. In this Letter a simple cubic lattice of polarisable spheres is considered. The lattice spacing is L, and the spheres are constrained to lie on the vertices of the lattice. Thus their response to an electric field is purely via polarisation. If the field at a lattice site $L\boldsymbol{m} = L(l, m, n)$ be $\boldsymbol{E}(\boldsymbol{m})$, then the dipole moment of the sphere at $L\boldsymbol{m}$ is

$$\boldsymbol{\mu}(\boldsymbol{m}) = \alpha\boldsymbol{E}(\boldsymbol{m}). \qquad (1)$$

Equation (1) implies that the electric field is fairly small at all points in the lattice, so that the response of the spheres may be considered as linear in the field.

We consider the case in which the sphere at (0, 0, 0) also contains a point dipole $\boldsymbol{\mu}$. The field at $L\boldsymbol{m}$ is then composed of two parts, the direct field

$$-t(\boldsymbol{m}) \cdot \boldsymbol{\mu}/L^3 \qquad (2)$$

and the indirect field

$$-\sum_{\boldsymbol{n}} L^{-3} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}), \qquad (3)$$

where

$$t(\boldsymbol{m}) = (1/|\boldsymbol{m}|^3)(I - 3\boldsymbol{m}\boldsymbol{m}/|\boldsymbol{m}|^3), \qquad \boldsymbol{m} \neq \boldsymbol{0}, \quad t(\boldsymbol{0}) = 0. \qquad (4)$$

Thus we obtain the sum equation

$$\boldsymbol{\mu}(\boldsymbol{m}) = -\beta t(\boldsymbol{m}) \cdot \boldsymbol{\mu} - \beta \sum_{\boldsymbol{n}} t(\boldsymbol{m}-\boldsymbol{n}) \cdot \boldsymbol{\mu}(\boldsymbol{n}), \qquad (5)$$

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where $\beta = \alpha/L^3$. We can solve equation (5) by Fourier series. Let

$$T(\boldsymbol{\xi}) = \sum_{\boldsymbol{m}\neq \boldsymbol{0}} t(\boldsymbol{m})\, \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}} \tag{6}$$

and

$$\boldsymbol{M}(\boldsymbol{\xi}) = \sum_{\boldsymbol{m}} \boldsymbol{\mu}(\boldsymbol{m})\, \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}}. \tag{7}$$

Then

$$\boldsymbol{M}(\boldsymbol{\xi}) = -\beta T(\boldsymbol{\xi}) \,.\, \boldsymbol{\mu} - \beta T(\boldsymbol{\xi}) \,.\, \boldsymbol{M}(\boldsymbol{\xi}). \tag{8}$$

We can now solve equation (8) for $\boldsymbol{M}(\boldsymbol{\xi})$, and then calculate $\boldsymbol{\mu}(\boldsymbol{m})$ from

$$\boldsymbol{\mu}(\boldsymbol{m}) = \frac{1}{(2\pi)^3} \int_{\Gamma_\pi} \boldsymbol{M}(\boldsymbol{\xi})\, \mathrm{e}^{-\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}}\, \mathrm{d}^3\boldsymbol{\xi}, \tag{9}$$

where Γ_π is the cube $[-\pi, \pi]^3$. Equations (8) and (9) give, in this way,

$$\boldsymbol{\mu}(\boldsymbol{m}) = -\left(\frac{1}{(2\pi)^3} \int_{\Gamma_\pi} (I + \beta T(\boldsymbol{\xi}))^{-1} \beta T(\boldsymbol{\xi})\, \mathrm{e}^{-\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}}\, \mathrm{d}^3\boldsymbol{\xi}\right) .\, \boldsymbol{\mu}. \tag{10}$$

Equation (10) forms a complete solution to the problem, but it is unfortunately not very useful in this form. We can set $\beta T(\boldsymbol{\xi}) = (I + \beta T(\boldsymbol{\xi}) - I)$ to give

$$\boldsymbol{\mu}(\boldsymbol{m}) = \left(\frac{1}{(2\pi)^3} \int_{\Gamma_\pi} (I + \beta T(\boldsymbol{\xi}))^{-1}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}}\, \mathrm{d}^3\boldsymbol{\xi}\right) .\, \boldsymbol{\mu} - \boldsymbol{\mu}\delta_{\boldsymbol{m},\boldsymbol{0}}. \tag{11}$$

We cannot proceed much further without a detailed numerical study, except to develop an expansion for large $|\boldsymbol{m}|$. If $|\boldsymbol{m}|$ be large, then we may write $\hat{\boldsymbol{m}} = \boldsymbol{m}/|\boldsymbol{m}|$, and then

$$\boldsymbol{\mu}(\boldsymbol{m}) = \left[\frac{1}{(2\pi|\boldsymbol{m}|)^3} \int_{\Gamma_{\pi|\boldsymbol{m}|}} \left(I + \beta T\left(\frac{\boldsymbol{\xi}}{|\boldsymbol{m}|}\right)\right)^{-1} \mathrm{e}^{-\mathrm{i}\boldsymbol{\xi}.\hat{\boldsymbol{m}}}\, \mathrm{d}^3\boldsymbol{\xi}\right] .\, \boldsymbol{\mu}. \tag{12}$$

The integral in (12) has an expansion in inverse powers of $|\boldsymbol{m}|$. We evaluate the leading term. DeLeeuw *et al* (1980) have shown that

$$\sum_{\boldsymbol{m}} t(\boldsymbol{m}) = -\nabla\nabla\phi(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{0}} + \frac{4\pi}{3} I, \tag{13}$$

while for $|\boldsymbol{\xi}|$ very small

$$\sum_{\boldsymbol{m}} t(\boldsymbol{m})\, \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}} = -\nabla\nabla\phi(\boldsymbol{r})|_{\boldsymbol{r}=\boldsymbol{0}} + 4\pi\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\boldsymbol{\xi}^2} + \mathrm{O}(\boldsymbol{\xi}^2), \tag{14}$$

with $\phi(\boldsymbol{r})$ given by

$$\phi(\boldsymbol{r}) = \sum_{\boldsymbol{m}} \frac{\operatorname{erfc}(a|\boldsymbol{m}+\boldsymbol{r}|)}{|\boldsymbol{m}+\boldsymbol{r}|} + \sum_{\boldsymbol{m}\neq\boldsymbol{0}} \frac{1}{\pi \boldsymbol{m}^2}\, \mathrm{e}^{-\pi^2\boldsymbol{m}^2/a^2 + 2\pi\mathrm{i}\boldsymbol{r}.\boldsymbol{m}}, \tag{15}$$

where a is a constant which may be chosen arbitrarily to aid the convergence of the two lattice sums.

We may also note that

$$\lim_{N\to\infty} \sum_{m_x=-N}^{N} \sum_{m_y=-N}^{N} \sum_{m_z=-N}^{N} t(\boldsymbol{m})$$

$$= \lim_{N\to\infty} \sum_{m_x=-N}^{N} \sum_{m_y=-N}^{N} \sum_{m_z=-N}^{N} (m_x^2+m_y^2+m_z^2)^{-5/2}$$

$$\times \begin{pmatrix} m_y^2+m_z^2-2m_x^2 & -3m_xm_y & -3m_xm_z \\ -3m_xm_y & m_x^2+m_z^2-2m_y^2 & -3m_ym_z \\ -3m_xm_z & -3m_ym_z & m_x^2+m_y^2-2m_z^2 \end{pmatrix}, \tag{16}$$

and the symmetries of the summand and region of summation ensure that this sum is zero. Thus for small $\boldsymbol{\xi}$

$$T(\boldsymbol{\xi}) = (4\pi/3)(I - 3\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2). \tag{17}$$

Thus the leading term in the expansion of equation (12) for large $|\boldsymbol{m}|$ may be written

$$\boldsymbol{\mu}(\boldsymbol{m}) \simeq \left\{\frac{1}{(2\pi)^3}\int_{\Gamma_\pi}\left[I - \frac{4\pi\beta}{3}\left(I - \frac{3\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2}\right)\right]^{-1} \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}}\, \mathrm{d}^3\boldsymbol{\xi}\right\} \cdot \boldsymbol{\mu}. \tag{18}$$

The matric in the integrand in this equation has inverse

$$\left[\left(1-\frac{4\pi\beta}{3}\right)I + 4\pi\beta\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2}\right]^{-1} = \frac{1}{1-4\pi\beta/3}I - \frac{4\pi\beta}{(1-4\pi\beta/3)(1+8\pi\beta/3)}\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2}, \tag{19}$$

which may be verified by noting that $(\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2)^2 = \boldsymbol{\xi}\boldsymbol{\xi}/\xi^2$. If we insert this inverse into equation (18), we note that the integral over the most matric term is zero for $\boldsymbol{m} \neq \boldsymbol{0}$, so that

$$\boldsymbol{\mu}(\boldsymbol{m}) \simeq -\frac{\beta}{F(\beta)}\frac{1}{2\pi^2}\int_{\Gamma_\pi}\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2}\mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{m}} \cdot \boldsymbol{\mu} \tag{20}$$

when $F(\beta) = (1-4\pi\beta/3)(1+8\pi\beta/3)$. We may write

$$\frac{1}{\xi^2} = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-t\xi^2}, \qquad \boldsymbol{\xi}\boldsymbol{\xi}\, \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{R}} = -\nabla\nabla\, \mathrm{e}^{\mathrm{i}\boldsymbol{\xi}.\boldsymbol{R}}, \tag{21}$$

so that

$$\boldsymbol{\mu}(\boldsymbol{m}) = \left(\frac{\beta}{F(\beta)}\nabla\nabla\int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\boldsymbol{R}^2/4t}\int_{\Gamma_\pi}\mathrm{e}^{-t(\boldsymbol{\xi}+\mathrm{i}\boldsymbol{R}/2t)^2}\,\mathrm{d}^3\boldsymbol{\xi}\right) \cdot \boldsymbol{\mu}. \tag{22}$$

The integral over $\boldsymbol{\xi}$ may be evaluated in terms of the error function. The argument of the error functions is always large when $\exp(-\boldsymbol{R}^2/4t)$ is not very small, so the error function may be replaced by 1. Finally we obtain

$$\boldsymbol{\mu}(\boldsymbol{m}) \simeq -\frac{\beta}{F(\beta)}\left(-\nabla\nabla\frac{1}{|\boldsymbol{R}|}\right)_{\boldsymbol{R}=\boldsymbol{m}} \cdot \boldsymbol{\mu} = -\frac{\beta}{F(\beta)}(t(\boldsymbol{m}) \cdot \boldsymbol{\mu}). \tag{23}$$

Thus the electric field at $\boldsymbol{m}$ is given by

$$\boldsymbol{E}(\boldsymbol{m}) = -\frac{1}{F(\beta)}\frac{1}{L^3}t(\boldsymbol{m}) \cdot \boldsymbol{\mu} \,.\, (1+\mathrm{O}(|\boldsymbol{m}|^{-2})). \tag{24}$$

The electric field at $L\boldsymbol{m}$ with respect to a dipole $\boldsymbol{\mu}$ in a continuum dielectric of dielectric constant ϵ is

$$\boldsymbol{E} = -(1/\epsilon L^3)t(\boldsymbol{m}) \cdot \boldsymbol{\mu}. \tag{25}$$

Thus for long-range interactions across the lattice of polarisable spheres we can treat the lattice as a continuum with dielectric constant

$$\epsilon(\alpha, L) = F(\beta) = (1 - 3\pi\alpha/3L^3)(1 + 8\pi\alpha/3L^3). \tag{26}$$

We note that this solution method fails for $\alpha \geqslant 3L^3/4\pi$, a reflection of the polarisation catastrophe. We may note that, for α/L^3 small, $\epsilon(\alpha, L) \simeq 1 + 4\pi\alpha/3L^3$.

The general result given in equation (11) is of some interest as it gives a method for making exact numerical studies of the reaction field in a rigid lattice. This problem and that of non-linear response of the polarisation in the lattice are at present under study.

Alder and Pollock (1977) have calculated the electric field at $\boldsymbol{r}$ with respect to a fixed dipole $\boldsymbol{\mu}$ in a dense system of polarisable particles to first order in α. In the notation of this Letter, for the model considered here, their result is

$$\boldsymbol{E}(\boldsymbol{m}) = -\left(1 - \frac{4\pi\alpha}{3L^3}\right)\frac{1}{L^3}t(\boldsymbol{m}) \cdot \boldsymbol{\mu} + \mathrm{O}(\alpha^2), \tag{27}$$

which, they point out, does not agree with the continuum theory result (Fröhlich 1949)

$$\boldsymbol{E}(\boldsymbol{m}) = -\left(1 - \frac{8\pi\alpha}{3L^3}\right)\frac{1}{L^3}t(\boldsymbol{m}) \cdot \boldsymbol{\mu} + \mathrm{O}(\alpha^2). \tag{28}$$

If we expand equation (24) in powers of β and then set $\beta = \alpha/L^3$, we obtain

$$\boldsymbol{E}(\boldsymbol{m}) = -\left(1 - \frac{3\pi\alpha}{3L^3}\right)\frac{1}{L^3}t(\boldsymbol{m}) \cdot \boldsymbol{\mu} + \mathrm{O}(\alpha^2), \tag{29}$$

in agreement with the result of Alder and Pollock.

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