ON THE DIELECTRIC PROPERTIES OF MOLECULAR CRYSTALS

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Introduction

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Introduction

The macroscopic dielectric properties of a system are characterized by the dielectric susceptibility. This quantity is in general a tensor and relates (in the linear theory) the polarization field linearly to the electric Maxwell field. One speaks about spatial dispersion if the polarization in a certain point in space is not only related to the Maxwell field in the same point but also to that field in all other points of space by means of an integral relation. If the medium under consideration is homogeneous and infinite this is expressed by the fact that after Fourier transformation the polarization in a certain point in the wave number space is related linearly to the Maxwell field in the same point by means of a wave number dependent complex dielectric susceptibility.

Our aim is to derive this wave number dependent dielectric susceptibility tensor from the microscopic properties of the system, in this case a molecular crystal. An electric field acting on a single molecule induces a dipole moment distribution which is supposed to depend linearly (also with spatial dispersion) on the electric field by means of a molecular polarizability tensor. This molecular polarizability tensor can be calculated quantum-mechanically.[1,2] We shall consider this quantity to be given. If the molecular crystal is subjected to a time dependent external electric field the effective field acting on a molecule consists of the external field and the secondary radiation fields of all molecules. The total microscopic polarization of the crystal thus induced can in the wave number space be written as sum over the reciprocal lattice in which each term is a product of an external susceptibility and the external field, both depending on the reciprocal lattice points. For a macroscopic description of the system one takes only into account those Fourier components of the polarization and the external field for which the wave number is lying in the first Brillouinzone. As a consequence only one term of the above mentioned reciprocal lattice sum survives and relates the polarization linearly to the external field for the same wave number. This yields the wave number dependent external susceptibility of the crystal which from then on can be considered as homogeneous (though in general anisotropic). [3] The phenomenological Maxwell theory provides the relation between this external susceptibility and the dielectric susceptibility from which an expression for the latter can be derived in terms of reciprocal lattice sums. In this derivation of the dielectric susceptibility we have only assumed that the external field is varying slowly over the intermolecular distance. No assumptions are made for the molecular radiation fields. The (formal) expression for the dielectric susceptibility can be worked out further by making a multipole expansion of the induced molecular dipole moment distribution. We shall investigate in how far it is permitted to break off this expansion.

The magnitude of the spatial dispersion (wave number dependence) of the dielectric susceptibility is given by the ratio between the smallest molecular distances or the molecular dimensions and the wave length of the macroscopic field. For optical wavelengths this ratio is small and spatial dispersion is a quantitatively small effect which can, however, give rise to qualitatively new effects. Thus e.g. the well known effect of optical activity (i.e. the rotation of the direction of polarization of linearly polarized light passing through a medium) is determined by the spatial dispersion of first order and so by the first order term in the expansion of the susceptibility in powers of the above mentioned ratio.

One can distinguish between spatial dispersion which is a consequence of the finite intermolecular distances (spatial dispersion with respect to the lattice) and spatial dispersion which is a consequence of the finite molecular dimensions (molecular spatial dispersion). If one deals with simple Bravais lattices (chapters I and II) it follows from symmetry considerations that with respect to the lattice there is no spatial dispersion of odd order. For this case optical activity can only be a consequence of molecular spatial dispersion. For simple point dipole lattices we have calculated in chapter I the effect of second order spatial dispersion (with respect to the lattice) which results e.g. in the effect of optical anisotropy of cubic point dipole lattices. In chapter II we have taken into account the molecular spatial dispersion in first order. This means that we have in addition to the electric dipole moment also considered the electric quadrupole and the magnetic dipole moment of the molecules. This gives rise to optical activity but, moreover, it appears also to be of influence on the zero wave number dielectric susceptibility. In chapter III we consider composite lattices, especially composite point dipole and quadrupole lattices. In contrast with the simple lattice the composite lattice can also show first order spatial dispersion if the molecules are represented by point dipoles.

The expressions for the dielectric susceptibility in the various cases contain lattice sums which are slowly convergent. Following a method developed by Ewald 4,5) and later generalized by Nijboer and De Wette 6) each of these lattice sums is transformed into two rapidly converging lattice sums, one over the original lattice and one over the reciprocal lattice. These rapidly converging lattice sums can easily be calculated numerically for the various types of crystals. The calculation is performed for a few simple examples.

References

1) Terwiel, R.H. and Mazur, P., Physica 30 (1964) 625.

2) Maaskant, W.J.A. and Oosterhoff, L.J., Molecular Physics 8 (1964) 319.

3) Agranovich, V.M. and Ginzburg, V.L., Spatial dispersion in Crystal Optics and the Theory of Excitons, Interscience (London, 1966).

4) Ewald, P.P., Ann. Phys. 49 (1916) 1, Ibid 49, 117.

5) Ewald, P.P., Ann. Phys. 64 (1921) 253.

6) Nijboer, B.R.A. and De Wette, F.W., Physica 23 (1957) 309.

I. FORMAL THEORY AND APPLICATION TO SIMPLE POINT-DIPOLE LATTICES

Synopsis

In this paper a general expression is given for the wave vector- and frequency-dependent dielectric-susceptibility tensor of a simple perfect lattice of fixed nonpolar molecules with given polarizability tensor. The general expression is applied to a lattice of point dipoles. For this point-dipole model the effect of second-order spatial dispersion is studied, especially for cubic lattices.

1. *Introduction.* In the present paper we shall give a general formal expression for the wave vector- and frequency-dependent dielectric-susceptibility tensor of a molecular crystal in terms of the polarizability tensor of the (nonpolar) molecules (section 2). These molecules are supposed to be identical, equally oriented and fixed at the lattice points of a Bravais lattice. We neglect lattice vibrations since for molecular crystals the influence of the molecular displacements on the dielectric properties is in general small. The small temperature dependence of the dielectric constant is sufficiently accounted for by the change of density (see, *e.g.*, ref. 1). The molecular-polarizability tensor is assumed to be given. The wave vector dependence (spatial dispersion) of the dielectric tensor is usually small in optics and is in crystals characterized by a parameter which is of order of the ratio between some characteristic length *e.g.* a lattice constant a and a distance l over which the fields in the crystal change. Although quantitatively small the effect of spatial dispersion gives rise to qualitatively different phenomena such as the well-known effect of optical activity (first order) and optical anisotropy of cubic crystals (second order).

The general formalism will be applied to a lattice of point dipoles (section 3). For this model the dielectric susceptibility is expressed in rapidly converging lattice sums involving gamma functions. In section 4 spatial dispersion is studied to second order. By the symmetry of the Bravais lattice with point dipoles there is no first-order spatial dispersion which means that the system is nongyrotropic (*i.e.*, there is no optical activity). To 0th order we have exactly the result obtained earlier by Vlieger for isotropic point dipoles[2]). To second order spatial dispersion is especially investigated for cubic lattices. The corrections to the refractive indices for different directions of propagation of light are calculated and compared with the result of Lorentz[3]).

The assumption of sections 3 and 4 that we are dealing with a point-dipole lattice means that no spatial dispersion is taken into account with respect to the molecules themselves or equivalently that we have neglected in the molecular polarizability terms of order of the ratio of the effective diameter d of the molecules to l. Since in crystals d is of the same order as the lattice constant a it is not very realistic to neglect terms of order d/l and at the same time take into account terms of order $(a/l)^2$. For nongyrotropic molecules, however, there is no contribution of first order in d/l so that the given results are valid for a lattice of nongyrotropic molecules with the assumption that d is sufficiently smaller than a so that $d^2 \ll a^2$. In the next paper we shall apply the formalism of section 2 to the case that we also take into account spatial dispersion with respect to the molecules by means of a multipole expansion. To first order this will imply optical activity.

2. *Formal theory.* Consider an infinite three-dimensional simple perfect lattice (Bravais lattice) of identical equally oriented molecules at fixed positions $\boldsymbol{R}_i$. The system is subjected to an arbitrary external electric field

$$\boldsymbol{E}^{\text{ext}}(\boldsymbol{R}, \omega) = \int \mathrm{e}^{\mathrm{i}\omega t}\, \boldsymbol{E}^{\text{ext}}(\boldsymbol{R}, t)\, \mathrm{d}t, \tag{2.1}$$

of frequency ω. The induced microscopic dipole-moment density $\boldsymbol{p}_i(\boldsymbol{R}, \omega)$ of the ith molecule is assumed to be linearly dependent on the effective field strength $\boldsymbol{E}_i^{\text{eff}}(\boldsymbol{R}, \omega)$ acting on molecule i:

$$\boldsymbol{p}_i(\boldsymbol{R}, \omega) = \int \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \cdot \boldsymbol{E}_i^{\text{eff}}(\boldsymbol{R}', \omega)\, \mathrm{d}\boldsymbol{R}', \tag{2.2}$$

where $\boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ is the molecular polarizability. In the semiclassical method we use classical fields whereas the polarizability tensor is calculated quantum-mechanically[4,5]). The effective field acting on the ith molecule is given by:

$$\begin{aligned}\boldsymbol{E}_i^{\text{eff}}(\boldsymbol{R}, \omega) = \boldsymbol{E}^{\text{ext}}(\boldsymbol{R}, \omega) &- \sum_{j \neq i} \mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) \cdot \boldsymbol{p}_j(\boldsymbol{R}', \omega)\, \mathrm{d}\boldsymbol{R}' \\ &- \int \tfrac{1}{2} [\mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) - \mathsf{F}^{+}(\boldsymbol{R} - \boldsymbol{R}', \omega)] \cdot \boldsymbol{p}_i(\boldsymbol{R}', \omega)\, \mathrm{d}\boldsymbol{R}',\end{aligned} \tag{2.3}$$

where the second term is the field induced by the other molecules and the third term is the reaction field of the ith molecule. The retarded vacuum propagator of the electromagnetic field is given by

$$\mathsf{F}(\boldsymbol{R}, \omega) = -(\nabla\nabla + \omega^2)\, \mathrm{e}^{\mathrm{i}(\omega + \mathrm{i}0)R}/4\pi R, \tag{2.4}$$

where $R = |\boldsymbol{R}|$ and i0 is an infinitesimal small positive imaginary number. We have chosen units such that the velocity of light is one. $\mathsf{F}^+(\boldsymbol{R}, \omega)$ is the advanced propagator which is the adjoint of $\mathsf{F}(\boldsymbol{R}, \omega)$. The choice of the reaction field is in essence the same as the choice originally made by Dirac[6,7]) for a system of point charges. See also refs. 8 and 9. From eqs. (2.2) and (2.3) follows:

$$\begin{aligned} \boldsymbol{p}_i(\boldsymbol{R}, \omega) = \int \mathrm{d}\boldsymbol{R}' \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \\ \cdot \Big(\boldsymbol{E}^{\mathrm{ext}}(\boldsymbol{R}', \omega) - \sum_{j \neq i} \int \mathsf{F}(\boldsymbol{R}' - \boldsymbol{R}'', \omega) \cdot \boldsymbol{p}_j(\boldsymbol{R}'', \omega)\, \mathrm{d}\boldsymbol{R}'' \\ - \int \tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R}' - \boldsymbol{R}'', \omega) - \mathsf{F}^+(\boldsymbol{R}' - \boldsymbol{R}'', \omega)\right] \cdot \boldsymbol{p}_i(\boldsymbol{R}'', \omega)\, \mathrm{d}\boldsymbol{R}''\Big). \end{aligned} \tag{2.5}$$

We assume that the molecules are not overlapping so that for each molecule, say the ith, we can choose a region g_i containing this molecule and no others. This implies that $\boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) = 0$ for $\boldsymbol{R} \notin g_i$ so that $\boldsymbol{p}_i(\boldsymbol{R}, \omega) = 0$ for $\boldsymbol{R} \notin g_i$. From the symmetry property of $\boldsymbol{\sigma}$ *viz.* $\sigma_{ij}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \sigma_{ji}(\boldsymbol{r}', \boldsymbol{r}; \omega)$[4]) we also have $\boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) = 0$ for $\boldsymbol{R}' \notin g_i$. Now define[8,9]):

$$\mathsf{H}_i(\boldsymbol{R}, \boldsymbol{R}'; \omega) \equiv \begin{cases} \mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) & \text{for} \quad \boldsymbol{R}' \notin g_i \\ \tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) - \mathsf{F}^+(\boldsymbol{R} - \boldsymbol{R}', \omega)\right] & \text{for} \quad \boldsymbol{R}' \in g_i \end{cases} \tag{2.6}$$

and further

$$\boldsymbol{P}(\boldsymbol{R}, \omega) \equiv \sum_i \boldsymbol{p}_i(\boldsymbol{R}, \omega). \tag{2.7}$$

Then it follows with (2.5), (2.6) and (2.7) that

$$\begin{aligned} \boldsymbol{P}(\boldsymbol{R}, \omega) = \int \mathrm{d}\boldsymbol{R}' \sum_i \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \cdot \boldsymbol{E}^{\mathrm{ext}}(\boldsymbol{R}', \omega) \\ - \int \mathrm{d}\boldsymbol{R}' \sum_i \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \\ \cdot \int \mathrm{d}\boldsymbol{R}'' \mathsf{H}_i(\boldsymbol{R}', \boldsymbol{R}''; \omega) \cdot \boldsymbol{P}(\boldsymbol{R}'', \omega). \end{aligned} \tag{2.8}$$

With the definitions

$$\boldsymbol{\alpha}(\boldsymbol{R}, \boldsymbol{R}'; \omega) \equiv \sum_i \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \tag{2.9}$$

and

$$\mathsf{H}_\sigma(\boldsymbol{R}, \boldsymbol{R}''; \omega) \equiv \sum_i \int \mathrm{d}\boldsymbol{R}' \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \cdot \mathsf{H}_i(\boldsymbol{R}', \boldsymbol{R}''; \omega) \tag{2.10}$$

eq. (2.8) becomes

$$P(R, \omega) = \int dR' \alpha (R, R'; \omega) \cdot E^{ext}(R', \omega) - \int dR' H_\sigma (R, R'; \omega) \cdot P(R', \omega). \tag{2.11}$$

In operator notation this can be written as

$$P = \alpha \cdot E^{ext} - H_\sigma \cdot P, \tag{2.12}$$

with the formal solution

$$P = (1 + H_\sigma)^{-1} \cdot \alpha \cdot E^{ext}. \tag{2.13}$$

From the definition (2.9) of α and the fact that H_σ [*cf.* eq. (2.10)] can be written as

$$H_\sigma (R, R''; \omega) = \sum_l h_\sigma (R - R_l, R'' - R_l; \omega), \tag{2.14}$$

with

$$h_\sigma (R, R''; \omega) = \int dR' \sigma (R, R'; \omega) \cdot H_{l=0}(R', R''; \omega), \tag{2.15}$$

it follows that (see appendix A): (i) α and H_σ are periodic so that in k representation

$$\alpha (k, k'; \omega) = \sum_\lambda \alpha^\lambda (k, \omega) \, \delta (k - k' - k_\lambda), \tag{2.16}$$

$$H_\sigma (k, k'; \omega) = \sum_\lambda H_\sigma^\lambda (k, \omega) \, \delta (k - k' - k_\lambda); \tag{2.17}$$

and (ii)

$$\alpha^\lambda (k, \omega) = (2\pi)^3 \varrho \sigma (k, k - k_\lambda; \omega), \tag{2.18}$$

$$H_\sigma^\lambda (k, \omega) = (2\pi)^3 \varrho h_\sigma (k, k - k_\lambda; \omega), \tag{2.19}$$

Here k_λ is a reciprocal-lattice vector and ϱ is the density such that $\varrho^{-1} = v$ is the volume of the unit cell of the lattice. The Fourier transform $f(k, k')$ of $f(R, R')$ is defined as

$$f(k, k') = (2\pi)^{-3} \int dR \, dR' f(R, R') \, e^{-ik \cdot R} \, e^{ik' \cdot R'}. \tag{2.20}$$

Since products and inverses of operators as (2.16) and (2.17) have the same form in this representation the operator $(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}$ in (2.13) can be written as

$$[(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]\,(\boldsymbol{k}, \boldsymbol{k}'; \omega)$$

$$= \sum_\lambda [(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]^\lambda\,(\boldsymbol{k}, \omega)\,\delta\,(\boldsymbol{k} - \boldsymbol{k}' - \boldsymbol{k}_\lambda). \tag{2.21}$$

Thus we get for eq. (2.13):

$$\boldsymbol{P}\,(\boldsymbol{k}, \omega) = \sum_\lambda [(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]^\lambda\,(\boldsymbol{k}, \omega) \cdot \boldsymbol{E}^{\text{ext}}\,(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega). \tag{2.22}$$

Now we assume that $\boldsymbol{E}^{\text{ext}}\,(\boldsymbol{k}', \omega) \neq 0$ only for $\boldsymbol{k}'$ in the first Brillouin zone, which is *e.g.* the case in optical experiments. This implies that in the sum of the r.h.s. of eq. (2.22) only one term survives. If we furthermore restrict ourselves to values of $\boldsymbol{k}$ lying in the first Brillouin zone this term is the $\boldsymbol{k}_\lambda = 0$ term so that

$$\boldsymbol{P}\,(\boldsymbol{k}, \omega) = [(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]^0\,(\boldsymbol{k}, \omega) \cdot \boldsymbol{E}^{\text{ext}}\,(\boldsymbol{k}, \omega). \tag{2.23}$$

It is this equation that should be used in the macroscopic, *i.e.*, long wavelength description of the optical properties of a crystal. On the other hand we have for the macroscopic susceptibility χ:

$$\boldsymbol{P}\,(\boldsymbol{k}, \omega) = \chi\,(\boldsymbol{k}, \omega) \cdot [\boldsymbol{E}^{\text{ext}}\,(\boldsymbol{k}, \omega) - \mathsf{F}\,(\boldsymbol{k}, \omega) \cdot \boldsymbol{P}\,(\boldsymbol{k}, \omega)]$$

$$= \chi\,(\boldsymbol{k}, \omega) \cdot \boldsymbol{E}\,(\boldsymbol{k}, \omega), \tag{2.24}$$

where $\boldsymbol{E}$ is the Maxwell field. Defining $\chi^{\text{ext}}\,(\boldsymbol{k}, \omega)$ by

$$\boldsymbol{P}\,(\boldsymbol{k}, \omega) = \chi^{\text{ext}}\,(\boldsymbol{k}, \omega) \cdot \boldsymbol{E}^{\text{ext}}\,(\boldsymbol{k}, \omega), \tag{2.25}$$

we obtain

$$\chi\,(\boldsymbol{k}, \omega) = \chi^{\text{ext}}\,(\boldsymbol{k}, \omega) \cdot [1 - \mathsf{F}\,(\boldsymbol{k}, \omega) \cdot \chi^{\text{ext}}\,(\boldsymbol{k}, \omega)]^{-1}. \tag{2.26}$$

By comparing eqs. (2.23) and (2.25) we get

$$\chi^{\text{ext}}\,(\boldsymbol{k}, \omega) = [(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]^0\,(\boldsymbol{k}, \omega). \tag{2.27}$$

Eq. (2.27) substituted into eq. (2.26) gives a formal expression for the macroscopic dielectric-susceptibility tensor $\chi\,(\boldsymbol{k}, \omega)$ and the dielectric tensor $\varepsilon\,(\boldsymbol{k}, \omega) = \chi(\boldsymbol{k},\omega) + 1$ for a Bravais lattice of molecules with given polarizability $\sigma\,(\boldsymbol{r}, \boldsymbol{r}'; \omega)$. In the next section we shall investigate this susceptibility tensor for a lattice of point dipoles.

3. *The dielectric-susceptibility tensor for a point-dipole lattice.* Consider the case that the molecular polarizability $\boldsymbol{\sigma}$ is given by

$$\boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \boldsymbol{\alpha}^0(\omega)\, \delta(\boldsymbol{r})\, \delta(\boldsymbol{r} - \boldsymbol{r}'). \tag{3.1}$$

By (2.2) we get for the induced dipole-moment density of molecule i:

$$\boldsymbol{p}_i(\boldsymbol{R}, \omega) = \boldsymbol{\alpha}^0(\omega) \cdot \boldsymbol{E}_i^{\mathrm{eff}}(\boldsymbol{R}, \omega)\, \delta(\boldsymbol{R} - \boldsymbol{R}_i). \tag{3.2}$$

We then have a lattice of point dipoles, the induced dipole moment of molecule i being

$$\boldsymbol{p}_i(\omega) = \int \boldsymbol{p}_i(\boldsymbol{R}, \omega)\, \mathrm{d}\boldsymbol{R} = \boldsymbol{\alpha}^0(\omega) \cdot \boldsymbol{E}_i^{\mathrm{eff}}(\boldsymbol{R}_i, \omega). \tag{3.3}$$

For this model we can take for the region g_i, containing molecule i and no others, a sufficiently small sphere of radius d centred at $\boldsymbol{R}_i$. Thus we can define the propagator $\mathsf{H}_i(\boldsymbol{R}, \boldsymbol{R}'; \omega)$ by[8])

$$\begin{aligned} \mathsf{H}_i(\boldsymbol{R}, \boldsymbol{R}'; \omega) &\equiv \mathsf{H}(\boldsymbol{R} - \boldsymbol{R}', \omega) \\ &\equiv \begin{cases} \mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) & \text{for} \quad |\boldsymbol{R} - \boldsymbol{R}'| > d, \\ \tfrac{1}{2}\,[\mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) - \mathsf{F}^{+}(\boldsymbol{R} - \boldsymbol{R}', \omega)] & \text{for} \quad |\boldsymbol{R} - \boldsymbol{R}'| \le d. \end{cases} \end{aligned} \tag{3.4}$$

With this definition we find from (2.9) and (2.10)

$$\mathsf{H}_{\sigma}(\boldsymbol{R}, \boldsymbol{R}''; \omega) = \int \mathrm{d}\boldsymbol{R}'\, \boldsymbol{\alpha}(\boldsymbol{R}, \boldsymbol{R}'; \omega) \cdot \mathsf{H}(\boldsymbol{R}' - \boldsymbol{R}'', \omega), \tag{3.5}$$

or in operator notation

$$\mathsf{H}_{\sigma} = \boldsymbol{\alpha} \cdot \mathsf{H}. \tag{3.6}$$

The expression (2.27) for the external dielectric susceptibility therefore becomes in this case

$$\boldsymbol{\chi}^{\mathrm{ext}}(\boldsymbol{R}, \omega) = [(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1} \cdot \boldsymbol{\alpha}]^0 (\boldsymbol{k}, \omega). \tag{3.7}$$

Now we have in the discrete representation introduced in appendix A [*cf.* eq. (A.9)]

$$\mathsf{H}^{\lambda}(\boldsymbol{k}, \omega) = \mathsf{H}(\boldsymbol{k}, \omega)\, \delta_{\lambda,0}. \tag{3.8}$$

Furthermore it follows from eqs. (2.9) and (3.1) that

$$\boldsymbol{\alpha}(\boldsymbol{R}, \boldsymbol{R}'; \omega) = \boldsymbol{\alpha}^0(\omega) \sum_i \delta(\boldsymbol{R} - \boldsymbol{R}_i)\, \delta(\boldsymbol{R} - \boldsymbol{R}'), \tag{3.9}$$

so that with eq. (A.6) we get

$$\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}, \omega) = \varrho \boldsymbol{\alpha}^{0}(\omega). \tag{3.10}$$

Using the product rule (A.4) we get for eq. (3.7)

$$\chi^{\mathrm{ext}}(\boldsymbol{k}, \omega) = \sum_{\lambda} [(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}]^{\lambda}(\boldsymbol{k}, \omega) \cdot \boldsymbol{\alpha}^{-\lambda}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega). \tag{3.11}$$

With eq. (3.10) this becomes

$$\chi^{\mathrm{ext}}(\boldsymbol{k}, \omega) = \sum_{\lambda} [(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}]^{\lambda}(\boldsymbol{k}, \omega) \cdot \varrho \boldsymbol{\alpha}^{0}(\omega). \tag{3.12}$$

The inverse operator $(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}$ with $\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}, \omega) = \varrho \boldsymbol{\alpha}^{0}(\omega)$ can easily be calculated (see appendix A). The result is [*cf.* eq. (A.17)]:

$$[(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}]^{\lambda}(\boldsymbol{k}, \omega) = \delta_{\lambda,0} - \Big(1 + \varrho \boldsymbol{\alpha}^{0}(\omega) \cdot \sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)\Big)^{-1} \cdot \varrho \boldsymbol{\alpha}^{0}(\omega) \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega). \tag{3.13}$$

From eqs. (3.12) and (3.13) we get

$$\chi^{\mathrm{ext}}(\boldsymbol{k}, \omega) = \Big(1 + \varrho \boldsymbol{\alpha}^{0}(\omega) \cdot \sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)\Big)^{-1} \cdot \varrho \boldsymbol{\alpha}^{0}(\omega). \tag{3.14}$$

Here the symbol -1 denotes simply tensor inversion.

Inserting (3.14) into (2.26) we get

$$\chi(\boldsymbol{k}, \omega) = \Big(1 + \varrho \boldsymbol{\alpha}^{0}(\omega) \cdot \sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) - \varrho \boldsymbol{\alpha}^{0}(\omega) \cdot \mathsf{F}(\boldsymbol{k}, \omega)\Big)^{-1} \cdot \varrho \boldsymbol{\alpha}^{0}(\omega). \tag{3.15}$$

For the lattice sum appearing in eq. (3.15) we can write

$$\begin{aligned}\varrho \sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) &= \varrho \sum_{\lambda} \int \mathsf{H}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-i(\boldsymbol{k}-\boldsymbol{k}_{\lambda})\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} = \sum_{l} \mathsf{H}(\boldsymbol{R}_{l}, \omega)\, \mathrm{e}^{-i\boldsymbol{k}\cdot \boldsymbol{R}_{l}} \\ &= \sum_{l}{}' \mathsf{F}(\boldsymbol{R}_{l}, \omega)\, \mathrm{e}^{-i\boldsymbol{k}\cdot \boldsymbol{R}_{l}} + \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}, \omega) - \mathsf{F}^{+}(\boldsymbol{R}, \omega)]_{\boldsymbol{R}=0},\end{aligned} \tag{3.16}$$

where we have used the definition of $\mathsf{H}(\boldsymbol{R}, \omega)$ and the equality10)

$$\varrho \sum_{\lambda} \mathrm{e}^{-i\boldsymbol{k}_{\lambda}\cdot \boldsymbol{R}} = \sum_{l} \delta(\boldsymbol{R} - \boldsymbol{R}_{l}). \tag{3.17}$$

In eq. (3.16) and in the following $\sum_{l}'$ denotes a sum over all the lattice points of the infinite crystal except the (arbitrarily chosen) origin $\boldsymbol{R}_{l} = 0$. Let us define

$$\begin{aligned}\varrho \mathsf{M}(\boldsymbol{k}, \omega) \equiv{}& \sum_{l}{}' \mathsf{F}(\boldsymbol{R}_{l}, \omega)\, \mathrm{e}^{-i\boldsymbol{k}\cdot \boldsymbol{R}_{l}} - \lim_{d \to 0} \varrho \int_{\varepsilon(d)} \mathsf{F}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-i\boldsymbol{k}\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} \\ &+ \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}, \omega) - \mathsf{F}^{+}(\boldsymbol{R}, \omega)]_{\boldsymbol{R}=0},\end{aligned} \tag{3.18}$$

where in the integral a small sphere of radius d around $\boldsymbol{R} = 0$ is cut out. Then we have

$$\sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) = \mathsf{M}(\boldsymbol{k}, \omega) + \lim_{d \to 0} \int_{\varepsilon(d)} \mathsf{F}(\boldsymbol{R}, \omega)\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, d\boldsymbol{R}$$

$$= \mathsf{M}(\boldsymbol{k}, \omega) + \mathsf{F}(\boldsymbol{k}, \omega) - \tfrac{1}{3}. \qquad (3.19)$$

Thus we get for eq. (3.15)

$$\chi(\boldsymbol{k}, \omega) = [1 - \tfrac{1}{3}\varrho\boldsymbol{\alpha}^0(\omega) + \varrho\boldsymbol{\alpha}^0(\omega)\cdot\mathsf{M}(\boldsymbol{k}, \omega)]^{-1}\cdot\varrho\boldsymbol{\alpha}^0(\omega). \qquad (3.20)$$

It is convenient to write (3.18) as

$$\varrho\mathsf{M}(\boldsymbol{k}, \omega) = \sum_{l}{}' \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}_l, \omega) + \mathsf{F}^{+}(\boldsymbol{R}_l, \omega)]\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$- \lim_{d \to 0} \varrho \int_{\varepsilon(d)} \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}, \omega) + \mathsf{F}^{+}(\boldsymbol{R}, \omega)]\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, d\boldsymbol{R}$$

$$+ \sum_{l} \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}_l, \omega) - \mathsf{F}^{+}(\boldsymbol{R}_l, \omega)]\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$- \varrho \int \tfrac{1}{2}[\mathsf{F}(\boldsymbol{R}, \omega) - \mathsf{F}^{+}(\boldsymbol{R}, \omega)]\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, d\boldsymbol{R}. \qquad (3.21)$$

The last two terms of the r.h.s. of this equation can be written as

$$\sum_{\lambda}{}' \tfrac{1}{2}[\mathsf{F}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) - \mathsf{F}^{+}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)] = i \sum_{\lambda}{}' \operatorname{Im} \mathsf{F}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega), \qquad (3.22)$$

since F is symmetric. Using the explicit form of $\mathsf{F}(\boldsymbol{k}, \omega)$ we have

$$\operatorname{Im} \mathsf{F}(\boldsymbol{k}, \omega) = \tfrac{1}{2}\pi k^{-1}[\delta(k + \omega) - \delta(k - \omega)](\boldsymbol{k}\boldsymbol{k} - \omega^2), \qquad (3.23)$$

so that

$$\sum_{\lambda}{}' \operatorname{Im} \mathsf{F}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) = \tfrac{1}{2}\pi \sum_{\lambda}{}' \frac{1}{|\boldsymbol{k} - \boldsymbol{k}_{\lambda}|}[\delta(|\boldsymbol{k} - \boldsymbol{k}_{\lambda}| + \omega) - \delta(|\boldsymbol{k} - \boldsymbol{k}_{\lambda}| - \omega)]$$

$$\times [(\boldsymbol{k} - \boldsymbol{k}_{\lambda})(\boldsymbol{k} - \boldsymbol{k}_{\lambda}) - \omega^2]. \qquad (3.24)$$

For frequencies ω smaller than the radius of the largest possible sphere in the first Brillouin zone with centre the origin this term vanishes since we have chosen $\boldsymbol{k}$ in the first Brillouin zone so that $|\boldsymbol{k} - \boldsymbol{k}_{\lambda}| \neq \omega$ for $\boldsymbol{k}_{\lambda} \neq 0$. Even for frequencies in the u.v. region this condition for ω is certainly fulfilled. The vanishing of the last two terms of the r.h.s. of eq. (3.21) and the corresponding contribution to the dielectric tensor implies the well-known fact that the ideal dipole lattice does not scatter light of optical frequencies. Consequently we have

$$\varrho \mathsf{M}(\boldsymbol{k}, \omega) = \sum_{l}{}' \tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R}_l, \omega) + \mathsf{F}^{+}(\boldsymbol{R}_l, \omega)\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$- \lim_{d\to 0} \varrho \int_{\varepsilon(d)} \tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R}, \omega) + \mathsf{F}^{+}(\boldsymbol{R}, \omega)\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \qquad (3.25)$$

From eq. (2.4) follows

$$\tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R}, \omega) + \mathsf{F}^{+}(\boldsymbol{R}, \omega)\right] = -(\boldsymbol{\nabla\nabla} + \omega^2)\left[(\cos \omega R)/4\pi R\right] \exp(-0R). \qquad (3.26)$$

The factor $\exp(-0R)$ which serves as a convergence factor and in which 0 is an infinitesimal small positive number [*cf.* also (2.4)] will in the following not be written explicitly. We can write $\mathsf{M}(\boldsymbol{k}, \omega)$ in terms of rapidly converging lattice sums by using a method introduced by Nijboer and De Wette[10]). The transformation will be done in appendix B. The result is [*cf.* eq. (B.13)]

$$4\pi\varrho \mathsf{M}(\boldsymbol{k}, \omega) = -\sum_{l}{}' (\boldsymbol{\nabla\nabla} + \omega^2)\left[\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right)\frac{\cos \omega R_l}{R_l}\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$+ 4\pi\varrho \sum_{\lambda}{}' \frac{(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2}{|\boldsymbol{k} - \boldsymbol{k}_\lambda|^2 - \omega^2} J(|\boldsymbol{k} - \boldsymbol{k}_\lambda|, \omega)$$

$$+ 4\pi\varrho \frac{\boldsymbol{k}\boldsymbol{k} - \omega^2}{k^2 - \omega^2}\left[J(k, \omega) - 1\right] + \frac{8\pi}{3a^3} + \frac{4\pi}{3}\varrho, \qquad (3.27)$$

where the functions $J(k, \omega)$ and $\bar{\Gamma}(n, x)$ are defined by

$$J(k, \omega) \equiv \frac{k - \omega}{2k}\left(1 - \frac{a^2 (k + \omega)^2}{2\pi}\right) \mathrm{e}^{-a^2 (k+\omega)^2/4\pi}$$

$$+ \frac{k + \omega}{2k}\left(1 - \frac{a^2 (k - \omega)^2}{2\pi}\right) \mathrm{e}^{-a^2 (k-\omega)^2/4\pi} \qquad (3.28)$$

and

$$\bar{\Gamma}(n, x) \equiv \left[1/\Gamma(n)\right] \int_{x}^{\infty} \mathrm{e}^{-t}\, t^{n-1}\, \mathrm{d}t. \qquad (3.29)$$

$\mathsf{M}(\boldsymbol{k}, \omega)$ as given by eq. (3.27) does not depend on the length a which serves as a "cut-off" parameter in the method of Nijboer and De Wette. In order to ensure the rapid convergence of both lattice sums a must be of the order of the lattice constant. In the following we will choose

$$a^3 = \varrho^{-1}. \tag{3.30}$$

In the next section we assume that $ak \ll 1$ and $a\omega \ll 1$ and expand $\mathsf{M}(\boldsymbol{k}, \omega)$ in powers of ak and $a\omega$ up to second order.

4. *Weak spatial dispersion.* We now assume that ω is an optical frequency such that $a\omega \ll 1$ and furthermore we assume that $ak \ll 1$ which means that we consider weak spatial dispersion. If we expand $\mathsf{M}(\boldsymbol{k}, \omega)$ in powers of ak and $a\omega$ we have no odd-order terms in ak by the symmetry of the lattice and no odd-order terms in $a\omega$ since $\mathsf{M}(\boldsymbol{k}, \omega) = \mathsf{M}(\boldsymbol{k}, -\omega)$. So up to second order we can write

$$\mathsf{M}(\boldsymbol{k}, \omega) = \mathsf{M}^{(0)} + \mathsf{M}''(\omega) + \mathsf{M}^{(2)}(\boldsymbol{k}), \tag{4.1}$$

with

$$\mathsf{M}''(\omega) = a^2\omega^2 \mathcal{M}'' \tag{4.2}$$

and

$$\mathsf{M}^{(2)}(\boldsymbol{k}) = a^2 \boldsymbol{k}\boldsymbol{k} : \mathcal{M}^{(2)}. \tag{4.3}$$

$\mathcal{M}^{(2)}$ is a tensor of fourth rank. With the expansion (4.1) we can expand the susceptibility (3.20):

$$\chi(\boldsymbol{k}, \omega) = \chi^{(0)}(\omega) + \chi^{(2)}(\boldsymbol{k}, \omega), \tag{4.4}$$

with

$$\chi^{(0)}(\omega) = [1 - \tfrac{1}{3}\varrho\boldsymbol{\alpha}^0(\omega) + \varrho\boldsymbol{\alpha}^0(\omega) \cdot \mathsf{M}^{(0)}]^{-1} \cdot \varrho\boldsymbol{\alpha}^0(\omega) \tag{4.5}$$

and

$$\chi^{(2)}(\boldsymbol{k}, \omega) = -\chi^{(0)}(\omega) \cdot [\mathsf{M}''(\omega) + \mathsf{M}^{(2)}(\boldsymbol{k})] \cdot \chi^{(0)}(\omega). \tag{4.6}$$

We shall treat successively the dielectric tensor to 0th order (section 4.1), to 2nd order (section 4.2) and the expansion of the inverse dielectric tensor (section 4.3).

4.1. The zeroth-order dielectric tensor. From eq. (3.27) we find to 0th order with use of eq. (3.30)

$$\mathsf{M}^{(0)} = \frac{a^3}{4\pi} \sum_l{}' \bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right) \frac{1 - 3\hat{\boldsymbol{R}}_l\hat{\boldsymbol{R}}_l}{R_l^3}$$

$$- \sum_l{}' \hat{\boldsymbol{R}}_l\hat{\boldsymbol{R}}_l \,\mathrm{e}^{-\pi R_l{}^2/a^2} + \sum_\lambda{}' \hat{\boldsymbol{k}}_\lambda\hat{\boldsymbol{k}}_\lambda \,\mathrm{e}^{-a^2 k_\lambda{}^2/4\pi}. \tag{4.7}$$

From eq. (4.5) we obtain the following expression for the dielectric tensor to 0th order

$$\begin{aligned}\boldsymbol{\varepsilon}^0(\omega) &= \boldsymbol{\chi}^{(0)}(\omega) + 1\\ &= [1 - \tfrac{1}{3}\varrho\boldsymbol{\alpha}^0(\omega) + \varrho\boldsymbol{\alpha}^0(\omega)\cdot\mathsf{M}^{(0)}]^{-1}\\ &\quad\cdot [1 + \tfrac{2}{3}\varrho\boldsymbol{\alpha}^0(\omega) + \varrho\boldsymbol{\alpha}^0(\omega)\cdot\mathsf{M}^{(0)}].\end{aligned} \tag{4.8}$$

In combination with eq. (4.7) this is exactly the result obtained earlier by Vlieger[2]) for isotropic molecules $[\boldsymbol{\alpha}^0(\omega) = \alpha^0(\omega)]$. Note that his expression G is equal to our $4\pi\mathsf{M}^{(0)}$. This result could have been obtained immediately by taking $\boldsymbol{k} = 0$ and $\omega = 0$ in eq. (3.25) giving the static dipole sum $(4\pi\varrho)^{-1}\sum_l' R_l^{-3}(1 - 3\hat{\boldsymbol{R}}_l\hat{\boldsymbol{R}}_l)$. The convergence of this sum is ensured by the convergence factor or equivalently by summing over a sphere of volume V and taking $V \to \infty$ (*cf.* ref. 11). If we apply the method of Nijboer and De Wette (*cf.* appendix B) to this static dipole sum we obtain immediately eq. (4.7) which consists of strongly converging sums. For a cubic lattice the first term of the r.h.s. of eq. (4.7) vanishes by symmetry while the last two terms cancel so that $\mathsf{M}^{(0)} = 0$. Then we have

$$\boldsymbol{\varepsilon}^0(\omega) = [1 - \tfrac{1}{3}\varrho\boldsymbol{\alpha}^0(\omega)]^{-1}\cdot[1 + \tfrac{2}{3}\varrho\boldsymbol{\alpha}^0(\omega)]. \tag{4.9}$$

If moreover the molecules are isotropic this becomes the Lorentz–Lorenz formula for the dielectric constant

$$\varepsilon^0(\omega) = [1 + \tfrac{2}{3}\varrho\alpha^0(\omega)]/[1 - \tfrac{1}{3}\varrho\alpha^0(\omega)]. \tag{4.10}$$

4.2. The second-order dielectric tensor. From eq. (3.27) we can calculate the tensors $\mathcal{M}''$ and $\mathcal{M}^{(2)}$. By straightforward calculations we find[‡]

$$\begin{aligned}4\pi\mathcal{M}'' = 2 &- \sum_\lambda{}' \tfrac{1}{2}\frac{a}{R_\lambda}\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R_\lambda^2}{a^2}\right)(1 + \hat{\boldsymbol{R}}_\lambda\hat{\boldsymbol{R}}_\lambda)\\ &- \sum_\lambda{}' \frac{4\pi}{a^2k_\lambda^2}\,\mathrm{e}^{-a^2k_\lambda{}^2/4\pi}(1 - \hat{\boldsymbol{k}}_\lambda\hat{\boldsymbol{k}}_\lambda) + \sum_\lambda{}' \mathrm{e}^{-a^2k_\lambda{}^2/4\pi}(1 + \hat{\boldsymbol{k}}_\lambda\hat{\boldsymbol{k}}_\lambda)\end{aligned} \tag{4.11}$$

and in cartesian components

$$\begin{aligned}4\pi\mathcal{M}^{(2)}_{mlij} = &\sum_\lambda{}' [\hat{R}^\lambda_m\hat{R}^\lambda_l\hat{R}^\lambda_i\hat{R}^\lambda_j f(R_\lambda) + \hat{R}^\lambda_m\hat{R}^\lambda_l\delta_{ij}g(R_\lambda)]\\ &+ \sum_\lambda{}' [\hat{k}^\lambda_m\hat{k}^\lambda_l\hat{k}^\lambda_i\hat{k}^\lambda_j a(k_\lambda) + \delta_{ml}\hat{k}^\lambda_i\hat{k}^\lambda_j b(k_\lambda) + (\delta_{mi}\hat{k}^\lambda_l\hat{k}^\lambda_j + \delta_{mj}\hat{k}^\lambda_l\hat{k}^\lambda_i)\,c(k_\lambda)\\ &+ (\delta_{li}\delta_{mj} + \delta_{lj}\delta_{mi})\,d(k_\lambda)] - \tfrac{1}{2}(\delta_{li}\delta_{mj} + \delta_{lj}\delta_{mi}),\end{aligned} \tag{4.12}$$

[‡] For a choice of a different from $a = \varrho^{-1/3}$ one should multiply the sums in $\boldsymbol{R}$-space in eqs. (4.11) and (4.12) with a factor $(a^3\varrho)^{-1}$.

where

$$f(R) \equiv \frac{3a}{2R}\,\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right) + 2\pi\,\frac{R^2}{a^2}\,\mathrm{e}^{-\pi R^2/a^2},$$

$$g(R) \equiv -\frac{a}{2R}\,\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right),$$

$$a(k) \equiv \left(4 + \frac{a^2k^2}{\pi} + \frac{a^4k^4}{8\pi^2}\right)\frac{4\pi}{a^2k^2}\,\mathrm{e}^{-a^2k^2/4\pi},$$

$$b(k) \equiv -\left(1 + \frac{4\pi}{a^2k^2}\right)\mathrm{e}^{-a^2k^2/4\pi},$$

$$c(k) \equiv 2b\,(k),$$

$$d(k) \equiv \frac{2\pi}{a^2k^2}\,\mathrm{e}^{-a^2k^2/4\pi}. \tag{4.13}$$

In eqs. (4.11) and (4.12) we have denoted lattice points by $\boldsymbol{R}_\lambda$ in order to avoid confusion with the cartesian index i. So $\hat{R}^\lambda_i$ is the i component of the unit vector in the direction of the lattice vector $\boldsymbol{R}_\lambda$ and similarly for $\hat{k}^\lambda_i$. Hence we get with eqs. (4.2), (4.3) and (4.6) for the expansion up to 2nd order of the dielectric tensor $\boldsymbol{\varepsilon}\,(\boldsymbol{k}, \omega) = \boldsymbol{\chi}\,(\boldsymbol{k}, \omega) + 1$ in cartesian components (with summation convention):

$$\varepsilon_{ij}\,(\boldsymbol{k}, \omega) = \varepsilon^0_{ij}(\omega) + \varepsilon''_{ij}(\omega) + \varepsilon^{(2)}_{ij}\,(\boldsymbol{k}, \omega), \tag{4.14}$$

where $\varepsilon^0_{ij}(\omega)$ is given by eq. (4.8),

$$\varepsilon''_{ij}(\omega) = -a^2\omega^2\,(\varepsilon^0_{ik}(\omega) - \delta_{ik})\,\mathscr{M}''_{kl}\,[\varepsilon^0_{lj}(\omega) - \delta_{lj}] \tag{4.15}$$

and

$$\varepsilon^{(2)}_{ij}\,(\boldsymbol{k}, \omega) = k_m k_n \alpha_{nmij}\,(\omega), \tag{4.16}$$

with

$$\alpha_{nmij}(\omega) = -a^2\,[\varepsilon^0_{ik}(\omega) - \delta_{ik}]\,\mathscr{M}^{(2)}_{nmkl}\,[\varepsilon^0_{lj}(\omega) - \delta_{lj}]. \tag{4.17}$$

The fourth-order tensor $\alpha_{nmij}(\omega)$ should not be confused with the polarizability tensor. We have chosen the notation of ref. 12. The evaluation of $\varepsilon\,(\boldsymbol{k}, \omega)$ for a particular type of lattice is now reduced to the numerical calculation of the strongly converging lattice sums $\mathrm{M}^{(0)}$, $\mathscr{M}''$ and $\mathscr{M}^{(2)}$.

As an example we consider the case of a simple cubic lattice with isotropic molecules. For a cubic lattice the tensor $\mathcal{M}''$ reduces to a scalar m'' which is for a simple cubic lattice [with eq. (3.30)] given by

$$4\pi m'' = 2 - \sum_{\lambda}{}' \frac{2a}{3R_\lambda} \operatorname{erfc}\left(\pi^{\frac{1}{2}} \frac{R_\lambda}{a}\right) - \sum_{\lambda}{}' \frac{2a^2}{3\pi R_\lambda^2} e^{-\pi R_\lambda^2/a^2}. \tag{4.18}$$

Here we have used the fact that

$$\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right) = \operatorname{erfc}\left(\pi^{\frac{1}{2}} \frac{R}{a}\right) + \frac{2R}{a} e^{-\pi R^2/a^2} \tag{4.19}$$

and that for a simple cubic lattice

$$\sum_{\lambda}{}' f(ak_\lambda/2\pi)\, g(\hat{k}_\lambda) = \sum_{\lambda}{}' f(R_\lambda/a)\, g(\hat{R}_\lambda). \tag{4.20}$$

For the dielectric tensor we then have

$$\varepsilon_{ij}(k, \omega) = [\varepsilon^0(\omega) + \varepsilon''(\omega)]\, \delta_{ij} + k_m k_n \alpha_{nmij}(\omega), \tag{4.21}$$

where $\varepsilon^0(\omega)$ is given by eq. (4.10) and where

$$\varepsilon''(\omega) = -a^2\omega^2\, [\varepsilon^0(\omega) - 1]^2\, m'' \tag{4.22}$$

and

$$\alpha_{nmij}(\omega) = -a^2\, [\varepsilon^0(\omega) - 1]^2\, \mathcal{M}^{(2)}_{nmij}. \tag{4.23}$$

The tensor $\mathcal{M}^{(2)}_{nmij}$ (hence also α_{nmij}) has in the case of a cubic lattice 2 independent components*. If we let the coordinate axes coincide with the three fourth-order axes of the cubic lattice we have

$$\begin{aligned} &\mathcal{M}^{(2)}_{xxxx} = m_1, \\ &\mathcal{M}^{(2)}_{xxyy} = \mathcal{M}^{(2)}_{yyxx} = m_2 = -\tfrac{1}{2}m_1, \\ &\mathcal{M}^{(2)}_{xyxy} = \mathcal{M}^{(2)}_{yxyx} = \mathcal{M}^{(2)}_{xyyx} = \mathcal{M}^{(2)}_{yxxy} = m_3 \\ &\text{and the cyclic permutations} \qquad xyz \rightarrow yzx \rightarrow zxy. \end{aligned} \tag{4.24}$$

The other components are zero by symmetry. The lattice sums can be computed to any desired accuracy; due to the strong convergence only a few points are

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* In general one has 3 independent components for these lattices[12]). The relation $m_2 = -\frac{1}{2}m_1$ in eq. (4.24) is a consequence of the point-dipole model.

sufficient to get a good result. We find for a simple cubic lattice

$$4\pi m_1 = 0.3297, \qquad 4\pi m_2 = -0.1648, \qquad 4\pi m_3 = -0.6377 \tag{4.25}$$

and from (4.18)

$$4\pi m'' = 1.8915. \tag{4.26}$$

Let us consider homogeneous normal waves in the crystal for which

$$\boldsymbol{k} = n(\hat{\boldsymbol{k}}, \omega)\, \omega \hat{\boldsymbol{k}}, \tag{4.27}$$

where $n(\hat{\boldsymbol{k}}, \omega)$ is the complex refractive index in the direction of $\boldsymbol{k}$. From the phenomenological theory (ch. 3 of ref. 12) follows the way in which this refractive index depends on the different directions of $\boldsymbol{k}$. As a first example let us consider transverse waves propagating along an edge of a cube. One then finds the following dispersion relation independent of the polarization.

$$n^2 = (\varepsilon^0 + \varepsilon'')/(1 - \alpha_2'). \tag{4.28}$$

Here and in the following

$$\alpha_p' \equiv \omega^2 \alpha_p = -a^2 \omega^2 (\varepsilon^0 - 1)^2 m_p \qquad (p = 1, 2, 3). \tag{4.29}$$

Using eqs. (4.22), (4.25), (4.26) and (4.29) and neglecting higher than second-order terms in $a\omega$ eq. (4.28) can be written as

$$n^2 = n_0^2 + (a^2\omega^2/4\pi)(n_0^2 - 1)^2 (0.1648 n_0^2 - 1.8915), \tag{4.30}$$

where $n_0^2 = \varepsilon^0$.

As a second example let us consider transverse waves propagating along a face diagonal of the cube. We then have the following dispersion relations depending on the polarization:

i) for transverse waves polarized perpendicular to the face plane:

$$n_1^2 = (\varepsilon^0 + \varepsilon'')/(1 - \alpha_2'); \tag{4.31}$$

ii) for transverse waves polarized in the face plane:

$$n_2^2 = (\varepsilon^0 + \varepsilon'')/(1 - \alpha_2' - \tfrac{1}{2}\tilde{\alpha}'), \tag{4.32}$$

where

$$\tilde{\alpha}' = \alpha_1' - \alpha_2' - 2\alpha_3'. \tag{4.33}$$

We then get with the numerical values (4.25) for the difference between the refractive indices:

$$n_1 - n_2 = 0.1106\,(a^2\omega^2/\pi)\,n_0\,(n_0^2 - 1)^2. \tag{4.34}$$

Note that this difference does not depend on ε'' since this correction is isotropic in the cubic case. The results (4.30) and (4.34) have already been obtained by Lorentz[3]).

Finally we consider transverse waves propagating along a main diagonal of the cube. In this case we have the dispersion relation (independent of the polarization)

$$n^2 = (\varepsilon^0 + \varepsilon'')/(1 - \alpha_2' - \tfrac{1}{3}\tilde{\alpha}') \tag{4.35}$$

and with the numerical values (4.25) and (4.26)

$$n^2 = n_0^2 - (a^2\omega^2/4\pi)\,(n_0^2 - 1)^2\,(0.4252 n_0^2 + 1.8915). \tag{4.36}$$

The same calculations can be done for the face-centred cubic and the body-centred cubic lattices. For the numerical values of m_1, m_2, m_3 and m'' we find for the f.c.c. lattice:

$$4\pi m_1 = -0.5974, \qquad 4\pi m_2 = 0.2987,$$

$$4\pi m_3 = -0.1827, \qquad 4\pi m'' = 1.9255,$$

and for the b.c.c. lattice:

$$4\pi m_1 = -0.5893, \qquad 4\pi m_2 = 0.2946,$$

$$4\pi m_3 = -0.1868, \qquad 4\pi m'' = 1.9256.$$

4.3. Expansion of the inverse dielectric tensor. We can also consider the expansion of the inverse dielectric tensor $\boldsymbol{\varepsilon}^{-1}(\boldsymbol{k}, \omega)$. This expansion is convenient near dipole transitions where $\varepsilon^0(\omega)$ may assume large values. Far away from transitions this expansion is equivalent to the expansion of $\boldsymbol{\varepsilon}(\boldsymbol{k}, \omega)$. From eq. (4.14) follows:

$$\begin{aligned}\boldsymbol{\varepsilon}^{-1}(\boldsymbol{k}, \omega) = {} & [\boldsymbol{\varepsilon}^0(\omega)]^{-1} - [\boldsymbol{\varepsilon}^0(\omega)]^{-1} \cdot \boldsymbol{\varepsilon}''(\omega) \cdot [\boldsymbol{\varepsilon}^0(\omega)]^{-1} \\ & - [\boldsymbol{\varepsilon}^0(\omega)]^{-1} \cdot \boldsymbol{\varepsilon}^{(2)}(\boldsymbol{k}, \omega) \cdot [\boldsymbol{\varepsilon}^0(\omega)]^{-1},\end{aligned} \tag{4.37}$$

where $\varepsilon''(\omega)$ and $\varepsilon^{(2)}(\boldsymbol{k}, \omega)$ are given by eqs. (4.15), (4.16) and (4.17). In the case of isotropic molecules on a simple cubic lattice eq. (4.37) becomes

$$\varepsilon^{-1}(\boldsymbol{k}, \omega) = \frac{1}{\varepsilon^0(\omega)} + a^2\omega^2 \left(1 - \frac{1}{\varepsilon^0(\omega)}\right)^2 m'' + \left(1 - \frac{1}{\varepsilon^0(\omega)}\right)^2 a^2 \boldsymbol{k}\boldsymbol{k} : \mathcal{M}^{(2)}, \tag{4.38}$$

where $\varepsilon^0(\omega)$ is given by (4.10).

Let the coordinate axes again coincide with the three fourth-order axes and let us consider transverse normal waves propagating in the crystal. For waves propagating along an edge of a cube we then have the following dispersion relation independent of the polarization[12]:

$$(1/n^2) = (1/\varepsilon^0) + a^2\omega^2 (1 - 1/\varepsilon^0)^2 (m'' + n^2 m_2). \tag{4.39}$$

In general we have two solutions for n^2 one of which is very close to ε^0 while for the other solution the condition $a^2k^2 \ll 1$ is violated. However, near a dipole transition at frequency ω_t, for which we may assume that ε^0 (without absorption) has the form $\varepsilon^0(\omega) = \varepsilon_{00} - A\omega_t^2/(\omega^2 - \omega_t^2)$ there can exist a second solution for which n^2 is large but the condition $a^2k^2 \ll 1$ is still satisfied. Then we can neglect m'' with respect to $n^2 m_2$ and eq. (4.39) becomes:

$$(1/n^2) = (1/\varepsilon^0) + n^2 m_2 a^2 \omega^2 (1 - 1/\varepsilon^0)^2. \tag{4.40}$$

We have similar expressions for the other main directions in the cubic crystal. For waves propagating along a face diagonal, with $\boldsymbol{D}$ polarized perpendicular to the plane:

$$(1/n^2) = (1/\varepsilon^0) + n^2 m_2 a^2 \omega^2 (1 - 1/\varepsilon^0)^2 \tag{4.41}$$

and polarized in the plane:

$$(1/n^2) = (1/\varepsilon^0) + n^2 (m_2 + \tfrac{1}{2}\tilde{m})\, a^2\omega^2 (1 - 1/\varepsilon^0)^2. \tag{4.42}$$

For waves propagating along one of the main diagonals of the cube:

$$(1/n^2) = (1/\varepsilon^0) + n^2 (m_2 + \tfrac{1}{3}\tilde{m})\, a^2\omega^2 (1 - 1/\varepsilon^0)^2. \tag{4.43}$$

In eqs. (4.42) and (4.43), $\tilde{m} \equiv m_1 - m_2 - 2m_3$. Using the numerical values (4.25) we find $m_2 = -0.1648/4\pi$, $m_2 + \frac{1}{2}\tilde{m} = 0.7202/4\pi$ and $m_2 + \frac{1}{3}\tilde{m} = 0.4252/4\pi$. We must distinguish between a positive coefficient of n^2 in the right-hand sides of (4.42) and (4.43) and a negative coefficient in (4.40) and (4.41). In the first case spatial dispersion induces the appearance of an anomalous wave propagating in a frequency region where with the assumed form of $\varepsilon^0(\omega)$ total internal reflection would occur if no spatial dispersion had been taken into account. In the second case there exists a region at the lower-frequency side of the dipole line where two waves may be propagating with the same frequency but with different refractive indices and thus different wave lengths[12]).

APPENDIX A

A.1. *Discrete operator representation.* In this appendix we shall give the relation between the continuous $\boldsymbol{k}$ representation and the discrete representation for periodic operators *i.e.* operators A for which in the $\boldsymbol{R}$ representation $A(\boldsymbol{R}, \boldsymbol{R}') = A(\boldsymbol{R} + \boldsymbol{R}_l, \boldsymbol{R}' + \boldsymbol{R}_l)$ for each lattice vector $\boldsymbol{R}_l$. In the $\boldsymbol{k}$ representation a periodic operator A can be written as

$$A(\boldsymbol{k}, \boldsymbol{k}') = \sum_{\lambda} A^{\lambda}(\boldsymbol{k})\, \delta(\boldsymbol{k} - \boldsymbol{k}' - \boldsymbol{k}_{\lambda}), \tag{A.1}$$

where $\boldsymbol{k}_{\lambda}$ is a reciprocal-lattice vector. Working on a function ψ this yields

$$(A\psi)(\boldsymbol{k}) = \int \mathrm{d}\boldsymbol{k}' A(\boldsymbol{k}, \boldsymbol{k}')\, \psi(\boldsymbol{k}') = \sum_{\lambda} A^{\lambda}(\boldsymbol{k})\, \psi(\boldsymbol{k} - \boldsymbol{k}_{\lambda}), \tag{A.2}$$

giving the relation between the continuous representation $A(\boldsymbol{k}, \boldsymbol{k}')$ and the discrete representation $A^{\lambda}(\boldsymbol{k})$. For a product of two periodic operators A and B we have

$$\begin{aligned}(AB)(\boldsymbol{k}, \boldsymbol{k}') &= \int \mathrm{d}\boldsymbol{k}'' \sum_{\lambda} A^{\lambda}(\boldsymbol{k})\, \delta(\boldsymbol{k} - \boldsymbol{k}'' - \boldsymbol{k}_{\lambda}) \sum_{\lambda'} B^{\lambda'}(\boldsymbol{k}'')\, \delta(\boldsymbol{k}'' - \boldsymbol{k}' - \boldsymbol{k}_{\lambda'}) \\ &= \sum_{\lambda} \sum_{\lambda'} A^{\lambda}(\boldsymbol{k})\, B^{\lambda'}(\boldsymbol{k} - \boldsymbol{k}_{\lambda})\, \delta(\boldsymbol{k} - \boldsymbol{k}' - \boldsymbol{k}_{\lambda} - \boldsymbol{k}_{\lambda'}) \\ &= \sum_{\mu} \sum_{\lambda} A^{\lambda}(\boldsymbol{k})\, B^{\mu-\lambda}(\boldsymbol{k} - \boldsymbol{k}_{\lambda})\, \delta(\boldsymbol{k} - \boldsymbol{k}' - \boldsymbol{k}_{\mu}),\end{aligned} \tag{A.3}$$

so that

$$(AB)^{\lambda}(\boldsymbol{k}) = \sum_{\mu} A^{\mu}(\boldsymbol{k})\, B^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}). \tag{A.4}$$

For the unit operator we have

$$1^{\lambda}(\boldsymbol{k}) = \delta_{\lambda,0} \equiv \begin{bmatrix} 1 & \text{for} & \boldsymbol{k}_{\lambda} = 0, \\ 0 & \text{for} & \boldsymbol{k}_{\lambda} \neq 0. \end{bmatrix} \tag{A.5}$$

A.2. *A property of periodic operators.* If the operator A is of the form $A(\boldsymbol{R}, \boldsymbol{R}') = \sum_l a(\boldsymbol{R} - \boldsymbol{R}_l, \boldsymbol{R}' - \boldsymbol{R}_l)$ it can easily be shown that

$$A^{\lambda}(\boldsymbol{k}) = (2\pi)^3 \varrho a(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{k}_{\lambda}), \tag{A.6}$$

where $\varrho^{-1} = v$ is the volume of the unit cell of the lattice. From eq. (A.4) we see that for a product of two such operators:

$$(AB)^{\lambda}(\boldsymbol{k}) = \varrho^2 \sum_{\lambda'} a(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{k}_{\lambda'})\, b(\boldsymbol{k} - \boldsymbol{k}_{\lambda'}, \boldsymbol{k} - \boldsymbol{k}_{\lambda}). \tag{A.7}$$

A.3. *A property of diagonal operators.* Suppose an operator H is diagonal in the $\boldsymbol{k}$ representation so that

$$H(\boldsymbol{k}, \boldsymbol{k}') = H(\boldsymbol{k})\, \delta(\boldsymbol{k} - \boldsymbol{k}'). \tag{A.8}$$

In this case

$$H^{\lambda}(\boldsymbol{k}) = H(\boldsymbol{k})\, \delta_{\lambda,0}, \tag{A.9}$$

so that with (A.4):

$$\begin{aligned}(AH)^{\lambda}(\boldsymbol{k}) &= \sum_{\mu} A^{\mu}(\boldsymbol{k})\, H^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}) \\ &= \sum_{\mu} A^{\mu}(\boldsymbol{k})\, H(\boldsymbol{k} - \boldsymbol{k}_{\mu})\, \delta_{\lambda,\mu} = A^{\lambda}(\boldsymbol{k})\, H(\boldsymbol{k} - \boldsymbol{k}_{\lambda}).\end{aligned} \tag{A.10}$$

If A is of the form (A.6):

$$(AH)^{\lambda}(\boldsymbol{k}) = (2\pi)^6 \varrho a(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{k}_{\lambda})\, H(\boldsymbol{k} - \boldsymbol{k}_{\lambda}) \tag{A.11}$$

A.4. *Calculation of* $[(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}]^{\lambda}(\boldsymbol{k}) \equiv \mathsf{f}^{\lambda}(\boldsymbol{k})$ *with* $\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}) = \varrho\boldsymbol{\alpha}^0$. The inverse operator is defined by the equations

$$[\mathsf{f} \cdot (1 + \boldsymbol{\alpha} \cdot \mathsf{H})]^{\lambda}(\boldsymbol{k}) = [(1 + \boldsymbol{\alpha} \cdot \mathsf{H}) \cdot \mathsf{f}]^{\lambda}(\boldsymbol{k}) = \delta_{\lambda,0}. \tag{A.12}$$

From eqs. (A.4), (A.10) and the fact that $\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}) = \varrho\boldsymbol{\alpha}^0$ is a constant, (3.10), we have

$$\begin{aligned}[\mathsf{f} \cdot (1 + \boldsymbol{\alpha} \cdot \mathsf{H})]^{\lambda}(\boldsymbol{k}) &= \sum_{\mu} \mathsf{f}^{\mu}(\boldsymbol{k}) \cdot [1 + \boldsymbol{\alpha} \cdot \mathsf{H}]^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}) \\ &= \sum_{\mu} \mathsf{f}^{\mu}(\boldsymbol{k}) \cdot [\delta_{\lambda,\mu} + \boldsymbol{\alpha}^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}) \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda})] \\ &= \mathsf{f}^{\lambda}(\boldsymbol{k}) + \mathsf{f}(\boldsymbol{k}) \cdot \varrho\boldsymbol{\alpha}^0 \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}),\end{aligned} \tag{A.13}$$

where

$$\mathrm{f}(\boldsymbol{k}) \equiv \sum_{\lambda} \mathrm{f}^{\lambda}(\boldsymbol{k}). \tag{A.14}$$

So with eq. (A.12),

$$\mathrm{f}^{\lambda}(\boldsymbol{k}) = \delta_{\lambda,0} - \varrho \mathrm{f}(\boldsymbol{k}) \cdot \boldsymbol{\alpha}^0 \cdot \mathrm{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}) \tag{A.15}$$

and with (A.14)

$$\mathrm{f}(\boldsymbol{k}) = \Bigl(1 + \varrho \boldsymbol{\alpha}^0 \cdot \sum_{\lambda'} \mathrm{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda})\Bigr)^{-1}. \tag{A.16}$$

Thus we get

$$\mathrm{f}^{\lambda}(\boldsymbol{k}) = \delta_{\lambda,0} - \Bigl(1 + \varrho \boldsymbol{\alpha}^0 \cdot \sum_{\lambda'} \mathrm{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda'})\Bigr)^{-1} \cdot \varrho \boldsymbol{\alpha}^0 \cdot \mathrm{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}). \tag{A.17}$$

The second equality of (A.12) can be easily verified.

APPENDIX B

In order to express $\mathrm{M}(\boldsymbol{k}, \omega)$ in rapidly converging lattice sums we write for eq. (3.25)

$$\begin{aligned} 4\pi\varrho \mathrm{M}(\boldsymbol{k}, \omega) = & -\sum_{l}{}' (\nabla\nabla + \omega^2) \left[\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right) \frac{\cos \omega R_l}{R_l} \right] \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{R}_l} \\ & - \sum_{l}{}' (\nabla\nabla + \omega^2) \left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right) \frac{\cos \omega R_l}{R_l} \right] \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{R}_l} \\ & - \lim_{d \to 0} 4\pi\varrho \int_{\varepsilon(d)} \tfrac{1}{2} [\mathrm{F}(\boldsymbol{R}, \omega) + \mathrm{F}^{+}(\boldsymbol{R}, \omega)]\, \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}, \end{aligned} \tag{B.1}$$

where

$$\bar{\Gamma}(n, x) \equiv [1/\Gamma(n)] \int_{x}^{\infty} \mathrm{e}^{-t} t^{n-1}\, \mathrm{d}t = \Gamma(n, x)/\Gamma(n) \tag{B.2}$$

and

$$\bar{\gamma}(n, x) \equiv 1 - \bar{\Gamma}(n, x). \tag{B.3}$$

$\Gamma(n) = \Gamma(n, 0)$ is the gamma function and $\Gamma(n, x)$ is the incomplete gamma function. We have introduced a "cut-off" parameter a which is of the order of the lattice constants. Since the function $\bar{\Gamma}(\frac{3}{2}, \pi R^2/a^2)$ is rapidly decreasing over a few lattice points the first term of the r.h.s. of eq. (B.1) is a rapidly converging lattice sum. The second term can be transformed into a rapidly converging lattice sum on the reciprocal lattice. If we use eq. (3.17) we can write

$$-\sum_{l}{}' (\nabla\nabla + \omega^2)\left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right)\frac{\cos \omega R_l}{R_l}\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$= \int \delta(\boldsymbol{R})\, (\nabla\nabla + \omega^2)\left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$- \varrho \sum_{\lambda} \mathrm{FT}_3 \left\{(\nabla\nabla + \omega^2)\left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\right]\right\}_{\boldsymbol{k}-\boldsymbol{k}_\lambda} \tag{B.4}$$

where

$$\mathrm{FT}_3\, [f(\boldsymbol{R})]_{\boldsymbol{k}-\boldsymbol{k}_\lambda} \equiv \int f(\boldsymbol{R})\, \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}_\lambda)\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \tag{B.5}$$

The first term of the r.h.s. of eq. (B.5) can be easily calculated. The result is

$$\int \delta(\boldsymbol{R})\, (\nabla\nabla + \omega^2)\left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} = \frac{8\pi}{3a^3}. \tag{B.6}$$

For the Fourier transform in the second term we have by integration by parts

$$-\int (\nabla\nabla + \omega^2)\left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$= (\boldsymbol{k}\boldsymbol{k} - \omega^2) \int \bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \tag{B.7}$$

Using spherical coordinates we find by straightforward calculations

$$\int \bar{\gamma}\left(\frac{3}{2}, \frac{\pi R^2}{a^2}\right)\frac{\cos \omega R}{R}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} = \frac{2\pi}{k}\, [I(k, \omega) + I(k, -\omega)], \tag{B.8}$$

with

$$I(k, \omega) = \mathscr{P} \frac{1}{k + \omega}\left(1 - \frac{a^2 (k + \omega)^2}{2\pi}\right) \mathrm{e}^{-a^2 (k+\omega)^2/4\pi} \tag{B.9}$$

in which $\mathscr{P}$ stands for "principal value".

Substituting (B.6)–(B.9) into (B.5) we get for the second term of the r.h.s. of (B.1), since k and ω are such that $|\boldsymbol{k} - \boldsymbol{k}_\lambda| > \omega$ for $\boldsymbol{k}_\lambda \neq 0$:

$$-\sum_l{}' (\boldsymbol{\nabla\nabla} + \omega^2) \left[\bar{\gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right) \frac{\cos \omega R_l}{R_l} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$= \frac{8\pi}{3a^3} + 4\pi\varrho \sum_\lambda{}' \frac{(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2}{|\boldsymbol{k} - \boldsymbol{k}_\lambda|^2 - \omega^2} J(|\boldsymbol{k} - \boldsymbol{k}_\lambda|, \omega)$$

$$+ 4\pi\varrho \mathscr{P} \frac{\boldsymbol{kk} - \omega^2}{k^2 - \omega^2} J(k, \omega), \tag{B.10}$$

where

$$J(k, \omega) \equiv \frac{k - \omega}{2k} \left(1 - \frac{a^2 (k + \omega)^2}{2\pi}\right) \mathrm{e}^{-a^2 (k+\omega)^2/4\pi}$$

$$+ \frac{k + \omega}{2k} \left(1 - \frac{a^2 (k - \omega)^2}{2\pi}\right) \mathrm{e}^{-a^2 (k-\omega)^2/4\pi}. \tag{B.11}$$

Furthermore we have

$$-\lim_{d\to 0} \int_{\varepsilon(d)} \tfrac{1}{2} [\mathsf{F}(\boldsymbol{R}, \omega) + \mathsf{F}^+(\boldsymbol{R}, \omega)] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \mathrm{d}\boldsymbol{R} = -\mathscr{P} \frac{\boldsymbol{kk} - \omega^2}{k^2 - \omega^2} + \frac{1}{3}. \tag{B.12}$$

From (B.1), (B.10) and (B.12) we then obtain

$$4\pi\varrho \mathsf{M}(\boldsymbol{k}, \omega) = -\sum_l{}' (\boldsymbol{\nabla\nabla} + \omega^2) \left[\bar{\Gamma}\left(\frac{3}{2}, \frac{\pi R_l^2}{a^2}\right) \frac{\cos \omega R_l}{R_l} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l}$$

$$+ 4\pi\varrho \sum_\lambda{}' \frac{(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2}{|\boldsymbol{k} - \boldsymbol{k}_\lambda|^2 - \omega^2} J(|\boldsymbol{k} - \boldsymbol{k}_\lambda|, \omega)$$

$$+ 4\pi\varrho \frac{\boldsymbol{kk} - \omega^2}{k^2 - \omega^2} [J(k, \omega) - 1] + \frac{8\pi}{3a^3} + \frac{4\pi}{3} \varrho. \tag{B.13}$$

Note that the poles of $(k^2 - \omega^2)^{-1}$ are cancelled by the zeros of $J(k, \omega) - 1$ in $k = \pm\omega$. By the gamma functions we now have two rapidly converging lattice sums.

REFERENCES

1) Brown jr., W.F., Handbuch der Physik XVII, Springer (Berlin, 1956).
2) Vlieger, J., Can. J. of Physics **49** (1971) 1384.
3) Lorentz, H.A., Collected Papers **3** (1936) 314; **2** (1936) 79.

4) Maaskant, W.J.A. and Oosterhoff, L.J., Molecular Physics **8** (1964) 319.
5) Terwiel, R.H. and Mazur, P., Physica **30** (1964) 625.
6) Dirac, P.A.M., Proc. Roy. Soc. London **A167** (1938) 148.
7) Wheeler, J.A. and Feynman, R.P., Rev. of Mod. Phys. **17** (1945) 157.
8) Bedeaux, D. and Mazur, P., Physica **67** (1973) 23.
9) Bedeaux, D. and Vlieger, J., Physica **73** (1974) 287.
10) Nijboer, B.R.A. and De Wette, F.W., Physica **23** (1957) 309.
11) Sipe, J.E. and Van Kranendonk, J., Phys. Rev., to be published.
12) Agranovich,V.M. and Ginzburg, V.L., Spatial Dispersion in Crystal Optics and the Theory of Excitons, Interscience (London, 1966).

II. FIRST-ORDER SPATIAL DISPERSION AND OPTICAL ACTIVITY

Synopsis

The general formal expression for the wavevector- and frequency-dependent dielectric susceptibility tensor of a simple molecular crystal, derived in paper I, is applied to the case of a Bravais lattice with gyrotropic molecules. The dielectric susceptibility tensor is calculated with first-order spatial dispersion and from this an expression for the gyration tensor is derived. As an example the optical rotatory power is calculated for light propagating along the optical axis of a gyrotropic tetragonal crystal.

1. *Introduction.* In our previous paper[1]), in the following denoted by I, we have derived a general expression for the wave vector- en frequency-dependent dielectric susceptibility tensor of a simple perfect lattice of fixed nonpolar molecules with given polarizability tensor. The general expression was applied to a lattice of point dipoles. The electric dipole moment can be considered as the first term of a multipole expansion of the continuous dipole distribution of the molecules.

In the present paper we shall extend the application of the formal theory of I with the second term of this expansion (electric quadrupole moment and magnetic dipole moment), which means that the ratio d/l of the linear dimensions of the molecule d and the length l over which the fields change appreciably, is not neglected but taken into account to first order (section 2).

In section 3 we derive the expression for the dielectric susceptibility tensor for the point dipole–quadrupole lattice. This tensor has the same form as the susceptibility of the point-dipole lattice, derived in I, but with the dipole polarizability $\boldsymbol{\alpha}^0$ now replaced by a structure- and $\boldsymbol{k}$-dependent tensor. The appearing lattice sums are transformed into rapidly converging sums. This susceptibility tensor is expanded in section 4 up to first order in dk. The zeroth-order term of this expansion is not exactly equal to the zeroth-order susceptibility calculated in I for the point-dipole lattice. The difference is that α^0 has still a correction which is of order d^2/a^2 where a is a length of order of the lattice constants. From the first-order term we derive a general expression for the gyration tensor of optically active molecular crystals.

In section 5 we use the expression for the gyration tensor to calculate the optical rotatory power ϕ for some special cases and compare ϕ with the results of Hoek[2]), Maaskant and Oosterhoff[3]) and Terwiel and Mazur[4]) for fluids. In the isotropic case the results are the same apart from statistical effects which have been neglected in the present paper: ϕ is proportional to $\frac{1}{3}(n_0^2 + 2)$, where n_0 is the zeroth-order refractive index. In general we have additional terms for crystals. We find for example in the case of a tetragonal crystal that for light propagating along the optical axis the expression for ϕ contains not only a term proportional to $\frac{1}{3}(n_\perp^2 + 2)$, but also a term proportional to $\frac{1}{3}(n_\perp^2 + 2)(n_\perp^2 - 1)$, where $n_\perp$ is the zeroth-order refractive index in that direction. Finally we give a discussion in section 6.

2. *The multipole expansion.* In paper I we have derived a general expression for the wavevector- and frequency-dependent dielectric susceptibility tensor $\chi(\boldsymbol{k}, \omega)$ of an infinite molecular crystal in which lattice vibrations are neglected. In our model the crystal consists of identical, equally oriented molecules with given molecular polarizability, fixed at the lattice points of a Bravais lattice. If we define the external susceptibility $\chi^{\text{ext}}(\boldsymbol{k}, \omega)$ by

$$\boldsymbol{P}(\boldsymbol{k}, \omega) = \chi^{\text{ext}}(\boldsymbol{k}, \omega) \cdot \boldsymbol{E}^{\text{ext}}(\boldsymbol{k}, \omega), \tag{2.1}$$

in which $\boldsymbol{P}(\boldsymbol{k}, \omega)$ is the polarization and $\boldsymbol{E}^{\text{ext}}(\boldsymbol{k}, \omega)$ is the external electric field, we can express the susceptibility $\chi(\boldsymbol{k}, \omega)$ in terms of $\chi^{\text{ext}}(\boldsymbol{k}, \omega)$ by the formula

$$\chi(\boldsymbol{k}, \omega) = \chi^{\text{ext}}(\boldsymbol{k}, \omega) \cdot [1 - \mathsf{F}(\boldsymbol{k}, \omega) \cdot \chi^{\text{ext}}(\boldsymbol{k}, \omega)]^{-1}. \tag{2.2}$$

$\mathsf{F}(\boldsymbol{k}, \omega)$ is the retarded vacuum propagator of the electromagnetic field and is given by

$$\mathsf{F}(\boldsymbol{k}, \omega) = \left(\mathscr{P} \frac{1}{k^2 - \omega^2} - \tfrac{1}{2} \mathrm{i} \pi k^{-1} [\delta(k + \omega) - \delta(k - \omega)] \right) (\boldsymbol{k}\boldsymbol{k} - \omega^2). \tag{2.3}$$

We have chosen units such that the velocity of light is unity. We note that all the information about, *e.g.*, the refractive indices and the optical activity, characterized by the gyration tensor, is contained in the wavevector- and frequency-dependent dielectric-susceptibility tensor $\chi(\boldsymbol{k}, \omega)$[5]). We have derived in I that for our model

$$\chi^{\text{ext}}(\boldsymbol{k}, \omega) = [(1 + \mathsf{H}_\sigma)^{-1} \cdot \boldsymbol{\alpha}]^0 (\boldsymbol{k}, \omega). \tag{2.4}$$

The expression on the r.h.s. of eq. (2.4) is an operator product, the general form of which is

$$(AB)^{\lambda}(\boldsymbol{k}) = \sum_{\mu} A^{\mu}(\boldsymbol{k})\, B^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}), \tag{2.5}$$

so that

$$(AB)^{0}(\boldsymbol{k}) = \sum_{\mu} A^{\mu}(\boldsymbol{k})\, B^{-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}), \tag{2.6}$$

see appendix A of I. The sums in eqs. (2.5) and (2.6) run over all lattice points $\boldsymbol{k}_{\mu}$ of the reciprocal lattice. The operator $\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}, \omega)$ in eq. (2.4) is related to the molecular polarizability as follows[‡]:

$$\boldsymbol{\alpha}^{\lambda}(\boldsymbol{k}, \omega) = (2\pi)^{3}\, \varrho \boldsymbol{\sigma}(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{k}_{\lambda}; \omega), \tag{2.7}$$

where ϱ is the density and

$$\boldsymbol{\sigma}(\boldsymbol{k}, \boldsymbol{k}'; \omega) = (2\pi)^{-3} \int \boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}'; \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'}\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'. \tag{2.8}$$

Here $\boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ is the molecular polarizability tensor, relating the dipole-moment distribution of a molecule (say the ith at lattice point $\boldsymbol{R}_i$) linearly to the effective field acting on that molecule:

$$\boldsymbol{p}^{i}(\boldsymbol{R}, \omega) = \int \boldsymbol{\sigma}(\boldsymbol{R} - \boldsymbol{R}_i, \boldsymbol{R}' - \boldsymbol{R}_i; \omega) \cdot \boldsymbol{E}^{\mathrm{eff}}(\boldsymbol{R}', \omega)\, \mathrm{d}\boldsymbol{R}'. \tag{2.9}$$

Similarly

$$\mathsf{H}^{\lambda}_{\sigma}(\boldsymbol{k}, \omega) = (2\pi)^{3}\, \varrho \mathsf{h}_{\sigma}(\boldsymbol{k}, \boldsymbol{k} - \boldsymbol{k}_{\lambda}; \omega), \tag{2.10}$$

where $\mathsf{h}_{\sigma}(\boldsymbol{k}, \boldsymbol{k}'; \omega)$ is the Fourier transform of $\mathsf{h}_{\sigma}(\boldsymbol{R}, \boldsymbol{R}'; \omega)$ defined by

$$\mathsf{h}_{\sigma}(\boldsymbol{R}, \boldsymbol{R}'; \omega) = \int \mathrm{d}\boldsymbol{R}'' \boldsymbol{\sigma}(\boldsymbol{R}, \boldsymbol{R}''; \omega) \cdot \mathsf{H}_{l=0}(\boldsymbol{R}'', \boldsymbol{R}'; \omega). \tag{2.11}$$

Here

$$\mathsf{H}_{l}(\boldsymbol{R}, \boldsymbol{R}'; \omega) = \begin{cases} \mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) & \text{for} \quad \boldsymbol{R}' \notin g_{l}, \\ \tfrac{1}{2}\left[\mathsf{F}(\boldsymbol{R} - \boldsymbol{R}', \omega) - \mathsf{F}^{\dagger}(\boldsymbol{R} - \boldsymbol{R}', \omega)\right] & \text{for} \quad \boldsymbol{R}' \in g_{l}, \end{cases} \tag{2.12}$$

in which g_l is a region in space containing molecule i and no others.

In principle the susceptibility is known if one knows the lattice, the form of the regions g_l and the molecular polarizability $\boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$. We shall now apply a multipole expansion[3]) to eq. (2.9) and write for the polarizability up to first order (in cartesian components with summation convention):

$$\sigma_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \alpha^0_{\alpha\beta}(\omega)\, \delta(\boldsymbol{r})\, \delta(\boldsymbol{r} - \boldsymbol{r}') - \beta'_{\alpha\beta\gamma}(\omega)\, \nabla_\gamma\, [\delta(\boldsymbol{r})\, \delta(\boldsymbol{r} - \boldsymbol{r}')] - \beta_{\alpha\beta\gamma}(\omega)\, \nabla'_\gamma\, [\delta(\boldsymbol{r})\, \delta(\boldsymbol{r} - \boldsymbol{r}')], \tag{2.13}$$

with

$$\alpha^0_{\alpha\beta}(\omega) \equiv \int \sigma_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}'; \omega)\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}', \tag{2.14}$$

$$\beta_{\alpha\beta\gamma}(\omega) \equiv \int \sigma_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}'; \omega)\, r'_\gamma\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}', \tag{2.15}$$

$$\beta'_{\alpha\beta\gamma}(\omega) \equiv \int \sigma_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}'; \omega)\, r_\gamma\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \tag{2.16}$$

and

$$\nabla_\gamma \equiv \left(\frac{\partial}{\partial \boldsymbol{r}}\right)_\gamma; \qquad \nabla'_\gamma \equiv \left(\frac{\partial}{\partial \boldsymbol{r}'}\right)_\gamma. \tag{2.17}$$

The first two moments of the continuous dipole distribution of molecule i then are with eqs. (2.9) and (2.13):

$$p^i_\alpha(\omega) \equiv \int p^i_\alpha(\boldsymbol{R}, \omega)\, \mathrm{d}\boldsymbol{R} = \alpha^0_{\alpha\beta}(\omega)\, E^{\mathrm{eff}}_\beta(\boldsymbol{R}_i, \omega) + \beta_{\alpha\beta\gamma}(\omega)\, \nabla_\gamma E^{\mathrm{eff}}_\beta(\boldsymbol{R}_i, \omega), \tag{2.18}$$

which is the electric dipole moment, and

$$q^i_{\alpha\beta}(\omega) \equiv \int p^i_\alpha(\boldsymbol{R}, \omega)\, (\boldsymbol{R} - \boldsymbol{R}_i)_\beta\, \mathrm{d}\boldsymbol{R} = \beta'_{\alpha\beta\gamma}(\omega)\, E^{\mathrm{eff}}_\gamma(\boldsymbol{R}_i, \omega), \tag{2.19}$$

which is a combination of the electric quadrupole moment and the magnetic dipole moment. Usually these molecular eqs. (2.18) and (2.19) are the starting point for calculations on optical activity[2-4]). We can, however, immediately use eq. (2.13), which becomes by Fourier transformation:

$$\sigma_{\alpha\beta}(\boldsymbol{k}, \boldsymbol{k}'; \omega) = (2\pi)^{-3}\, [\alpha^0_{\alpha\beta}(\omega) - \mathrm{i}\beta'_{\alpha\beta\gamma}(\omega)\, k_\gamma + \mathrm{i}\beta_{\alpha\beta\gamma}(\omega)\, k'_\gamma], \tag{2.20}$$

in the general expression (2.2) with (2.4) for the dielectric susceptibility. In the rest of this paper we shall restrict ourselves to a molecular polarizability of the form (2.20). This implies of course that the variation of the effective electric field over the diameter of a molecule is only taken into account up to first order in $\boldsymbol{k}'$ (*i.e.* the first spatial derivative of this field). This is certainly appropriate for the variation of the external electric field, it is less appropriate for the fields of the neighbouring particles. In the derivation of eq. (2.4) in paper I the only assumption is that the external electric field varies slowly over the molecular diameter. We shall therefore be able to calculate the corrections due to the linear terms in $\boldsymbol{k}$

and k' in eq. (2.20) to the zeroth-order result for the susceptibility $[\chi(k = 0)]$. It will turn out that in extreme cases (β and β' large) this correction is not negligeable. We shall come back to this point in the discussion (section 6) where we also shall give an estimate of the order of magnitude of corrections due to higher-order terms in the multipole expansion.

The multipole expansion offers the advantage that we can choose for g_i small spheres of radius $b < d$ around the centres of the molecules, so that for each i:

$$\mathsf{H}_i(R, R'; \omega) \equiv \mathsf{H}(R - R', \omega) \equiv \begin{cases} \mathsf{F}(R - R', \omega) & \text{for} \quad |R - R'| > b, \\ \frac{1}{2}[\mathsf{F}(R - R', \omega) - \mathsf{F}^\dagger(R - R', \omega)] & \text{for} \quad |R - R'| \leqslant b. \end{cases} \tag{2.21}$$

Hence

$$\mathsf{h}_\sigma(R, R'; \omega) = \int \mathrm{d}R''\sigma(R, R''; \omega) \cdot \mathsf{H}(R'' - R', \omega), \tag{2.22}$$

so that

$$\mathsf{H}_\sigma^\lambda(k, \omega) = \boldsymbol{\alpha}^\lambda(k, \omega) \cdot \mathsf{H}(k - k_\lambda, \omega). \tag{2.23}$$

As a consequence the expression (2.4) for the external susceptibility becomes:

$$\chi^{\text{ext}}(k, \omega) = [(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1} \cdot \boldsymbol{\alpha}]^0(k, \omega). \tag{2.24}$$

With expression (2.21) for H and with (2.7) and (2.20) for $\boldsymbol{\alpha}$ we can calculate the dielectric susceptibility, which will be done in the next section.

3. *The dielectric susceptibility of a point dipole and quadrupole lattice.* Now we use the molecular polarizability tensor given by eq. (2.20) so that, using eq. (2.7), the operator $\boldsymbol{\alpha}$ in eq. (2.24) is given by

$$\alpha_{\alpha\beta}^\lambda(k, \omega) = \varrho\alpha_{\alpha\beta}^0(\omega) - \mathrm{i}\varrho\beta'_{\alpha\beta\gamma}(\omega)\,k_\gamma + \mathrm{i}\varrho\beta_{\alpha\beta\gamma}(\omega)\,(k - k_\lambda)_\gamma, \tag{3.1}$$

or in tensor notation:

$$\boldsymbol{\alpha}^\lambda(k, \omega) = \varrho\boldsymbol{\alpha}^0(\omega) - \mathrm{i}\varrho\boldsymbol{\beta}'(\omega) \cdot k + \mathrm{i}\varrho\boldsymbol{\beta}(\omega) \cdot (k - k_\lambda). \tag{3.2}$$

With this expression for $\boldsymbol{\alpha}$ we can calculate exactly the corresponding dielectric susceptibility. First we shall calculate the inverse operator $(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}$ in eq. (2.24). Defining

$$\mathsf{f}^\lambda(k, \omega) \equiv [(1 + \boldsymbol{\alpha} \cdot \mathsf{H})^{-1}]^\lambda(k, \omega), \tag{3.3}$$

we obtain with eqs. (2.6) and (2.24):

$$\chi^{\mathrm{ext}}(\boldsymbol{k}, \omega) = \sum_{\lambda} \mathsf{f}^{\lambda}(\boldsymbol{k}, \omega) \cdot \boldsymbol{\alpha}^{-\lambda}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega). \tag{3.4}$$

From def. (3.3) and eq. (2.5) then follows

$$\sum_{\mu} \mathsf{f}^{\mu}(\boldsymbol{k}, \omega) \cdot [\delta_{\lambda,\mu} + (\boldsymbol{\alpha} \cdot \mathsf{H})^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}, \omega)] = \delta_{\lambda,0}. \tag{3.5}$$

Since we have (see appendix A.3 of I)

$$\mathsf{H}^{\lambda}(\boldsymbol{k}, \omega) = \mathsf{H}(\boldsymbol{k}, \omega)\, \delta_{\lambda,0}, \tag{3.6}$$

eq. (3.5) can be written as

$$\mathsf{f}^{\lambda}(\boldsymbol{k}, \omega) + \sum_{\mu} \mathsf{f}^{\mu}(\boldsymbol{k}, \omega) \cdot \boldsymbol{\alpha}^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}, \omega) \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) = \delta_{\lambda,0}. \tag{3.7}$$

From eq. (3.2) follows that

$$\begin{aligned} \boldsymbol{\alpha}^{\lambda-\mu}(\boldsymbol{k} - \boldsymbol{k}_{\mu}, \omega) &= \varrho\boldsymbol{\alpha}^{0}(\omega) - \mathrm{i}\varrho\boldsymbol{\beta}'(\omega) \cdot (\boldsymbol{k} - \boldsymbol{k}_{\mu}) + \mathrm{i}\varrho\boldsymbol{\beta}(\omega) \cdot (\boldsymbol{k} - \boldsymbol{k}_{\lambda}) \\ &= \mathsf{a}(\boldsymbol{k}, \omega) + \mathrm{i}\varrho\boldsymbol{\beta}'(\omega) \cdot \boldsymbol{k}_{\mu} - \mathrm{i}\varrho\boldsymbol{\beta}(\omega) \cdot \boldsymbol{k}_{\lambda}, \end{aligned} \tag{3.8}$$

where $\mathsf{a}(\boldsymbol{k}, \omega)$ is defined as

$$\mathsf{a}(\boldsymbol{k}, \omega) \equiv \varrho\boldsymbol{\alpha}^{0}(\omega) - \mathrm{i}\varrho\boldsymbol{\beta}'(\omega) \cdot \boldsymbol{k} + \mathrm{i}\varrho\boldsymbol{\beta}(\omega) \cdot \boldsymbol{k}. \tag{3.9}$$

Inserting eq. (3.8) into eq. (3.7) we obtain

$$\begin{aligned} &\mathsf{f}^{\lambda}(\boldsymbol{k}, \omega) + \mathsf{f}(\boldsymbol{k}, \omega) \cdot \mathsf{a}(\boldsymbol{k}, \omega) \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) + \mathsf{g}(\boldsymbol{k}, \omega) \cdot \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) \\ &\quad - \mathrm{i}\mathsf{f}(\boldsymbol{k}, \omega) \cdot \varrho\boldsymbol{\beta}(\omega) : \boldsymbol{k}_{\lambda}\mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) = \delta_{\lambda,0}, \end{aligned} \tag{3.10}$$

in which $\mathsf{f}(\boldsymbol{k}, \omega)$ and $\mathsf{g}(\boldsymbol{k}, \omega)$ are defined as

$$\mathsf{f}(\boldsymbol{k}, \omega) \equiv \sum_{\lambda} \mathsf{f}^{\lambda}(\boldsymbol{k}, \omega) \tag{3.11}$$

and

$$\mathsf{g}(\boldsymbol{k}, \omega) \equiv \mathrm{i} \sum_{\lambda} \mathsf{f}^{\lambda}(\boldsymbol{k}, \omega) \cdot \varrho\boldsymbol{\beta}'(\omega) \cdot \boldsymbol{k}_{\lambda}. \tag{3.12}$$

The quantity f can be obtained by summing eq. (3.10) over λ, and g from eq. (3.10) by multiplying this equation on the right with $\mathrm{i}\varrho\boldsymbol{\beta}'(\omega) \cdot \boldsymbol{k}_{\lambda}$ and then summing over λ. This yields:

$$\mathsf{f} \cdot (1 + \mathsf{a} \cdot \mathsf{A} - \mathsf{D}) + \mathsf{g} \cdot \mathsf{A} = 1 \tag{3.13}$$

and

$$\mathsf{f}\cdot(\mathsf{a}\cdot\mathsf{D}' + \mathsf{E}) + \mathsf{g}\cdot(1 + \mathsf{D}') = 0. \tag{3.14}$$

All quantities depend on $\boldsymbol{k}$ and ω, which will not always be written explicitly. The quantities A, D, D′ and E are defined as

$$\mathsf{A}(\boldsymbol{k}, \omega) \equiv \sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega), \tag{3.15}$$

$$\mathsf{D}(\boldsymbol{k}, \omega) \equiv \mathrm{i}\sum_{\lambda} \varrho\boldsymbol{\beta}(\omega) : \boldsymbol{k}_{\lambda}\mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega), \tag{3.16}$$

$$\mathsf{D}'(\boldsymbol{k}, \omega) \equiv \mathrm{i}\sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)\cdot\varrho\boldsymbol{\beta}'(\omega)\cdot\boldsymbol{k}_{\lambda}, \tag{3.17}$$

$$\mathsf{E}(\boldsymbol{k}, \omega) \equiv \sum_{\lambda} \varrho\boldsymbol{\beta}(\omega) : \boldsymbol{k}_{\lambda}\mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)\cdot\varrho\boldsymbol{\beta}'(\omega)\cdot\boldsymbol{k}_{\lambda}. \tag{3.18}$$

From eqs. (3.13) and (3.14) we can solve f and g and so $\mathsf{f}^{\lambda}(\boldsymbol{k}, \omega)$ is known from eq. (3.10). Now we are interested in the susceptibility, given by eq. (3.4). From eqs. (3.2) and (3.9) follows that

$$\boldsymbol{\alpha}^{-\lambda}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) = \mathsf{a}(\boldsymbol{k}, \omega) + \mathrm{i}\varrho\boldsymbol{\beta}'(\omega)\cdot\boldsymbol{k}_{\lambda}, \tag{3.19}$$

so that with eq. (3.4) and defs. (3.11) and (3.12):

$$\boldsymbol{\chi}^{\mathrm{ext}}(\boldsymbol{k}, \omega) = \mathsf{f}(\boldsymbol{k}, \omega)\cdot\mathsf{a}(\boldsymbol{k}, \omega) + \mathsf{g}(\boldsymbol{k}, \omega). \tag{3.20}$$

From eqs. (3.13) and (3.14) we obtain

$$\mathsf{g} = -\mathsf{f}\cdot(\mathsf{a}\cdot\mathsf{D}' + \mathsf{E})\cdot(1 + \mathsf{D}')^{-1} \tag{3.21}$$

and

$$\mathsf{f} = [1 + \mathsf{a}\cdot\mathsf{A} - \mathsf{D} - (\mathsf{a}\cdot\mathsf{D}' + \mathsf{E})\cdot(1 + \mathsf{D}')^{-1}\cdot\mathsf{A}]^{-1}. \tag{3.22}$$

Using eqs. (3.20)–(3.22) we find after some calculations

$$\boldsymbol{\chi}^{\mathrm{ext}} = [(1 + \mathsf{D}')\cdot(\mathsf{a} - \mathsf{E})^{-1}\cdot(1 - \mathsf{D}) + \mathsf{A}]^{-1}. \tag{3.23}$$

With eq. (2.2) we finally obtain for the dielectric susceptibility tensor:

$$\begin{aligned}\boldsymbol{\chi}(\boldsymbol{k}, \omega) = \{&\mathsf{A}(\boldsymbol{k}, \omega) - \mathsf{F}(\boldsymbol{k}, \omega)\\ &+ [1 + \mathsf{D}'(\boldsymbol{k}, \omega)]\cdot[\mathsf{a}(\boldsymbol{k}, \omega) - \mathsf{E}(\boldsymbol{k}, \omega)]^{-1}\cdot[1 - \mathsf{D}(\boldsymbol{k}, \omega)]\}^{-1}.\end{aligned} \tag{3.24}$$

In I we have introduced a quantity $\mathsf{M}(\boldsymbol{k}, \omega)$, defined as

$$\mathsf{M}(\boldsymbol{k}, \omega) \equiv \varrho^{-1} \sum_{l} \mathsf{F}(\boldsymbol{R}_l, \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_l} - \lim_{d \to 0} \int_{\varepsilon(d)} \mathsf{F}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$+ \tfrac{1}{2}\varrho^{-1} [\mathsf{F}(\boldsymbol{R}, \omega) - \mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)]_{\boldsymbol{R}=0}, \tag{3.25}$$

where $\sum_l'$ denotes a sum over all lattice points except an arbitrarily chosen origin $\boldsymbol{R}_l = 0$, and where in the integral a sphere of radius d around the origin is excluded. With this definition and with definitions (3.15) and (2.21) we have

$$\mathsf{A}(\boldsymbol{k}, \omega) = \mathsf{M}(\boldsymbol{k}, \omega) + \mathsf{F}(\boldsymbol{k}, \omega) - \tfrac{1}{3}. \tag{3.26}$$

For a more detailed derivation see I where $\mathsf{M}(\boldsymbol{k}, \omega)$ is expressed in terms of rapidly converging lattice sums [*cf.* eqs. (I.3.27)–(I.3.29)]. Using eq. (3.26) the expression (3.24) for $\chi(\boldsymbol{k}, \omega)$ becomes:

$$\chi(\boldsymbol{k}, \omega) = \{\mathsf{I} + \mathscr{A}(\boldsymbol{k}, \omega) \cdot [\mathsf{M}(\boldsymbol{k}, \omega) - \tfrac{1}{3}]\}^{-1} \cdot \mathscr{A}(\boldsymbol{k}, \omega), \tag{3.27}$$

with

$$\mathscr{A}(\boldsymbol{k}, \omega) \equiv [\mathsf{I} - \mathsf{D}(\boldsymbol{k}, \omega)]^{-1} \cdot [\mathsf{a}(\boldsymbol{k}, \omega) - \mathsf{E}(\boldsymbol{k}, \omega)] \cdot [\mathsf{I} + \mathsf{D}'(\boldsymbol{k}, \omega)]^{-1}. \tag{3.28}$$

This expression for $\chi(\boldsymbol{k}, \omega)$ has the same form as the susceptibility for a simple point-dipole lattice as found in I. The only difference is that $\varrho\alpha^0(\omega)$ is replaced here by the more complicated expression $\mathscr{A}(\boldsymbol{k}, \omega)$ which is depending on the structure of the lattice.

The tensors $\mathsf{D}(\boldsymbol{k}, \omega)$, $\mathsf{D}'(\boldsymbol{k}, \omega)$ and $\mathsf{E}(\boldsymbol{k}, \omega)$ defined by eqs. (3.16)–(3.18) contain the lattice sums

$$\mathsf{B}(\boldsymbol{k}, \omega) \equiv \sum_{\lambda} \boldsymbol{k}_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega) \tag{3.29}$$

and

$$\mathsf{C}(\boldsymbol{k}, \omega) \equiv \sum_{\lambda} \boldsymbol{k}_{\lambda} \boldsymbol{k}_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega). \tag{3.30}$$

We can transform these sums into rapidly converging lattice sums in a similar way as we did with the sum $\sum_{\lambda} \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega)$ in I. Here we shall give the results and leave the details of the calculations to the appendix. For the sum $\mathsf{B}(\boldsymbol{k}, \omega)$ we find:

$$\mathsf{B}(\boldsymbol{k}, \omega) = \boldsymbol{k}\mathsf{M}(\boldsymbol{k}, \omega) - \tfrac{1}{3}\boldsymbol{k}\mathsf{U} + \mathrm{i}\mathsf{N}(\boldsymbol{k}, \omega), \tag{3.31}$$

where U is the second-order unit tensor and where

$$\mathrm{N}(\boldsymbol{k},\omega) = -\varrho^{-1}\sum_{\lambda}{}' \nabla(\nabla\nabla+\omega^2)\left[\operatorname{erfc}\left(\pi^{\frac{1}{2}}\frac{R_\lambda}{a}\right)\frac{\cos\omega R_\lambda}{4\pi R_\lambda}\right]\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda}$$

$$+\,\mathrm{i}\sum_{\lambda}{}'(\boldsymbol{k}-\boldsymbol{k}_\lambda)\frac{(\boldsymbol{k}-\boldsymbol{k}_\lambda)(\boldsymbol{k}-\boldsymbol{k}_\lambda)-\omega^2}{|\boldsymbol{k}-\boldsymbol{k}_\lambda|^2-\omega^2}\mathscr{L}(|\boldsymbol{k}-\boldsymbol{k}_\lambda|,\omega)$$

$$+\,\mathrm{i}\boldsymbol{k}\frac{\boldsymbol{k}\boldsymbol{k}-\omega^2}{k^2-\omega^2}[\mathscr{L}(k,\omega)-1], \tag{3.32}$$

in which

$$\mathscr{L}(k,\omega) \equiv \frac{k-\omega}{2k}\mathrm{e}^{-a^2(k+\omega)^2/4\pi}+\frac{k+\omega}{2k}\mathrm{e}^{-a^2(k-\omega)^2/4\pi}, \tag{3.33}$$

For the sum C $(\boldsymbol{k},\omega)$ we find (in components):

$$C_{ijkl}(\boldsymbol{k},\omega) = k_ik_jM_{kl}(\boldsymbol{k},\omega)-\tfrac{1}{3}k_ik_j\delta_{kl}+\mathrm{i}k_iN_{jkl}(\boldsymbol{k},\omega)$$

$$+\,\mathrm{i}k_jN_{ikl}(\boldsymbol{k},\omega)+O_{ijkl}(\boldsymbol{k},\omega), \tag{3.34}$$

in which

$$O_{ijkl}(\boldsymbol{k},\omega) = \varrho^{-1}\sum_{\lambda}{}'\nabla_i\nabla_j(\nabla_k\nabla_l+\omega^2\delta_{kl})\left[\operatorname{erfc}\left(\pi^{\frac{1}{2}}\frac{R_\lambda}{a}\right)\frac{\cos\omega R_\lambda}{4\pi R_\lambda}\right]\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda}$$

$$+\sum_{\lambda}{}'(\boldsymbol{k}-\boldsymbol{k}_\lambda)_i(\boldsymbol{k}-\boldsymbol{k}_\lambda)_j\frac{(\boldsymbol{k}-\boldsymbol{k}_\lambda)_k(\boldsymbol{k}-\boldsymbol{k}_\lambda)_l-\omega^2\delta_{kl}}{|\boldsymbol{k}-\boldsymbol{k}_\lambda|^2-\omega^2}$$

$$\times\,\mathscr{L}(|\boldsymbol{k}-\boldsymbol{k}_\lambda|,\omega)+k_ik_j\frac{k_kk_l-\omega^2\delta_{kl}}{k^2-\omega^2}[\mathscr{L}(k,\omega)-1]$$

$$-\frac{1}{\varrho a^5}\left[\left(\tfrac{2}{5}\pi+\tfrac{2}{3}a^2\omega^2+\frac{1}{6\pi}a^4\omega^4\right)(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\right.$$

$$\left.-\left(\tfrac{1}{3}a^2\omega^2+\frac{1}{2\pi}a^4\omega^4\right)\delta_{ij}\delta_{kl}\right]. \tag{3.35}$$

We have denoted the lattice points by $\boldsymbol{R}_\lambda$ in order to avoid confusion with the suffix *i*. The expressions (I.3.27), (3.32) and (3.35) for the quantities M $(\boldsymbol{k},\omega)$, N $(\boldsymbol{k},\omega)$ and O $(\boldsymbol{k},\omega)$ do not depend on the parameter *a* as can be checked by differentiation. This parameter *a* serves as a "cutoff" parameter and must be chosen of order of the lattice constants to ensure rapid convergence of all lattice sums. We can choose, *e.g.*, $a^3 = \varrho^{-1}$.

Because of the inversion symmetry of the Bravais lattice and the reciprocal lattice, $\mathsf{M}(\boldsymbol{k}, \omega)$ and $\mathsf{C}(\boldsymbol{k}, \omega)$ are even functions of $\boldsymbol{k}$ whereas $\mathsf{B}(\boldsymbol{k}, \omega)$ is an odd function of $\boldsymbol{k}$. These quantities are all even functions of ω. If we make an expansion of these tensors in powers of ak and $a\omega$, the main term of $\mathsf{M}(\boldsymbol{k}, \omega)$ is of order 1, $\mathsf{B}(\boldsymbol{k}, \omega)$ is of order k and $a^2\mathsf{C}(\boldsymbol{k}, \omega)$ is of order 1, all with corrections of second and higher orders in ak and $a\omega$. Furthermore we know that the components of $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ are of order d with respect to the components of $\boldsymbol{\alpha}^0$. For the quantities $\mathsf{M}(\boldsymbol{k}, \omega)$, $\mathsf{D}(\boldsymbol{k}, \omega)$, $\mathsf{D}'(\boldsymbol{k}, \omega)$ and $\mathsf{E}(\boldsymbol{k}, \omega)$, appearing in expression (3.27) for the susceptibility, this means that $\mathsf{M}(\boldsymbol{k}, \omega)$ is of order 1, $\mathsf{D}(\boldsymbol{k}, \omega)$ and $\mathsf{D}'(\boldsymbol{k}, \omega)$ are of order dk and $\mathsf{E}(\boldsymbol{k}, \omega)$ is of order d^2/a^2 (to the extent to which $\varrho\boldsymbol{\alpha}^0$ is of order 1), all with corrections of at least second order in ak and $a\omega$ relative to the leading term. We shall restrict ourselves to optical frequencies and small values of $\boldsymbol{k}$, so that we can neglect the terms of order a^2k^2 and $a^2\omega^2$. We shall do this in the next section and investigate the dielectric susceptibility to first order in k (first-order spatial dispersion).

4. *First-order spatial dispersion and optical activity*. For an expansion of the dielectric susceptibility [eq. (3.27)] up to first order in k we only need the zeroth order of $\mathsf{M}(\boldsymbol{k}, \omega)$ and $\mathsf{E}(\boldsymbol{k}, \omega)$, and the first order of $\mathsf{D}(\boldsymbol{k}, \omega)$ and $\mathsf{D}'(\boldsymbol{k}, \omega)$, which we shall call respectively: $\mathsf{M}^{(0)}$, $\mathsf{E}^{(0)}(\omega)$, $\mathsf{D}^{(1)}(\boldsymbol{k}, \omega)$ and $\mathsf{D}'^{(1)}(\boldsymbol{k}, \omega)$. If we write

$$\chi(\boldsymbol{k}, \omega) = \chi^{(0)}(\omega) + \chi^{(1)}(\boldsymbol{k}, \omega) + \cdots \tag{4.1}$$

and

$$\mathscr{A}(\boldsymbol{k}, \omega) = \mathscr{A}^{(0)}(\omega) + \mathscr{A}^{(1)}(\boldsymbol{k}, \omega) + \cdots, \tag{4.2}$$

then it is easily derived from eq. (3.27) that to first order:

$$\chi^{(0)}(\omega) = [1 + \mathscr{A}^{(0)}(\omega) \cdot (\mathsf{M}^{(0)} - \tfrac{1}{3})]^{-1} \cdot \mathscr{A}^{(0)}(\omega) \tag{4.3}$$

and

$$\chi^{(1)}(\boldsymbol{k}, \omega) = [1 + \mathscr{A}^{(0)}(\omega) \cdot (\mathsf{M}^{(0)} - \tfrac{1}{3})]^{-1} \cdot \mathscr{A}^{(1)}(\boldsymbol{k}, \omega) \cdot [1 + (\mathsf{M}^{(0)} - \tfrac{1}{3}) \cdot \mathscr{A}^{(0)}(\omega)]^{-1}. \tag{4.4}$$

$\chi^{(1)}(\boldsymbol{k}, \omega)$ and $\mathscr{A}^{(1)}(\boldsymbol{k}, \omega)$ are linear in $\boldsymbol{k}$. From eq. (3.28) we find for the expansion (4.2) of $\mathscr{A}(\boldsymbol{k}, \omega)$:

$$\mathscr{A}^{(0)}(\omega) = \mathsf{a}^{(0)}(\omega) - \mathsf{E}^{(0)}(\omega) \tag{4.5}$$

and

$$\mathscr{A}^{(1)}(\boldsymbol{k}, \omega) = \mathsf{D}^{(1)}(\boldsymbol{k}, \omega) \cdot [\mathsf{a}^{(0)}(\omega) - \mathsf{E}^{(0)}(\omega)] - [\mathsf{a}^{(0)}(\omega) - \mathsf{E}^{(0)}(\omega)] \cdot \mathsf{D}'^{(1)}(\boldsymbol{k}, \omega) + \mathsf{a}^{(1)}(\boldsymbol{k}, \omega). \tag{4.6}$$

From eq. (3.9) it follows that

$$\mathsf{a}^{(0)}(\omega) = \varrho\boldsymbol{\alpha}^{(0)}(\omega) \tag{4.7}$$

and

$$\mathsf{a}^{(1)}(\boldsymbol{k},\omega) = -\mathrm{i}\varrho\boldsymbol{\beta}'(\omega)\cdot\boldsymbol{k} + \mathrm{i}\varrho\boldsymbol{\beta}(\omega)\cdot\boldsymbol{k}. \tag{4.8}$$

We shall successively treat the susceptibility without spatial dispersion in subsection 4.1 and with first-order spatial dispersion in subsection 4.2.

4.1. Dielectric susceptibility without spatial dispersion. The dielectric susceptibility in zeroth order in k is given by eqs. (4.3), (4.5) and (4.7). Inserting eqs. (4.5) and (4.7) into eq. (4.3) we obtain

$$\boldsymbol{\chi}^{(0)}(\omega) = \{1 + [\varrho\boldsymbol{\alpha}^{(0)}(\omega) - \mathsf{E}^{(0)}(\omega)]\cdot(\mathsf{M}^{(0)} - \tfrac{1}{3})\}^{-1} \cdot [\varrho\boldsymbol{\alpha}^{(0)}(\omega) - \mathsf{E}^{(0)}(\omega)]. \tag{4.9}$$

This equation has the same form as the equations for the susceptibility of a point-dipole lattice [eq. (I.4.5)], but with $\varrho\boldsymbol{\alpha}^0(\omega)$ now replaced by $\varrho\boldsymbol{\alpha}^0(\omega) - \mathsf{E}^{(0)}(\omega)$. From eqs. (3.18) and (3.34) follows that

$$E_{ij}(\boldsymbol{k},\omega) = \varrho^2\beta_{ikl}(\omega)\,\beta'_{mjn}(\omega)\,C_{lnkm}(\boldsymbol{k},\omega). \tag{4.10}$$

From eqs. (2.13)–(2.15) and $\sigma_{ij}(\boldsymbol{r},\boldsymbol{r}';\omega) = \sigma_{ji}(\boldsymbol{r}',\boldsymbol{r};\omega)$[3]) follow $\alpha^0_{ij}(\omega) = \alpha^0_{ji}(\omega)$ and $\beta'_{mjn}(\omega) = \beta_{jmn}(\omega)$. So eq. (4.10) can be written as

$$E_{ij}(\boldsymbol{k},\omega) = \varrho^2\beta_{ikl}(\omega)\,\beta_{jmn}(\omega)\,C_{lnkm}(\boldsymbol{k},\omega). \tag{4.11}$$

Furthermore, from

$$C_{lnkm}(\boldsymbol{k},\omega) = C_{nlkm}(\boldsymbol{k},\omega) = C_{nlmk}(\boldsymbol{k},\omega), \tag{4.12}$$

follows

$$E_{ij}(\boldsymbol{k},\omega) = E_{ji}(\boldsymbol{k},\omega). \tag{4.13}$$

For $\mathsf{E}^{(0)}(\omega)$ in eq. (4.5) we have

$$E^{(0)}_{ij}(\omega) = \varrho^2\beta_{ikl}(\omega)\,\beta_{jmn}(\omega)\,C_{lnkm}(0,0). \tag{4.14}$$

$C_{lnkm}(0,0)$ follows from eqs. (3.33), (3.34) and (3.35). After some calculations we find

$$C_{lnkm}(0,0) = \frac{1}{a^2}\Bigg[(\delta_{ln}\delta_{km} + \delta_{lk}\delta_{nm} + \delta_{nk}\delta_{lm})\,\frac{1}{\varrho a^3}\Bigg(\sum_{\lambda}{}'\,\frac{a^2}{R_\lambda^2}\,f'(R_\lambda) - \frac{2\pi}{5}\Bigg)$$

$$- \frac{1}{\varrho a^3}\sum_{\lambda}{}'\,\frac{a^2}{R_\lambda^2}\,g'(R_\lambda)\,\{\delta_{ln}\hat{R}_k^\lambda\hat{R}_m^\lambda\}^{\mathrm{P}}$$

$$+ \frac{1}{\varrho a^3}\sum_{\lambda}{}'\,\frac{a^2}{R_\lambda^2}\,h'(R_\lambda)\,\hat{R}_l^\lambda\hat{R}_n^\lambda\hat{R}_k^\lambda\hat{R}_m^\lambda + \sum_{\lambda}{}'\,a^2k_\lambda^2a'(k_\lambda)\,\hat{k}_l^\lambda\hat{k}_n^\lambda\hat{k}_k^\lambda\hat{k}_m^\lambda\Bigg], \tag{4.15}$$

where

$$\{\delta_{ln}\hat{R}_k\hat{R}_m\}^{\mathrm{P}} \equiv \delta_{ln}\hat{R}_k\hat{R}_m + \delta_{lk}\hat{R}_n\hat{R}_m + \delta_{nk}\hat{R}_l\hat{R}_m + \delta_{lm}\hat{R}_n\hat{R}_k$$

$$+ \delta_{nm}\hat{R}_l\hat{R}_k + \delta_{km}\hat{R}_l\hat{R}_n. \tag{4.16}$$

$$f'(R) \equiv \frac{3a^3}{4\pi R^3}\,\mathrm{erfc}\left(\pi^{\frac{1}{2}}\frac{R}{a}\right) + \left(\frac{3}{2}\,\frac{a^2}{\pi R^2} + 1\right)\mathrm{e}^{-\pi R^2/a^2}, \tag{4.17}$$

$$g'(R) \equiv \frac{15a^3}{4\pi R^3}\,\mathrm{erfc}\left(\pi^{\frac{1}{2}}\frac{R}{a}\right) + \left(\frac{15}{2}\,\frac{a^2}{\pi R^2} + 5 + 2\,\frac{\pi R^2}{a^2}\right)\mathrm{e}^{-\pi R^2/a^2}, \tag{4.18}$$

$$h'(R) \equiv \frac{105a^3}{4\pi R^3}\,\mathrm{erfc}\left(\pi^{\frac{1}{2}}\frac{R}{a}\right)$$

$$+ \left(\frac{105}{2}\,\frac{a^2}{\pi R^2} + 35 + 14\,\frac{\pi R^2}{a^2} + 4\,\frac{\pi^2R^4}{a^4}\right)\mathrm{e}^{-\pi R^2/a^2} \tag{4.19}$$

and

$$a'(k) \equiv \mathrm{e}^{-a^2k^2/4\pi}. \tag{4.20}$$

Furthermore $\hat{R}_l^\lambda \equiv (\boldsymbol{R}_\lambda)_l/|\boldsymbol{R}_\lambda|$ and $\hat{k}_l^\lambda \equiv (\boldsymbol{k}_\lambda)_l/|\boldsymbol{k}_\lambda|$.

Since for molecular crystals $\boldsymbol{\sigma}(\boldsymbol{r},\boldsymbol{r}';\omega)$ is supposed to be zero for $|\boldsymbol{r}|, |\boldsymbol{r}'| > \frac{1}{2}d$, where d is of order of the linear dimensions of the molecules, we see from eqs. (2.14)-(2.16) that the ratios of the components of $\boldsymbol{\beta}$ and $\boldsymbol{\beta}'$ and the components of $\boldsymbol{\alpha}^0$: β/α^0 and β'/α^0 are of order d. So the quantity $\mathsf{E}^{(0)}(\omega)$ is a correction on $\varrho\boldsymbol{\alpha}^0$ of order $(d^2/a^2)(\varrho\alpha^0)^2$, where a is of order of the intermolecular distance. Since this correction does not need to be small we have derived the explicit expression for $\mathsf{E}^{(0)}(\omega)$. However, for a medium with an optical rotatory power (see next section) of 10 rad/cm or less at a wavelength of say 5×10^{-5} cm (as is the case for most optically active crystals), $\varrho\beta$ is of order 10^{-9} cm, if we suppose that $\varrho\alpha^0$ is of order one. This means that the ratio $(\varrho\beta/a)^2$ (and therefore $E^{(0)}$) is of order 10^{-2} if a is of order 10^{-8} cm. In this case the correction $\mathsf{E}^{(0)}$ in eq. (4.5) may be neglected. This correction is zero in the case that $\beta_{ljk} = b\delta_{ljk}$ where δ_{ljk} is the permutation tensor. (We may think of molecules with random orientation, averaged over all orientations, as is the case in fluids[2-4].) In this case the contribution $\mathsf{E}^{(0)}$ vanishes by the symmetry properties of $\mathsf{C}\,(0, 0)$. For crystals with a higher optical rotatory power, $\mathsf{E}^{(0)}$ is in general not small. In that case we may also expect contributions to $\chi^{(0)}(\omega)$ arising from the higher-order terms in the multipole expansion (2.19) (see also section 6).

4.2. First-order spatial dispersion. Eqs. (4.4)–(4.8) determine the first-order spatial dispersion of the dielectric susceptibility. First we note that from definitions (3.16) and (3.17), the symmetry of $\mathsf{H}\,(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega)$ and $\beta'_{ljk} = \beta_{jlk}$ it follows that $D'_{lj}\,(\boldsymbol{k}, \omega) = D_{jl}\,(\boldsymbol{k}, \omega)$. Together with the symmetry of $\boldsymbol{\alpha}^0(\omega)$ and $\mathsf{E}^{(0)}(\omega)$ then follows that $\mathscr{A}^{(1)}\,(\boldsymbol{k}, \omega)$ [eq. (4.6)] can be written as

$$\mathscr{A}^{(1)}\,(\boldsymbol{k}, \omega) = \mathsf{Y}\,(\boldsymbol{k}, \omega) - \mathsf{Y}^{\mathrm{T}}\,(\boldsymbol{k}, \omega), \tag{4.21}$$

where

$$\mathsf{Y}\,(\boldsymbol{k}, \omega) = \mathsf{D}^{(1)}\,(\boldsymbol{k}, \omega) \cdot \mathscr{A}^{(0)}(\omega) + \mathrm{i}\varrho\boldsymbol{\beta}\,(\omega) \cdot \boldsymbol{k} \tag{4.22}$$

and $\mathsf{Y}^{\mathrm{T}}\,(\boldsymbol{k}, \omega)$ is the transpose of $\mathsf{Y}\,(\boldsymbol{k}, \omega)$. From eqs. (3.16) and (3.31) we furthermore obtain for $\mathsf{D}^{(1)}\,(\boldsymbol{k}, \omega)$:

$$\mathsf{D}^{(1)}\,(\boldsymbol{k}, \omega) = \mathrm{i}\varrho\boldsymbol{\beta}\,(\omega) : (\boldsymbol{k}\mathsf{M}^{(0)} - \tfrac{1}{3}\boldsymbol{k}\mathsf{U} - \boldsymbol{k} \cdot \mathsf{L}). \tag{4.23}$$

In this equation the fourth-order tensor L is defined by

$$\mathrm{i}\boldsymbol{k} \cdot \mathsf{L} \equiv \mathsf{N}^{(1)}(\boldsymbol{k}), \tag{4.24}$$

where $\mathsf{N}^{(1)}(\boldsymbol{k})$ is the first term in the expansion (3.32) of $\mathsf{N}\,(\boldsymbol{k}, \omega)$, which is linear in $\boldsymbol{k}$ and in which terms of order $a^2\omega^2$ are neglected. Hence follows for $\mathsf{Y}\,(\boldsymbol{k}, \omega)$ in cartesian components:

$$\begin{aligned} Y_{lj}\,(\boldsymbol{k}, \omega) = \mathrm{i}\varrho\beta_{ilm}\,\{&k_m\,[\delta_{lj} + M^{(0)}_{lk}\mathscr{A}^{(0)}_{kj}(\omega) - \tfrac{1}{3}\delta_{lk}\mathscr{A}^{(0)}_{kj}(\omega)] \\ &- k_n L_{nmlk}\mathscr{A}^{(0)}_{kj}\,(\omega)\}. \end{aligned} \tag{4.25}$$

Let us define

$$\mathsf{S}(\omega) \equiv 1 + (\mathsf{M}^{(0)} - \tfrac{1}{3}) \cdot \mathscr{A}^{(0)}(\omega), \tag{4.26}$$

so that

$$\mathsf{S}^{\mathrm{T}}(\omega) = 1 + \mathscr{A}^{(0)}(\omega) \cdot (\mathsf{M}^{(0)} - \tfrac{1}{3}). \tag{4.27}$$

Then it follows from eqs. (4.4) and (4.21) that

$$\chi_{ij}^{(1)}(\boldsymbol{k}, \omega) = \Phi_{ij}(\boldsymbol{k}, \omega) - \Phi_{ji}(\boldsymbol{k}, \omega), \tag{4.28}$$

where

$$\Phi_{ij}(\boldsymbol{k}, \omega) = \{[\mathsf{S}^{\mathrm{T}}(\omega)]^{-1} \cdot \mathsf{Y}(\boldsymbol{k}, \omega) \cdot \mathsf{S}^{-1}(\omega)\}_{ij} = S_{ki}^{-1}(\omega)\, Y_{kl}(\boldsymbol{k}, \omega)\, S_{lj}^{-1}(\omega). \tag{4.29}$$

Using eq. (4.25) we can write this as

$$\Phi_{ij}(\boldsymbol{k}, \omega) = \mathrm{i}\psi_{ijl}(\omega)\, k_l, \tag{4.30}$$

with

$$\psi_{ijl}(\omega) = S_{ki}^{-1}(\omega)\, \varrho\beta_{kjl}(\omega) - S_{ki}^{-1}(\omega)\, \varrho\beta_{knm}(\omega)\, L_{lmnp}\mathscr{A}_{pq}^{(0)}(\omega)\, S_{qj}^{-1}(\omega). \tag{4.31}$$

Thus we have found the first-order spatial dispersion term of the dielectric susceptibility and so of the dielectric tensor $\boldsymbol{\varepsilon}(\boldsymbol{k}, \omega) = \boldsymbol{\chi}(\boldsymbol{k}, \omega) + 1$. If we write for the expansion of the dielectric tensor:

$$\varepsilon_{ij}(\boldsymbol{k}, \omega) = \varepsilon_{ij}^{(0)}(\omega) + \mathrm{i}\gamma_{ijl}(\omega)\, k_l, \tag{4.32}$$

then it follows with eq. (4.30) that $\gamma_{ijl}(\omega)$ is given by

$$\gamma_{ijl}(\omega) = \psi_{ijl}(\omega) - \psi_{jil}(\omega). \tag{4.33}$$

The gyration tensor $\mathsf{g}(\omega)$ is now defined by

$$\gamma_{ijl}(\omega) \equiv \delta_{ijk} g_{kl}(\omega), \tag{4.34}$$

where δ_{ijk} is the permutation tensor or Levi-Civita tensor. From eq. (4.33) and the rule $\delta_{ijk}\delta_{pqk} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}$ then follows

$$g_{kl}(\omega) = \delta_{ijk}\psi_{ijl}(\omega). \tag{4.35}$$

Finally the fourth-order tensor L, defined by eq. (4.24), can be obtained from eq. (3.32). The result is:

$$\begin{aligned} L_{ijkl} = {} & (1/\varrho a^3) \sum_{\lambda}{}' f'(R_\lambda)\, (\delta_{ij}\hat{R}_k^\lambda \hat{R}_l^\lambda + \delta_{ik}\hat{R}_j^\lambda \hat{R}_l^\lambda + \delta_{jk}\hat{R}_i^\lambda \hat{R}_l^\lambda) \\ & - (1/\varrho a^3) \sum_{\lambda}{}' g'(R_\lambda)\, \hat{R}_i^\lambda \hat{R}_j^\lambda \hat{R}_k^\lambda \hat{R}_l^\lambda \\ & + \sum_{\lambda}{}' a'(k_\lambda)\, (\hat{k}_i^\lambda \hat{k}_j^\lambda \delta_{kl} + \hat{k}_i^\lambda \hat{k}_k^\lambda \delta_{jl} + \hat{k}_j^\lambda \hat{k}_k^\lambda \delta_{il}) - \sum_{\lambda}{}' b'(k_\lambda)\, \hat{k}_i^\lambda \hat{k}_j^\lambda \hat{k}_k^\lambda \hat{k}_l^\lambda. \end{aligned} \tag{4.36}$$

In this equation the functions $f'(R)$, $g'(R)$ and $a'(k)$ are given by eqs. (4.17), (4.18) and (4.20) whereas $b'(k)$ is defined by

$$b'(k) \equiv 2\,(1 + a^2k^2/4\pi)\,\mathrm{e}^{-a^2k^2/4\pi} \tag{4.37}$$

Eqs. (4.35) with (4.31) give the general expression for the gyration tensor of a Bravais lattice with molecules with polarizability given by eq. (2.19). In the next section we shall treat some special cases in which the gyration tensor reduces to a simpler form.

5. *Special cases.* Consider the case of a cubic lattice with molecules for which the generalized polarizability tensors are:

$$\varrho\alpha^0_{ij}(\omega) = a_0(\omega)\,\delta_{ij} \tag{5.1}$$

and

$$\varrho\beta_{ijk}(\omega) = b_0(\omega)\,\delta_{ijk}. \tag{5.2}$$

One might think of gyrotropic molecules with random orientation, averaged over all orientations. In this case

$$\mathscr{A}^{(0)}_{ij}(\omega) = \varrho\alpha^0_{ij}(\omega), \tag{5.3}$$

as we saw at the end of subsection 4.1. As a consequence of eq. (5.2) the second term in eq. (4.31) vanishes since $L_{lmnp} = L_{lnmp}$ as follows from eq. (4.36). Furthermore the tensor $\mathsf{S}(\omega)$, defined by eq. (4.26) reduces to a scalar

$$S(\omega) = 1 - \tfrac{1}{3}a_0(\omega), \tag{5.4}$$

since for a cubic lattice $\mathsf{M}^{(0)} = 0$ 1). In the given case eq. (4.31) becomes

$$\psi_{ijl}(\omega) = \frac{b_0(\omega)}{1 - \frac{1}{3}a_0(\omega)}\,\delta_{ijl}, \tag{5.5}$$

so that we get for the gyration tensor [eq. (4.35)]:

$$g_{kl}(\omega) = \frac{b_0(\omega)}{1 - \frac{1}{3}a_0(\omega)}\,\delta_{ijk}\delta_{ijl} = \frac{2b_0(\omega)}{1 - \frac{1}{3}a_0(\omega)}\,\delta_{kl}. \tag{5.6}$$

From the phenomenological theory (see, *e.g.*, refs. 5 or 6) then follows for the optical rotatory power (*i.e.*, the rotation to the right, for an observer viewing the light beam in the direction opposite to the direction of propagation, of the plane of polarization of linearly polarized light, measured in rad/cm):

$$\phi = -\frac{2\pi^2}{\lambda_0^2}\,\frac{2b_0(\omega)}{1-\frac{1}{3}a_0(\omega)}, \tag{5.7}$$

where λ_0 is the vacuum wavelength. If we use eq. (4.3) for the zeroth-order susceptibility we get with eq. (5.1)

$$\varepsilon^{(0)}(\omega) = \frac{1+\frac{2}{3}a_0(\omega)}{1-\frac{1}{3}a_0(\omega)} \equiv n_0^2, \tag{5.8}$$

where n_0 is the zeroth-order refractive index. Using eq. (5.8) we get for ϕ:

$$\phi = -(2\pi^2/\lambda_0^2)\,\tfrac{1}{3}\,(n_0^2+2)\,2b_0(\omega). \tag{5.9}$$

This expression agrees with the results obtained by Hoek^{2}), Maaskant and Oosterhoff^{3}) and Terwiel and Mazur^{4}) for fluids (when neglecting statistical effects). Note that we have $2b_0$ in eq. (5.9) instead of two different terms as in refs. 2, 3 and 4 since we have used the symmetry property $\beta_{ijk} = \beta'_{jik}$.

As a second example we consider a tetragonal crystal of class 4 (or C4) in which the molecules are fixed on a cubic lattice. We shall calculate the optical rotatory power for light propagating along the optical axis of this uniaxial crystal. We shall choose the coordinate axes (right handed) along the edges of the cube such that the z axis (3) coincides with the 4th-order axis (which is the optical axis) of the crystal. From the symmetry properties of crystal class 4 follows that the third-order tensor ψ_{ijk} has the following nonvanishing components:

$$\begin{aligned} &\psi_{113} = \psi_{223} \equiv \psi_1; \qquad \psi_{131} = \psi_{232} \equiv \psi_2; \qquad \psi_{311} = \psi_{322} \equiv \psi_3; \\ &\psi_{123} = -\psi_{213} \equiv \psi_4; \qquad \psi_{132} = -\psi_{231} \equiv \psi_5; \qquad \psi_{312} = -\psi_{321} \equiv \psi_6; \\ &\psi_{333} \equiv \psi_7. \end{aligned} \tag{5.10}$$

Hence the gyration tensor $g_{kl} = \delta_{ijk}\psi_{ijl}$ [eq. (4.35)] has the following form:

$$\mathsf{g} = \begin{pmatrix} \psi_6-\psi_5 & \psi_2-\psi_3 & 0 \\ \psi_3-\psi_2 & \psi_6-\psi_5 & 0 \\ 0 & 0 & 2\psi_4 \end{pmatrix}, \tag{5.11}$$

so that the symmetrical part g^s of g, which is essential for the optical activity, can be written as

$$\mathsf{g}^s = \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\parallel \end{pmatrix}, \tag{5.12}$$

with

$$g_{\perp} = \psi_6 - \psi_5 \tag{5.13}$$

and

$$g_{\parallel} = 2\psi_4 . \tag{5.14}$$

From the phenomenological theory (see, *e.g.*, ref. 5 or 6) follows that the optical rotatory power for propagation along the optical axis then is given by

$$\phi = -(2\pi^2/\lambda_0^2)\, g_{\parallel} , \tag{5.15}$$

where λ_0 is the vacuum wavelength. So we still have to calculate ψ_4. From eqs. (4.31) and (5.10) follows

$$\psi_4 = \psi_{123} = S_{k1}^{-1} \varrho\beta_{k23} - S_{k1}^{-1} \varrho\beta_{knm} L_{3mnp} \mathscr{A}_{pq}^{(0)} S_{q2}^{-1} . \tag{5.16}$$

We can reduce this expression using the symmetry properties of the tensors appearing in eq. (5.16). From the symmetry of crystal class 4 it follows that symmetrical second-order tensors such as S and $\mathscr{A}^{(0)}$ have the form

$$\mathsf{T} = \begin{pmatrix} T_{\perp} & 0 & 0 \\ 0 & T_{\perp} & 0 \\ 0 & 0 & T_{\parallel} \end{pmatrix} . \tag{5.17}$$

For our model of identical equally oriented molecules, the molecules must have the same symmetry elements as this crystal. This means that the nonvanishing components of the third-order tensor $\boldsymbol{\beta}$ are the following:

$$\varrho\beta_{113} = \varrho\beta_{223} \equiv b_1 ; \qquad \varrho\beta_{131} = \varrho\beta_{232} \equiv b_2 ;$$

$$\varrho\beta_{311} = \varrho\beta_{322} \equiv b_3 ; \qquad \varrho\beta_{123} = -\varrho\beta_{213} \equiv b_4 ;$$

$$\varrho\beta_{132} = -\varrho\beta_{231} \equiv b_5 ; \qquad \varrho\beta_{312} = -\varrho\beta_{321} \equiv b_6 ; \qquad \varrho\beta_{333} \equiv b_7 . \tag{5.18}$$

The fourth-order tensor L only depends on the lattice, in this case a cubic lattice. For the given choice of axes the nonvanishing components of L therefore are: $L_{1111} = L_{2222} = L_{3333} = l_1$; and the components with indices equal in pairs (L_{1122}, L_{1331}, *etc.*) are equal to l_2. The consequence of the above symmetry properties is that eq. (5.16) becomes:

$$\psi_{123} = (b_4/S_{\perp}) - (\mathscr{A}_{\perp}^{(0)}/S_{\perp}^2)\, l_2\, (b_4 + b_5) . \tag{5.19}$$

Furthermore it follows with eq. (4.26) that

$$S_\perp = 1 - \tfrac{1}{3}\mathscr{A}_\perp^{(0)}, \tag{5.20}$$

since for a cubic lattice $\mathsf{M}^{(0)} = 0$. With eq. (4.3) we have for the orthogonal component of the zeroth-order dielectric tensor:

$$\varepsilon_\perp^0 = [1 + \tfrac{2}{3}\mathscr{A}_\perp^{(0)}]/[1 - \tfrac{1}{3}\mathscr{A}_\perp^{(0)}]. \tag{5.21}$$

Defining

$$\varepsilon_\perp^0 \equiv n_\perp^2, \tag{5.22}$$

we have

$$1/S_\perp = \tfrac{1}{3}(n_\perp^2 + 2); \qquad \mathscr{A}_\perp^{(0)}/S_\perp = n_\perp^2 - 1, \tag{5.23}$$

so that eq. (5.19) becomes

$$\psi_{123} = \tfrac{1}{3}(n_\perp^2 + 2)\,[b_4 - (n_\perp^2 - 1)\, l_2\,(b_4 + b_5)]. \tag{5.24}$$

With eqs. (5.14) and (5.15) the optical rotatory power then is given by

$$\phi = -(2\pi^2/\lambda_0^2)\,\tfrac{1}{3}(n_\perp^2 + 2)\,[2b_4 - 2\,(n_\perp^2 - 1)\, l_2\,(b_4 + b_5)]. \tag{5.25}$$

As to the quantity $\mathscr{A}_\perp^{(0)}$ we remark that with eqs. (4.5) and (4.7) we have

$$\mathscr{A}_\perp^{(0)} = \varrho\alpha_\perp^0 - E_\perp^{(0)}. \tag{5.26}$$

From eqs. (4.14) and (5.18) and the fact that the nonvanishing components of the fourth-order tensor C are: $C_{1111} = C_{2222} = C_{3333} = c_1$ and all components with indices equal in pairs (C_{1122}, *etc.*) are equal to c_2, follows

$$E_\perp^{(0)} = c_2\,[(b_1 + b_2)^2 + (b_4 + b_5)^2]. \tag{5.27}$$

The numbers l_1, l_2, c_1 and c_2 can easily be calculated with the formulae (4.36) and (4.15). The numbers l_1 and l_2 are dependent and so are c_1 and c_2. From the definitions of C and L: (3.34) and (4.24) [or from the expressions (4.15) and (4.36)] one finds

$$l_1 = -2l_2 - 1 \tag{5.28}$$

and

$$c_1 = -2c_2. \tag{5.29}$$

Using eqs. (4.15) and (4.36) we find the following values for the simple cubic (SC), the body-centered cubic (BCC) and the face-centered cubic (FCC) lattices:

$$
\begin{aligned}
\text{SC:}\ l_2 &= 0.1716,\\
\text{BCC:}\ l_2 &= -0.3146,\\
\text{FCC:}\ l_2 &= -0.3019
\end{aligned}
\tag{5.30}
$$

and, if we choose a such that $\varrho a^3 = 1$:

$$
\begin{aligned}
\text{SC:}\ a^2 c_2 &= -2.9681,\\
\text{BCC:}\ a^2 c_2 &= 0.9344,\\
\text{FCC:}\ a^2 c_2 &= 0.7130.
\end{aligned}
\tag{5.31}
$$

So we can write for eqs. (5.25) and (5.27) in the case of a simple cubic lattice:

$$\phi = -(2\pi^2/\lambda_0^2)\,\tfrac{1}{3}\,(n_\perp^2 + 2)\,2\,[b_4 - 0.1716\,(n_\perp^2 - 1)\,(b_4 + b_5)] \tag{5.32}$$

and

$$E_\perp^{(0)} = -2.9681\,(1/a^2)\,[(b_1 + b_2)^2 + (b_4 + b_5)^2]. \tag{5.33}$$

From these two equations we can make an estimate of the size of the correction $E_\perp^{(0)}$ if we know the order of magnitude of ϕ, as we did at the end of subsection 4.1. Furthermore we can also see that in the case that $\boldsymbol{\beta}$ has the form $\beta_{ijk} = b_0\delta_{ijk}$, $b_4 = -b_5 = b_0$ and $b_1 = b_2 = 0$, so that then $E_\perp^{(0)} = 0$ and the correction on ϕ proportional to l_2 [*cf.*, eq. (5.25)] vanishes too.

Finally we consider the case that the molecules that constituted this tetragonal crystal now are oriented at random and an orientational averaging is performed *a priori*. In this case we can write$^{2-4}$)

$$\varrho\bar{\beta}_{ijk} = \bar{b}_0\delta_{ijk}, \tag{5.34}$$

with

$$\bar{b}_0 = \tfrac{1}{6}\varrho\delta_{lmn}\beta_{lmn} \tag{5.35}$$

and

$$\varrho\bar{\alpha}^0_{ij} = \bar{a}_0\delta_{ij}, \tag{5.36}$$

with

$$\bar{a}_0 = \tfrac{1}{3}\varrho\alpha^0_{kl}\delta_{kl}. \tag{5.37}$$

From eq. (5.18) then follows

$$\bar{b}_0 = \tfrac{1}{3}(b_4 + b_6 - b_5). \tag{5.38}$$

We then have the isotropic case as treated in the beginning of this section. With eqs. (5.7) and (5.8) we find:

$$\phi = -(2\pi^2/\lambda_0^2)\,\tfrac{1}{3}(n_0^2 + 2)\,\tfrac{1}{3}(b_4 + b_6 - b_5), \tag{5.39}$$

in which n_0 is given by

$$n_0^2 = (1 + \tfrac{2}{3}\bar{a}_0)/(1 - \tfrac{1}{3}\bar{a}_0) \tag{5.40}$$

and

$$\bar{a}_0 = \tfrac{1}{3}\varrho\alpha_{kl}^0\delta_{kl} = \tfrac{1}{3}\varrho\,(2\alpha_\perp^0 + \alpha_\parallel^0). \tag{5.41}$$

Here $\alpha_\perp^0$ and $\alpha_\parallel^0$ are the two independent components of the tensor $\boldsymbol{\alpha}^0$, which is of the form (5.17) in a coordinate frame with the z axis along the symmetry or fourth-order axis of the molecule.

6. *Discussion.* In this paper and in the previous paper we have calculated the susceptibility for a zero-temperature crystal with one molecule per unit cell. In both papers a multipole expansion was used for the polarizability of the molecules. In the first paper we only considered the lowest-order term in this expansion (point dipoles), whereas in the present paper we went to the next order. The use of the multipole expansion implies the assumption that the effective field acting on a molecule varies sufficiently slowly over the molecular diameter. Whereas this assumption is valid for the external field, within the context of the theory, it is certainly less appropriate for the contribution to the effective field due to the neighbouring molecules. We note that in the subsequent evaluation of the susceptibility it is only assumed that the external field varies slowly over the molecular diameter. It is clear that the multipole expansion will be correct if the higher-order multipoles are sufficiently small. By comparison of the results in the present paper with those obtained in paper I for the $\boldsymbol{k} = 0$ susceptibility, it is now possible to indicate explicitly how large the higher-order generalized polarizabilities [higher moments of the continuous polarizability $\boldsymbol{\sigma}(\boldsymbol{r}, \boldsymbol{r}')$] are allowed to be. We can write the multipole expansion as (suppressing the frequencies):

$$\sigma_{ij}(\boldsymbol{k}, \boldsymbol{k}') = \sum_{m,n=0}^{\infty} \alpha_{ijp_1\cdots p_{m+n}}^{m,n} k_{p_1} \cdots k_{p_m} k'_{p_{n+1}} \cdots k'_{p_{m+n}}, \tag{6.1}$$

where $\boldsymbol{\alpha}^{m,n}$ is a tensor of order $m + n + 2$ and summation convention is used. Then it turns out that in the equations from which the $\boldsymbol{k} = 0$ susceptibility can be solved, the generalized polarizabilities $\varrho\boldsymbol{\alpha}^{m,n}$ are always contracted with the tensor sums $\sum_\lambda \boldsymbol{k}_\lambda \cdots \boldsymbol{k}_\lambda \mathsf{H}(\boldsymbol{k}_\lambda)$ of order $m + n + 2$. Since the components of $a^{m+n} \sum_\lambda \boldsymbol{k}_\lambda \cdots \boldsymbol{k}_\lambda \mathsf{H}(\boldsymbol{k}_\lambda)$ are dimensionless numbers of order one (which can be calculated in the same way as we did in the present paper for $m + n = 1, 2$), the convergence of the susceptibility of the crystal will be good if the components of $\varrho\boldsymbol{\alpha}^{m,n}/a^{m+n}$ approach zero sufficiently rapidly for $m + n \rightarrow \infty$. If one defines an "electromagnetic diameter" for $m + n \geqslant 1$:

$$d_{\mathrm{el}} \equiv \sup \left[\left(\varrho \left| \alpha^{m,n}_{p_1 \cdots p_{m+n+2}} \right| \right)^{1/(m+n)} \right], \tag{6.2}$$

the criterion for rapid convergence will be: $d_{\mathrm{el}} \ll a$.

We shall now consider explicitly the contributions up to order $(d_{\mathrm{el}}/a)^2$. Then we must take into account generalized polarizabilities for which $m + n = 0, 1, 2$ and take for the continuous polarizability:

$$\boldsymbol{\sigma}(\boldsymbol{k}, \boldsymbol{k}') = (2\pi)^{-3} (\boldsymbol{\alpha}^0 - \mathrm{i}\boldsymbol{\beta}' \cdot \boldsymbol{k} + \mathrm{i}\boldsymbol{\beta} \cdot \boldsymbol{k}' - \boldsymbol{\gamma} : \boldsymbol{k}\boldsymbol{k} + \boldsymbol{\gamma}' : \boldsymbol{k}\boldsymbol{k}' - \boldsymbol{\gamma}'' : \boldsymbol{k}'\boldsymbol{k}'). \tag{6.3}$$

For the zeroth-order susceptibility we then find

$$\begin{aligned} \boldsymbol{\chi}^{(0)} = {} & [1 + (\varrho\boldsymbol{\alpha}^0 + \varrho\boldsymbol{\alpha}^0 \cdot \mathsf{G}^{\mathrm{T}} + \mathsf{G} \cdot \varrho\boldsymbol{\alpha}^{(0)} - \mathsf{E}^{(0)}) \cdot (\mathsf{M}^{(0)} - \tfrac{1}{3})]^{-1} \\ & \cdot (\varrho\boldsymbol{\alpha}^0 + \varrho\boldsymbol{\alpha}^0 \cdot \mathsf{G}^{\mathrm{T}} + \mathsf{G} \cdot \varrho\boldsymbol{\alpha} - \mathsf{E}^{(0)}), \end{aligned} \tag{6.4}$$

which has the same form as the zeroth-order susceptibility of the point-dipole lattice (derived in paper I), but now with $\varrho\boldsymbol{\alpha}^0$ replaced by $\varrho\boldsymbol{\alpha}^0 + \varrho\boldsymbol{\alpha}^0 \cdot \mathsf{G}^{\mathrm{T}} + \mathsf{G} \cdot \varrho\boldsymbol{\alpha}^0 - \mathsf{E}^{(0)}$. In this formula

$$\mathsf{G} \equiv \varrho\boldsymbol{\gamma}'' : \mathsf{C}(0, 0) \tag{6.5}$$

and G^{T} is the transpose of G. Furthermore $\mathsf{E}^{(0)}$ and $\mathsf{C}(0, 0)$ are given by eqs. (4.14) and (4.15). Comparing result (6.4) with that of subsection 4.1, we see that we get an additional correction of order $(d_{\mathrm{el}}/a)^2$ on $\varrho\boldsymbol{\alpha}^0$ from octupole moments.

It is interesting to consider again the case of isotropic molecules on a cubic lattice. For isotropic molecules $\boldsymbol{\gamma}''$ must be of the form (see, *e.g.*, ref. 8):

$$\gamma''_{ikmp} = \lambda \delta_{ik} \delta_{mp} + \mu (\delta_{im} \delta_{kp} + \delta_{ip} \delta_{km}) + \nu (\delta_{im} \delta_{kp} - \delta_{ip} \delta_{km}), \tag{6.6}$$

so that

$$G_{ij} = (\lambda + 2\mu)(c_1 + 2c_2) \delta_{ij}, \tag{6.7}$$

which is zero because of eq. (5.29): $c_1 = -2c_2$. Since in this case also $\mathsf{E}^{(0)} = 0$ we have only corrections on $\varrho\boldsymbol{\alpha}^0$ of order $a^2\omega^2$ which can be neglected. In this isotropic case the multipole expansion is good even if $\varrho\beta/a$ and $\varrho\gamma''/a^2$ are not much smaller than one.

Finally we note that we have a nonvanishing correction G in the anisotropic tetragonal case which we treated as an example in section 5. Then, for the proper choice of coordinate axes used in section 5, G has the form (5.17), where $G_\perp$ and $G_\parallel$ can easily be expressed in terms of the nonvanishing components of γ'' and the number c_2 [see eq. (5.31)].

APPENDIX

In this appendix we shall give the derivation of the rapidly converging expressions for the lattice sums $\mathsf{B}(\boldsymbol{k}, \omega)$ [eqs. (3.31), (3.32)] and $\mathsf{C}(\boldsymbol{k}, \omega)$ [eqs. (3.34), (3.35)]. *Cf.* also appendix B of I. First we have with eqs. (3.15), (3.26) and (3.29):

$$\mathsf{B}(\boldsymbol{k}, \omega) = \boldsymbol{k}\mathsf{M}(\boldsymbol{k}, \omega) + \boldsymbol{k}\mathsf{F}(\boldsymbol{k}, \omega) - \tfrac{1}{3}\boldsymbol{k}\mathsf{U} - \sum_\lambda (\boldsymbol{k} - \boldsymbol{k}_\lambda)\, \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega). \quad \text{(A.1)}$$

With the definition (2.20) of H and using the equality

$$\varrho \sum_\lambda e^{-i\boldsymbol{k}_\lambda \cdot \boldsymbol{R}} = \sum_\lambda \delta(\boldsymbol{R} - \boldsymbol{R}_\lambda), \quad \text{(A.2)}$$

we can write for the last term on the r.h.s. of (A.1):

$$\begin{aligned}\sum_\lambda (\boldsymbol{k} - \boldsymbol{k}_\lambda)\, \mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega) &= -\mathrm{i} \sum_\lambda \int \nabla \mathsf{H}(\boldsymbol{R}, \omega)\, e^{-i(\boldsymbol{k}-\boldsymbol{k}_\lambda)\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} \\ &= -\mathrm{i}\varrho^{-1} \sum_\lambda \nabla \mathsf{H}(\boldsymbol{R}_\lambda, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}_\lambda} \\ &= -\mathrm{i}\varrho^{-1} \sum_\lambda{}' \nabla \mathsf{F}(\boldsymbol{R}_\lambda, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}_\lambda} \\ &\quad - \mathrm{i}\varrho^{-1}\tfrac{1}{2}\, [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)]_{\boldsymbol{R}=0}. \end{aligned} \quad \text{(A.3)}$$

Defining

$$\begin{aligned}\mathsf{N}'(\boldsymbol{k}, \omega) \equiv{}& \varrho^{-1} \sum_\lambda{}' \nabla \mathsf{F}(\boldsymbol{R}_\lambda, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}_\lambda} - \lim_{d\to 0} \int_{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} \\ &+ \varrho^{-1}\tfrac{1}{2}\, [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)]_{\boldsymbol{R}=0}, \end{aligned} \quad \text{(A.4)}$$

we have for $\mathsf{B}(\boldsymbol{k}, \omega)$:

$$\begin{aligned}\mathsf{B}(\boldsymbol{k}, \omega) ={}& \boldsymbol{k}\mathsf{M}(\boldsymbol{k}, \omega) + \boldsymbol{k}\mathsf{F}(\boldsymbol{k}, \omega) - \tfrac{1}{3}\boldsymbol{k}\mathsf{U} \\ &+ \mathrm{i}\mathsf{N}'(\boldsymbol{k}, \omega) + \lim_{d\to 0} \mathrm{i} \int_{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} \\ ={}& \boldsymbol{k}\mathsf{M}(\boldsymbol{k}, \omega) - \tfrac{1}{3}\boldsymbol{k}\mathsf{U} + \mathrm{i}\mathsf{N}'(\boldsymbol{k}, \omega) - \lim_{d\to 0} \mathrm{i} \int^{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, e^{-i\boldsymbol{k}\cdot \boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \end{aligned} \quad \text{(A.5)}$$

The symbol $\int^{\varepsilon(d)}$ denotes integration over a sphere of radius d around $\boldsymbol{R} = 0$ whereas $\int_{\varepsilon(d)}$ stands for integration over the whole space excluding this sphere. As the next step we write $\mathsf{N}'(\boldsymbol{k}, \omega)$ in the following form:

$$\begin{aligned}
\mathsf{N}'(\boldsymbol{k}, \omega) &= \varrho^{-1} \sum_{\lambda}{}' \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}_\lambda, \omega) + \nabla \mathsf{F}^\dagger(\boldsymbol{R}_\lambda, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda} \\
&\quad - \lim_{d\to 0} \int_{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) + \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R} \\
&\quad + \varrho^{-1} \sum_{\lambda} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}_\lambda, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}_\lambda, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda} \\
&\quad - \int \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R}.
\end{aligned} \tag{A.6}$$

The last integral is taken over the whole space since

$$\lim_{d\to 0} \int^{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R} = 0.$$

With eq. (A.2) and (2.3) we can show that

$$\begin{aligned}
&\varrho^{-1} \sum_{\lambda} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}_\lambda, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}_\lambda, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda} \\
&\qquad - \int \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R} \\
&\quad = \sum_{\lambda}{}' \int \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) - \nabla \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}_\lambda)\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R} \\
&\quad = -\tfrac{1}{2} \sum_{\lambda}{}' (\boldsymbol{k} - \boldsymbol{k}_\lambda) \, \mathrm{Im}\, \mathsf{F}(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega) \\
&\quad = \tfrac{1}{4}\pi \sum_{\lambda}{}' \frac{\boldsymbol{k} - \boldsymbol{k}_\lambda}{|\boldsymbol{k} - \boldsymbol{k}_\lambda|} [(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2] \\
&\qquad \times [\delta(|\boldsymbol{k} - \boldsymbol{k}_\lambda| + \omega) - \delta(|\boldsymbol{k} - \boldsymbol{k}_\lambda| - \omega)].
\end{aligned} \tag{A.7}$$

Cf. eqs. (I.3.21)–(I.3.24). For frequencies ω smaller than the radius of the largest possible sphere in the first Brillouin zone with centre at the origin this expression vanishes since we have chosen $\boldsymbol{k}$ in the first Brillouin zone so that $|\boldsymbol{k} - \boldsymbol{k}_\lambda| \neq \omega$ for $\boldsymbol{k}_\lambda \neq 0$. For the first two terms on the r.h.s. of eq. (A.6) we use the formula

$$\tfrac{1}{2} [\mathsf{F}(\boldsymbol{R}, \omega) + \mathsf{F}^\dagger(\boldsymbol{R}, \omega)] = -(\nabla\nabla + \omega^2) \frac{\cos \omega R}{4\pi R}, \tag{A.8}$$

and apply the method, introduced by Nijboer and De Wette[7]), as we did in I. For $\mathsf{N}'(\boldsymbol{k}, \omega)$ we write:

$$\mathsf{N}'(\boldsymbol{k}, \omega) = -\varrho^{-1} \sum_{\lambda}{}' \nabla (\nabla\nabla + \omega^2) \left[\mathrm{erfc}\left(\pi^{\frac{1}{2}} \frac{R_\lambda}{a}\right) \frac{\cos \omega R_\lambda}{4\pi R_\lambda} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda}$$

$$- \varrho^{-1} \sum_{\lambda}{}' \boldsymbol{\nabla} (\boldsymbol{\nabla}\boldsymbol{\nabla} + \omega^2) \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R_\lambda}{a} \right) \frac{\cos \omega R_\lambda}{4\pi R_\lambda} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda}$$

$$- \lim_{d\to 0} \int_{\varepsilon(d)} \tfrac{1}{2} [\boldsymbol{\nabla}\mathsf{F}(\boldsymbol{R}, \omega) + \boldsymbol{\nabla}\mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)] \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R}. \qquad (A.9)$$

where

$$\operatorname{erfc}(x) \equiv (2/\sqrt{\pi}) \int_x^{\infty} \mathrm{e}^{-t^2} \, \mathrm{d}t \qquad (A.10)$$

and

$$\operatorname{erf}(x) \equiv (2/\sqrt{\pi}) \int_0^{x} \mathrm{e}^{-t^2} \, \mathrm{d}t = 1 - \operatorname{erfc}(x). \qquad (A.11)$$

Since the function $\operatorname{erfc}(\pi^{\frac{1}{2}} R_\lambda / a)$ is rapidly decreasing over a few lattice distances the first term on the r.h.s. of eq. (A.9) is a strongly converging lattice sum. The second term can be transformed into a rapidly converging sum on the reciprocal lattice. If we use eq. (A.2) we can write:

$$-\varrho^{-1} \sum_{\lambda}{}' \boldsymbol{\nabla} (\boldsymbol{\nabla}\boldsymbol{\nabla} + \omega^2) \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R_\lambda}{a} \right) \frac{\cos \omega R_\lambda}{4\pi R_\lambda} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_\lambda}$$

$$= \varrho^{-1} \int \delta(\boldsymbol{R}) \, \boldsymbol{\nabla} (\boldsymbol{\nabla}\boldsymbol{\nabla} + \omega^2) \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R}{a} \right) \frac{\cos \omega R}{4\pi R} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \, \mathrm{d}\boldsymbol{R}$$

$$- \sum_{\lambda} \mathrm{FT}_3 \left(\boldsymbol{\nabla} (\boldsymbol{\nabla}\boldsymbol{\nabla} + \omega^2) \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R}{a} \right) \frac{\cos \omega R}{4\pi R} \right] \right)_{\boldsymbol{k}-\boldsymbol{k}_\lambda}, \qquad (A.12)$$

where FT_3 [ ] means the 3-dimensional Fourier transform. For the first term on the r.h.s. of (A.12) we find zero. For the second term we get after straightforward calculations:

$$-\sum_{\lambda} \mathrm{FT}_3 \left(\boldsymbol{\nabla} (\boldsymbol{\nabla}\boldsymbol{\nabla} + \omega^2) \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R}{a} \right) \frac{\cos \omega R}{4\pi R} \right] \right)_{\boldsymbol{k}-\boldsymbol{k}_\lambda}$$

$$= \mathrm{i} \sum_{\lambda} (\boldsymbol{k} - \boldsymbol{k}_\lambda) [(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2] \, \mathrm{FT}_3 \left[\operatorname{erf} \left(\pi^{\frac{1}{2}} \frac{R}{a} \right) \frac{\cos \omega R}{4\pi R} \right]_{\boldsymbol{k}-\boldsymbol{k}_\lambda}$$

$$= \mathrm{i} \sum_{\lambda}{}' (\boldsymbol{k} - \boldsymbol{k}_\lambda) \frac{(\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda) - \omega^2}{|\boldsymbol{k} - \boldsymbol{k}_\lambda|^2 - \omega^2} \mathscr{L}(|\boldsymbol{k} - \boldsymbol{k}_\lambda|, \omega)$$

$$+ \mathrm{i}\mathscr{P}\boldsymbol{k} \frac{\boldsymbol{k}\boldsymbol{k} - \omega^2}{k^2 - \omega^2} \mathscr{L}(k, \omega), \qquad (A.13)$$

where

$$\mathscr{L}(k, \omega) \equiv \frac{k - \omega}{2k} \mathrm{e}^{-a^2 (k+\omega)^2 / 4\pi} + \frac{k + \omega}{2k} \mathrm{e}^{-a^2 (k-\omega)^2 / 4\pi}. \qquad (A.14)$$

Finally we have for the third term on the r.h.s. of eq. (A.9):

$$-\lim_{d\to 0} \int_{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) + \nabla \mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)]\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$= -\mathrm{i}\boldsymbol{k}\, \mathrm{Re}\, \mathsf{F}(\boldsymbol{k}, \omega) + \lim_{d\to 0} \int^{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) + \nabla \mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)]\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$= -\mathrm{i}\mathscr{P}\boldsymbol{k}\, \frac{\boldsymbol{k}\boldsymbol{k} - \omega^2}{k^2 - \omega^2} + \lim_{d\to 0} \int^{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) + \nabla \mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)]\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \quad \text{(A.15)}$$

Furthermore

$$\lim_{d\to 0} \int^{\varepsilon(d)} \tfrac{1}{2} [\nabla \mathsf{F}(\boldsymbol{R}, \omega) + \nabla \mathsf{F}^{\dagger}(\boldsymbol{R}, \omega)]\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R} = \lim_{d\to 0} \int^{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}. \quad \text{(A.16)}$$

Substituting the results (A.12) with (A.13) and (A.15) with (A.16) into the r.h.s. of (A.9) we find:

$$\begin{aligned}
\mathsf{N}'(\boldsymbol{k}, \omega) = {} & -\varrho^{-1} \sum_{\lambda}{}' \nabla(\nabla\nabla + \omega^2) \left[\operatorname{erfc}\left(\pi^{\frac{1}{2}} \frac{R_{\lambda}}{a} \right) \frac{\cos \omega R_{\lambda}}{4\pi R_{\lambda}} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{\lambda}} \\
& + \mathrm{i} \sum_{\lambda}{}' (\boldsymbol{k} - \boldsymbol{k}_{\lambda}) \frac{(\boldsymbol{k} - \boldsymbol{k}_{\lambda})(\boldsymbol{k} - \boldsymbol{k}_{\lambda}) - \omega^2}{|\boldsymbol{k} - \boldsymbol{k}_{\lambda}|^2 - \omega^2} \mathscr{L}(|\boldsymbol{k} - \boldsymbol{k}_{\lambda}|, \omega) \\
& + \mathrm{i}\boldsymbol{k} \frac{\boldsymbol{k}\boldsymbol{k} - \omega^2}{k^2 - \omega^2} [\mathscr{L}(k, \omega) - 1] + \lim_{d\to 0} \int^{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}.
\end{aligned} \quad \text{(A.17)}$$

Defining $\mathsf{N}(\boldsymbol{k}, \omega)$ by

$$\mathsf{N}(\boldsymbol{k}, \omega) \equiv \mathsf{N}'(\boldsymbol{k}, \omega) - \lim_{d\to 0} \int^{\varepsilon(d)} \nabla \mathsf{F}(\boldsymbol{R}, \omega)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}, \quad \text{(A.18)}$$

we obtain from eq. (A.5) the expression (3.31) for $\mathsf{B}(\boldsymbol{k}, \omega)$ with $\mathsf{N}(\boldsymbol{k}, \omega)$ given by eq. (3.32).

For the derivation of eqs. (3.34) with (3.35) for $C_{ijkl}(\boldsymbol{k}, \omega)$ we first write:

$$\begin{aligned}
C_{ijkl}(\boldsymbol{k}, \omega) = {} & k_i B_{jkl}(\boldsymbol{k}, \omega) + k_j B_{ikl}(\boldsymbol{k}, \omega) - k_i k_j A_{kl}(\boldsymbol{k}, \omega) \\
& + \sum_{\lambda} (\boldsymbol{k} - \boldsymbol{k}_{\lambda})_i (\boldsymbol{k} - \boldsymbol{k}_{\lambda})_j H_{kl}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega),
\end{aligned} \quad \text{(A.19)}$$

or with eqs. (3.26) and (3.31)

$$\begin{aligned}
C_{ijkl}(\boldsymbol{k}, \omega) = {} & k_i k_j M_{kl}(\boldsymbol{k}, \omega) - \tfrac{1}{3} k_i k_j \delta_{kl} + \mathrm{i} k_i N_{jkl}(\boldsymbol{k}, \omega) + \mathrm{i} k_j N_{ikl}(\boldsymbol{k}, \omega) \\
& - k_i k_j F_{kl}(\boldsymbol{k}, \omega) + \sum_{\lambda} (\boldsymbol{k} - \boldsymbol{k}_{\lambda})_i (\boldsymbol{k} - \boldsymbol{k}_{\lambda})_j H_{kl}(\boldsymbol{k} - \boldsymbol{k}_{\lambda}, \omega).
\end{aligned} \quad \text{(A.20)}$$

The transformation of $\sum_\lambda (\boldsymbol{k} - \boldsymbol{k}_\lambda)(\boldsymbol{k} - \boldsymbol{k}_\lambda)\,\mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega)$ is very similar to the transformation of $\sum_\lambda (\boldsymbol{k} - \boldsymbol{k}_\lambda)\,\mathsf{H}(\boldsymbol{k} - \boldsymbol{k}_\lambda, \omega)$ as we have done above. An important difference is that the integral corresponding to the integral in eq. (A.12) now gives a contribution *viz.*:

$$\varrho^{-1} \int \delta(\boldsymbol{R})\, \nabla_i \nabla_j (\nabla_k \nabla_l + \omega^2 \delta_{kl}) \left[\operatorname{erf}\left(\pi^{\frac{1}{2}} \frac{R}{a} \right) \frac{\cos \omega R}{4\pi R} \right] \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\, \mathrm{d}\boldsymbol{R}$$

$$= \frac{1}{\varrho a^5} \left[\left(\frac{2\pi}{5} + \tfrac{2}{3} a^2 \omega^2 + \frac{1}{6\pi} a^4 \omega^4 \right) (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \left(\tfrac{1}{3} a^2 \omega^2 + \frac{1}{2\pi} a^4 \omega^4 \right) \delta_{ij}\delta_{kl} \right]. \tag{A.21}$$

By straightforward calculations, following the same line as in the derivation of $\mathsf{B}(\boldsymbol{k}, \omega)$, we arrive at eqs. (3.34) and (3.35). Finally we remark that the transformation of $\mathsf{M}(\boldsymbol{k}, \omega)$ in terms of rapidly converging lattice sums, which was done in I with the function $\bar{\Gamma}(\frac{3}{2}, \pi R^2/a^2)$ can be done faster with the function $\operatorname{erfc}(\pi^{\frac{1}{2}} R/a) = \bar{\Gamma}(\frac{1}{2}, \pi R^2/a^2)$. The results (I.4.7), (I.4.11) and (I.4.12) with (I.4.13) remain unchanged.

REFERENCES

1) Hafkenscheid, L.M. and Vlieger, J., Physica **75** (1974) 57.
2) Hoek, H., Physica **8** (1941) 209.
3) Maaskant, W.J.A. and Oosterhoff, L.J., Molecular Phys. **8** (1964) 319.
4) Terwiel, R.H. and Mazur, P., Physica **30** (1964) 625.
5) Agranovich, V.M. and Ginzburg, V.L., Spatial Dispersion in Crystal Optics and the Theory of Excitons, Interscience (London, 1966).
6) Nye, J.F., Physical Properties of Crystals, Oxford University Press (London, 1957).
7) Nijboer, B.R.A. and De Wette, F.W., Physica **23** (1957) 309.
8) Jeffreys, H., Cartesian Tensors, Cambridge University Press (London, 1963).

III. COMPOSITE LATTICES

Synopsis

In this paper a general expression is given for the wave vector- and frequency-dependent dielectric susceptibility tensor of a composite perfect lattice with an arbitrary number of fixed nonpolar molecules with given polarizability tensor in a unit cell. The general expression is applied to a lattice of point dipoles and quadrupoles. The dielectric susceptibility tensor is in particular studied with first order spatial dispersion.

1. Introduction

In a previous paper [1], in the following denoted by I, we have derived a general expression for the wave vector- and frequency-dependent dielectric susceptibility tensor $\overset{\leftrightarrow}{\chi}(\vec{k},\omega)$ of a simple perfect lattice of fixed nonpolar molecules with given molecular polarizability tensor. The formal theory was worked out in detail for point dipole lattices. In a second paper [2], denoted hereafter by II, the theory was applied to point dipole and quadrupole lattices for which we considered especially the 0th and 1st order spatial dispersion.

In the present paper we shall extend the theory to the case of composite lattices, i.e. Bravais lattices, with more than one molecule in a unit cell. In section 2 we shall develope the formal theory for the composite lattice in a similar way as it was done in paper I for the simple lattice. This theory is applied to the case of a composite dipole and quadrupole lattice in section 3. The formalism is a direct generalization of that of paper II section 3. We consider the 0th and 1st order spatial dispersion of the dielectric susceptibility tensor for this point dipole and quadrupole lattice in section 4 and for the pure point dipole lattice in section 5.

2. Formal theory

Consider an infinite three-dimensional Bravais lattice in which each unit cell (numbered with index i) contains N molecules (numbered with index k). The lattice points are given by the vectors $\vec{R}_i$, whereas the centres of the individual molecules are at the positions $\vec{R}_{i,k} = \vec{R}_i + \vec{r}_k$. If this system is subjected to an external electric field of frequency ω: $\vec{E}^{ext}(\vec{R},\omega)$, the induced microscopic dipole-moment density $\vec{p}_{i,k}(\vec{R},\omega)$ of molecule i,k is given by (see also I and II):

$$\vec{p}_{i,k}(\vec{R},\omega) = \int \overset{\leftrightarrow}{\alpha}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)\cdot\vec{E}^{eff}_{i,k}(\vec{R}',\omega)\,d\vec{R}'. \qquad (2.1)$$

Here $\overset{\leftrightarrow}{\alpha}_k(\vec{r},\vec{r}';\omega)$ is the molecular polarizability tensor of the kth molecule of a unit cell. The effective field acting on molecule i,k is given by

$$\vec{E}^{eff}_{i,k}(\vec{R},\omega) = \vec{E}^{ext}(\vec{R},\omega) - \sum_{j\neq i}\sum_{\ell=1}^{N}\int \overset{\leftrightarrow}{F}(\vec{R}-\vec{R}',\omega)\cdot\vec{p}_{j,\ell}(\vec{R}',\omega)\,d\vec{R}'$$

$$-\sum_{\substack{\ell=1\\ \ell\neq k}}^{N}\int \vec{\vec{F}}(\vec{R}-\vec{R}',\omega)\cdot\vec{p}_{i,\ell}(\vec{R}',\omega)d\vec{R}'$$

$$-\tfrac{1}{2}\int\{\vec{\vec{F}}(\vec{R}-\vec{R}',\omega)-\vec{\vec{F}}^{\dagger}(\vec{R}-\vec{R}',\omega)\}\cdot\vec{p}_{ik}(\vec{R}',\omega)d\vec{R}'. \qquad (2.2)$$

The retarded vacuum propagator of the electromagnetic field is given by

$$\vec{\vec{F}}(\vec{R},\omega) = -(\vec{\nabla}\vec{\nabla}+\omega^2)e^{i(\omega+i0)R}/4\pi R. \qquad (2.3)$$

where $R = |\vec{R}|$ and i0 is an infinitesimal small positive imaginary number. We have chosen units such that the velocity of light is one. $\vec{\vec{F}}^{\dagger}(\vec{R},\omega)$ is the adjoint of $\vec{\vec{F}}(\vec{R},\omega)$. We assume that the molecules are not overlapping so that for each molecule, say molecule i,k, we can choose a region $g_{i,k}$ containing this molecule and no others. This implies that $\vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)=0$ for $\vec{R} \notin g_{i,k}$ so that $\vec{p}_{i,k}(\vec{R},\omega)=0$ for $\vec{R} \notin g_{i,k}$. From the symmetry property of $\vec{\vec{\sigma}}_k$ viz. $(\vec{\vec{\sigma}}_k)_{ij}(\vec{r},\vec{r}';\omega) = (\vec{\vec{\sigma}}_k)_{ji}(\vec{r}',\vec{r};\omega)$ 3) we also have $\vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)=0$ for $\vec{R}' \notin g_{i,k}$. Now define 1):

$$\vec{\vec{H}}_{i,k}(\vec{R},\vec{R}';\omega) \equiv \begin{cases} \vec{\vec{F}}(\vec{R}-\vec{R}',\omega) & \text{for } \vec{R}' \notin g_{i,k} \\ \tfrac{1}{2}\left[\vec{\vec{F}}(\vec{R}-\vec{R}',\omega)-\vec{\vec{F}}^{\dagger}(\vec{R}-\vec{R}',\omega)\right] & \text{for } \vec{R}' \in g_{i,k} \end{cases} \qquad (2.4)$$

and further

$$\vec{P}(\vec{R},\omega) \equiv \sum_i \sum_{k=1}^{N} \vec{p}_{i,k}(\vec{R},\omega). \qquad (2.5)$$

Then it follows with (2.1), (2.2), (2.4) and (2.5) that

$$\vec{P}(\vec{R},\omega) = \int d\vec{R}' \sum_i \sum_{k=1}^{N} \vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)\cdot\vec{E}^{ext}(\vec{R}',\omega)$$

$$-\int d\vec{R}' \sum_{i} \sum_{k=1}^{N} \vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)\cdot\int d\vec{R}''\ \vec{\vec{H}}_{i,k}(\vec{R}',\vec{R}'';\omega)\cdot\vec{P}(\vec{R}'',\omega). \tag{2.6}$$

With the definitions

$$\vec{\vec{\alpha}}(\vec{R},\vec{R}';\omega) \equiv \sum_{i} \sum_{k=1}^{N} \vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega) \tag{2.7}$$

and

$$\vec{\vec{H}}_\sigma(\vec{R},\vec{R}'';\omega) \equiv \sum_{i} \sum_{k=1}^{N} \int d\vec{R}'\ \vec{\vec{\sigma}}_k(\vec{R}-\vec{R}_{i,k},\vec{R}'-\vec{R}_{i,k};\omega)\cdot\vec{\vec{H}}_{i,k}(\vec{R}',\vec{R}'';\omega) \tag{2.8}$$

eq. (2.6) becomes

$$\vec{P}(\vec{R},\omega) = \int d\vec{R}'\ \vec{\vec{\alpha}}(\vec{R},\vec{R}';\omega)\cdot\vec{E}^{ext}(\vec{R}',\omega)-\int d\vec{R}'\ \vec{\vec{H}}_\sigma(\vec{R},\vec{R}';\omega)\cdot\vec{P}(\vec{R},\omega). \tag{2.9}$$

In operator notation this can be written as

$$\vec{P} = \vec{\vec{\alpha}}\cdot\vec{E}^{ext}-\vec{\vec{H}}_\sigma\cdot\vec{P} \tag{2.10}$$

with the formal solution

$$\vec{P} = (1+\vec{\vec{H}}_\sigma)^{-1}\cdot\vec{\vec{\alpha}}\cdot\vec{E}^{ext} \tag{2.11}$$

(cf. eqs. (2.11) - (2.13) in paper I).

Now evaluate the Fourier transform of $\vec{\vec{H}}_\sigma$:

$$\vec{\vec{H}}_\sigma(\vec{k},\vec{k}';\omega) \equiv \frac{1}{(2\pi)^3}\int d\vec{R}\ d\vec{R}'\ \vec{\vec{H}}_\sigma(\vec{R},\vec{R}';\omega)e^{-i\vec{k}\cdot\vec{R}}e^{i\vec{k}'\cdot\vec{R}'}$$

$$= \frac{1}{(2\pi)^3}\sum_{i}\sum_{k=1}^{N}\int\vec{\vec{\sigma}}_k(\vec{r},\vec{r}'';\omega)\cdot\vec{\vec{H}}_{i,k}(\vec{r}''+\vec{R}_{i,k},\vec{r}'+\vec{R}_{i,k};\omega)$$

$$\times\, e^{-i\vec{k}\cdot\vec{r}}e^{i\vec{k}'\cdot\vec{r}'}d\vec{r}\ d\vec{r}'\ d\vec{r}''\ e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_{i,k}}, \tag{2.12}$$

where we have used eq. (2.8) and shifted the integration variables.

Using the fact that

$$\vec{\vec{H}}_{i,k}(\vec{r}''+\vec{R}_{i,k},\vec{r}'+\vec{R}_{i,k};\omega) = \vec{\vec{H}}_{0,k}(\vec{r}''+\vec{r}_k,\vec{r}'+\vec{r}_k;\omega), \tag{2.13}$$

where we have chosen

$$\vec{R}_0=0 \tag{2.14}$$

and the definition

$$\vec{\vec{h}}_{\sigma,k}(\vec{r},\vec{r}';\omega) \equiv \int d\vec{r}''\, \vec{\vec{\sigma}}_k(\vec{r},\vec{r}'';\omega)\cdot\vec{\vec{H}}_{0,k}(\vec{r}''+\vec{r}_k,\vec{r}'+\vec{r}_k;\omega), \tag{2.15}$$

we find

$$\vec{\vec{H}}_\sigma(\vec{k},\vec{k}';\omega) = \frac{1}{(2\pi)^3}\sum_i\sum_{k=1}^{N}\int\vec{\vec{h}}_{\sigma,k}(\vec{r},\vec{r}';\omega)e^{-i\vec{k}\cdot\vec{r}}e^{i\vec{k}'\cdot\vec{r}'}d\vec{r}\,d\vec{r}'$$

$$\times\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_{i,k}} = \sum_i\sum_{k=1}^{N}\vec{\vec{h}}_{\sigma,k}(\vec{k},\vec{k}';\omega)e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_{i,k}}. \tag{2.16}$$

With the relation

$$\sum_i e^{-i\vec{k}\cdot\vec{R}_i} = (2\pi)^3\rho\sum_\lambda\delta(\vec{k}-\vec{k}_\lambda), \tag{2.17}$$

where $\vec{k}_\lambda$ is a reciprocal lattice vector and ρ is such that $\rho^{-1}=v$ is the volume of the unit cell of the lattice, we finally obtain

$$\vec{\vec{H}}_\sigma(\vec{k},\vec{k}';\omega) = (2\pi)^3\rho\sum_\lambda\delta(\vec{k}-\vec{k}'-\vec{k}_\lambda)\sum_k\vec{\vec{h}}_{\sigma,k}(\vec{k},\vec{k}-\vec{k}_\lambda;\omega)e^{-i\vec{k}_\lambda\cdot\vec{r}_k}. \tag{2.18}$$

Similarly we find with eq. (2.7)

$$\vec{\vec{\alpha}}(\vec{k},\vec{k}';\omega) = (2\pi)^3\rho\sum_\lambda\delta(\vec{k}-\vec{k}'-\vec{k}_\lambda)\sum_k\vec{\vec{\sigma}}_k(\vec{k},\vec{k}-\vec{k}_\lambda)e^{-i\vec{k}_\lambda\cdot\vec{r}_k}. \tag{2.19}$$

So, if we use the discrete representation introduced in appendix A of I and define $\vec{\vec{H}}^\lambda_\sigma(\vec{k},\omega)$ and $\vec{\vec{\alpha}}^\lambda(\vec{k},\omega)$ by

$$\vec{\vec{H}}_\sigma(\vec{k},\vec{k}';\omega) \equiv \sum_\lambda\vec{\vec{H}}^\lambda_\sigma(\vec{k},\omega)\delta(\vec{k}-\vec{k}'-\vec{k}_\lambda) \tag{2.20}$$

and

$$\vec{\vec{\alpha}}(\vec{k},\vec{k}';\omega) \equiv \sum_{\lambda} \vec{\vec{\alpha}}^{\lambda}(\vec{k},\omega)\,\delta(\vec{k}-\vec{k}'-\vec{k}_{\lambda}), \tag{2.21}$$

we have

$$\vec{\vec{H}}^{\lambda}_{\sigma}(\vec{k},\omega) = (2\pi)^3\rho \sum_{k=1}^{N} \vec{\vec{h}}_{\sigma,k}(\vec{k},\vec{k}-\vec{k}_{\lambda};\omega)\,e^{-i\vec{k}_{\lambda}\cdot\vec{r}_k} \tag{2.22}$$

and

$$\vec{\vec{\alpha}}^{\lambda}(\vec{k},\omega) = (2\pi)^3\rho \sum_{k=1}^{N} \vec{\vec{\sigma}}_{k}(\vec{k},\vec{k}-\vec{k}_{\lambda};\omega)\,e^{-i\vec{k}_{\lambda}\cdot\vec{r}_k}. \tag{2.23}$$

Now we can apply the same arguments as in section 2 of paper I. Under the condition that $\vec{k}$ lies in the first Brillouinzone and that $\vec{E}^{ext}(\vec{k}',\omega)\neq 0$ only for $\vec{k}'$ in the first Brillouinzone we find for the macroscopic dielectric susceptibility

$$\vec{\vec{\chi}}(\vec{k},\omega) = \vec{\vec{\chi}}^{ext}(\vec{k},\omega)\cdot\left[1-\vec{\vec{F}}(\vec{k},\omega)\cdot\vec{\vec{\chi}}^{ext}(\vec{k},\omega)\right]^{-1}, \tag{2.24}$$

with

$$\begin{aligned}\vec{\vec{\chi}}^{ext}(\vec{k},\omega) &= \left[(1+\vec{\vec{H}}_{\sigma})^{-1}\cdot\vec{\vec{\alpha}}\right]^{0}(\vec{k},\omega)\\ &= \sum_{\lambda}\left[(1+\vec{\vec{H}}_{\sigma})^{-1}\right]^{\lambda}(\vec{k},\omega)\cdot\vec{\vec{\alpha}}^{-\lambda}(\vec{k},\omega).\end{aligned} \tag{2.25}$$

The result of section 2 of paper I is a special case of the above expressions viz. the case that we have one molecule in a unit cell (N=1) with $\vec{r}_1=0$.

In the rest of this paper we shall apply this general formalism to some special cases of point multipoles. In those cases we can take for the regions $g_{i,k}$ small spheres of radius d centered at $\vec{R}_{i,k}$. Then we can define $\vec{\vec{H}}_{i,k}(\vec{R},\vec{R}';\omega)$ by

$$\vec{\vec{H}}_{i,k}(\vec{R},\vec{R}';\omega) \equiv \vec{\vec{H}}(\vec{R}-\vec{R}',\omega) \equiv \begin{cases} \vec{\vec{F}}(\vec{R}-\vec{R}',\omega) & \text{for } |\vec{R}-\vec{R}'|>d \\ \frac{1}{2}\left[\vec{\vec{F}}(\vec{R}-\vec{R}',\omega)-\vec{\vec{F}}^{\dagger}(\vec{R}-\vec{R}',\omega)\right] & \text{for } |\vec{R}-\vec{R}'|<d. \end{cases} \tag{2.26}$$

With this definition eq. (2.6) remains unchanged but it follows from eqs. (2.7) and (2.8) that

$$\vec{\vec{H}}_\sigma(\vec{R},\vec{R}'';\omega) = \int d\vec{R}'\ \vec{\vec{\alpha}}(\vec{R},\vec{R}';\omega)\cdot\vec{\vec{H}}(\vec{R}'-\vec{R}'',\omega), \tag{2.27}$$

or in operator notation

$$\vec{\vec{H}}_\sigma = \vec{\vec{\alpha}}\cdot\vec{\vec{H}}. \tag{2.28}$$

The expression (2.25) then becomes

$$\vec{\vec{\chi}}^{ext}(\vec{k},\omega) = \left[(1+\vec{\vec{\alpha}}\cdot H)^{-1}\cdot\vec{\vec{\alpha}}\right]^{0}(\vec{k},\omega) \tag{2.29}$$

with $\vec{\vec{\alpha}}^{\lambda}(\vec{k},\omega)$ given by eq. (2.23) and

$$\vec{\vec{H}}^{\lambda}(\vec{k},\omega) = \vec{\vec{H}}(\vec{k},\omega)\delta_{\lambda,0}, \tag{2.30}$$

(see appendix A of paper I).

In the next section we shall evaluate this expression for a lattice in which each of the N molecules in a unit cell is considered as a point dipole-quadrupole.

3. The dielectric susceptibility for a composite point dipole and quadrupole lattice

In the case of a composite point dipole-quadrupole lattice the molecular polarizability tensors $\vec{\vec{\sigma}}_\ell(\vec{k},\vec{k}';\omega)$ in eq. (2.23) are, in cartesian components, given by (cf. eq.(II.2.20)):

$$\left[\vec{\vec{\sigma}}_\ell(\vec{k},\vec{k}';\omega)\right]_{\alpha\beta} = (2\pi)^{-3}\{\left[\vec{\vec{\alpha}}^{0}_{\ell}(\omega)\right]_{\alpha\beta} - i\left[\vec{\vec{\vec{\beta}}}{}'_{\ell}(\omega)\right]_{\alpha\beta\gamma}k_\gamma + i\left[\vec{\vec{\vec{\beta}}}_{\ell}(\omega)\right]_{\alpha\beta\gamma}k'_\gamma\}. \tag{3.1}$$

Equation (2.23) then becomes (in tensor notation)

$$\vec{\vec{\alpha}}^{\lambda}(\vec{k},\omega) = \rho\sum_{\ell=1}^{N}\{\vec{\vec{\alpha}}^{0}_{\ell}(\omega) - i\vec{\vec{\vec{\beta}}}{}'_{\ell}(\omega)\cdot\vec{k} + i\vec{\vec{\vec{\beta}}}_{\ell}(\omega)\cdot(\vec{k}-\vec{k}_\lambda)\}e^{-i\vec{k}_\lambda\cdot\vec{r}_\ell}. \tag{3.2}$$

We shall use this expression in eq. (2.29) in order to evaluate $\vec{\vec{\chi}}^{ext}(\vec{k},\omega)$ for this case.

First we define (cf. eqs. (II. 3.3) and (II.3.4))

$$\vec{\vec{f}}^{\lambda}(\vec{k},\omega) \equiv \left[(1+\vec{\vec{\alpha}}\cdot\vec{\vec{H}})^{-1}\right]^{\lambda}(\vec{k},\omega), \tag{3.3}$$

so that eq. (2.29) becomes:

$$\vec{\vec{\chi}}^{ext}(\vec{k},\omega) = \sum_{\lambda} \vec{\vec{f}}^{\lambda}(\vec{k},\omega)\cdot\vec{\vec{\alpha}}^{-\lambda}(\vec{k}-\vec{k}_{\lambda},\omega). \tag{3.4}$$

As we have shown in paper II (cf. eq. (II.3.7)) $\vec{\vec{f}}^{\lambda}(\vec{k},\omega)$ satisfies the equation

$$\vec{\vec{f}}^{\lambda}(\vec{k},\omega)+\sum_{\mu}\vec{\vec{f}}^{\mu}(\vec{k},\omega)\cdot\vec{\vec{\alpha}}^{\lambda-\mu}(\vec{k}-\vec{k}_{\mu},\omega)\cdot\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega) = \delta_{\lambda,0}. \tag{3.5}$$

From eq. (3.2) follows that

$$\begin{aligned}
\vec{\vec{\alpha}}^{\lambda-\mu}(\vec{k}-\vec{k}_{\mu},\omega) &= \rho\sum_{\ell=1}^{N}\{\vec{\vec{\alpha}}^{0}_{\ell}(\omega)-i\vec{\vec{\beta}}'_{\ell}(\omega)\cdot(\vec{k}-\vec{k}_{\mu})+i\vec{\vec{\beta}}_{\ell}(\omega)\cdot(\vec{k}-\vec{k}_{\lambda})\}e^{-i(\vec{k}_{\lambda}-\vec{k}_{\mu})\cdot\vec{r}_{\ell}} \\
&= \sum_{\ell=1}^{N}\vec{\vec{a}}_{\ell}(\vec{k},\omega)e^{-i(\vec{k}_{\lambda}-\vec{k}_{\mu})\cdot\vec{r}_{\ell}}+i\rho\sum_{\ell=1}^{N}\vec{\vec{\beta}}'_{\ell}(\omega)\cdot\vec{k}_{\mu}e^{-i(\vec{k}_{\lambda}-\vec{k}_{\mu})\cdot\vec{r}_{\ell}} \\
&\quad -i\rho\sum_{\ell=1}^{N}\vec{\vec{\beta}}_{\ell}(\omega)\cdot\vec{k}_{\lambda}e^{-i(\vec{k}_{\lambda}-\vec{k}_{\mu})\cdot\vec{r}_{\ell}},
\end{aligned} \tag{3.6}$$

in which

$$\vec{\vec{a}}_{\ell}(\vec{k},\omega) \equiv \rho\vec{\vec{\alpha}}^{0}_{\ell}(\omega) - i\rho\vec{\vec{\beta}}'_{\ell}(\omega)\cdot\vec{k} + i\rho\vec{\vec{\beta}}_{\ell}(\omega)\cdot\vec{k}. \tag{3.7}$$

Inserting eq. (3.6) into eq. (3.5) and using the definitions

$$\vec{\vec{f}}_{\ell}(\vec{k},\omega) \equiv \sum_{\mu}\vec{\vec{f}}^{\mu}(\vec{k},\omega)e^{i\vec{k}_{\mu}\cdot\vec{r}_{\ell}} \tag{3.8}$$

and

$$\vec{\vec{g}}_{\ell}(\vec{k},\omega) \equiv i\sum_{\mu}\vec{\vec{f}}^{\mu}(\vec{k},\omega)\cdot\rho\vec{\vec{\beta}}'_{\ell}(\omega)\cdot\vec{k}_{\mu}e^{i\vec{k}_{\mu}\cdot\vec{r}_{\ell}} \tag{3.9}$$

we obtain the equation for $\vec{\vec{f}}^{\lambda}(\vec{k},\omega)$:

$$\vec{\vec{f}}^{\lambda}(\vec{k},\omega)+\sum_{\ell=1}^{N}\vec{\vec{f}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{a}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell}}$$

$$+\sum_{\ell=1}^{N}\vec{\vec{g}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell}}$$

$$-i\sum_{\ell=1}^{N}\vec{\vec{f}}_{\ell}(\vec{k},\omega)\cdot\rho\vec{\vec{\vec{\beta}}}_{\ell}(\omega):\vec{k}_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell}}=\delta_{\lambda,0}. \tag{3.10}$$

Multiplying eq. (3.10) with $e^{i\vec{k}_{\lambda}\cdot\vec{r}_{m}}$ and summing over λ (i.e. summing over the reciprocal lattice) we obtain

$$\sum_{\ell=1}^{N}\vec{\vec{f}}_{\ell}(\vec{k},\omega)\cdot\{\delta_{\ell m}+\vec{\vec{a}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{A}}_{\ell,m}(\vec{k},\omega)-\vec{\vec{D}}_{\ell,m}(\vec{k},\omega)\}$$

$$+\sum_{\ell=1}^{N}\vec{\vec{g}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{A}}_{\ell,m}(\vec{k},\omega)=1, \tag{3.11}$$

where

$$\vec{\vec{A}}_{\ell,m}(\vec{k},\omega)\equiv\sum_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}}, \tag{3.12}$$

$$\vec{\vec{D}}_{\ell,m}(\vec{k},\omega)\equiv i\sum_{\lambda}\rho\vec{\vec{\vec{\beta}}}_{\ell}(\omega):\vec{k}_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}} \tag{3.13}$$

and

$$\vec{r}_{\ell m}=\vec{r}_{\ell}-\vec{r}_{m}. \tag{3.14}$$

Multiplying eq. (3.10) on the right with $i\rho\vec{\vec{\vec{\beta}}}'_{m}(\omega)\cdot\vec{k}_{\lambda}e^{i\vec{k}_{\lambda}\cdot\vec{r}_{m}}$ and summing over λ we furthermore obtain:

$$\sum_{\ell=1}^{N}\vec{\vec{f}}_{\ell}(\vec{k},\omega)\cdot\{\vec{\vec{a}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{D}}'_{\ell,m}(\vec{k},\omega)+\vec{\vec{E}}_{\ell,m}(\vec{k},\omega)\}$$

$$+\sum_{\ell=1}^{N}\vec{\vec{g}}_{\ell}(\vec{k},\omega)\cdot\{\delta_{\ell m}+\vec{\vec{D}}'_{\ell,m}(\vec{k},\omega)\}=0, \tag{3.15}$$

where

$$\vec{D}'_{\ell,m}(\vec{k},\omega) \equiv i\sum_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)\cdot\rho\vec{\vec{\beta}}'_{m}(\omega)\cdot\vec{k}_{\lambda}e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}} \qquad (3.16)$$

and

$$\vec{\vec{E}}_{\ell,m}(\vec{k},\omega) \equiv \sum_{\lambda}\rho\vec{\vec{\beta}}_{\ell}(\omega):\vec{k}_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)\cdot\rho\vec{\vec{\beta}}'_{m}(\omega)\cdot\vec{k}_{\lambda}e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}}. \qquad (3.17)$$

Thus the two sets of equations (3.11) and (3.15) determine $\vec{\vec{f}}_{\ell}(\vec{k},\omega)$ and $\vec{\vec{g}}_{\ell}(\vec{k},\omega)$. On the other hand we find from eqs. (3.2) and (3.4) together with the definitions (3.7), (3.8) and (3.9):

$$\vec{\vec{\chi}}^{ext}(\vec{k},\omega) = \sum_{\ell=1}^{N}\{\vec{\vec{f}}_{\ell}(\vec{k},\omega)\cdot\vec{\vec{a}}_{\ell}(\vec{k},\omega)+\vec{\vec{g}}_{\ell}(\vec{k},\omega)\}, \qquad (3.18)$$

(cf. eq. (II.3.20)).

So $\vec{\vec{\chi}}^{ext}(\vec{k},\omega)$ is known if the sets of equations (3.11) and (3.15) are solved. We are, however, interested in $\vec{\vec{\chi}}(\vec{k},\omega)$ which is related to $\vec{\vec{\chi}}^{ext}(\vec{k},\omega)$ by eq. (2.24). It is easily shown that we can write $\vec{\vec{\chi}}(\vec{k},\omega)$ in the form (cf. eqs. (II.3.26) and (II.3.27)):

$$\vec{\vec{\chi}}(\vec{k},\omega) = \{\vec{\vec{\mathcal{A}}}(\vec{k},\omega)\cdot\left[\vec{\vec{A}}(\vec{k},\omega)-\vec{\vec{F}}(\vec{k},\omega)\right]+1\}^{-1}\cdot\vec{\vec{\mathcal{A}}}(\vec{k},\omega), \qquad (3.19)$$

with

$$\vec{\vec{\mathcal{A}}}(\vec{k},\omega) = \{1-\vec{\vec{\chi}}^{ext}(\vec{k},\omega)\cdot\vec{\vec{A}}(\vec{k},\omega)\}^{-1}\cdot\vec{\vec{\chi}}^{ext}(\vec{k},\omega). \qquad (3.20)$$

Here we will choose (see eq. (3.12))

$$\vec{\vec{A}}(\vec{k},\omega) \equiv \vec{\vec{A}}_{\ell,\ell}(\vec{k},\omega) = \sum_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega). \qquad (3.21)$$

It then follows from eqs. (II.3.15) and (II.3.26) that eq. (3.19) can be written as

$$\vec{\vec{\chi}}(\vec{k},\omega) = \{\vec{\vec{\mathcal{A}}}(\vec{k},\omega)\cdot\left[\vec{\vec{M}}(\vec{k},\omega)-\tfrac{1}{3}\right]+1\}^{-1}\cdot\vec{\vec{\mathcal{A}}}(\vec{k},\omega), \qquad (3.22)$$

where the tensor $\vec{\vec{M}}(\vec{k},\omega)$ is defined by eq. (I.3.18).

Now we can rewrite eq. (3.11) as

$$\sum_{\ell=1}^{N} \vec{\vec{f}}_{\ell}\cdot\{\delta_{\ell m}+\vec{\vec{a}}_{\ell}\cdot(\vec{\vec{A}}_{\ell,m}-\vec{\vec{A}})-\vec{\vec{D}}_{\ell,m}\}+\sum_{\ell=1}^{N}\vec{\vec{g}}_{\ell}\cdot(\vec{\vec{A}}_{\ell,m}-\vec{\vec{A}})$$

$$= 1-\sum_{\ell=1}^{N}(\vec{\vec{f}}_{\ell}\cdot\vec{\vec{a}}_{\ell}+\vec{\vec{g}}_{\ell})\cdot\vec{\vec{A}}. \tag{3.23}$$

Defining

$$\vec{\vec{Q}}_{\ell,m}(\vec{k},\omega) \equiv \vec{\vec{A}}_{\ell,m}(\vec{k},\omega)-\vec{\vec{A}}(\vec{k},\omega) \tag{3.24}$$

and using eq. (3.18), eq. (3.23) becomes

$$\sum_{\ell=1}^{N} \vec{\vec{f}}_{\ell}\cdot\{\delta_{\ell m}+\vec{\vec{a}}_{\ell}\cdot\vec{\vec{Q}}_{\ell,m}-\vec{\vec{D}}_{\ell,m}\}+\sum_{\ell=1}^{N}\vec{\vec{g}}_{\ell}\cdot\vec{\vec{Q}}_{\ell,m} = 1-\vec{\vec{\chi}}^{ext}\cdot\vec{\vec{A}}. \tag{3.25}$$

So, if we define

$$\vec{\vec{f}}'_{\ell} \equiv (1-\vec{\vec{\chi}}^{ext}\cdot\vec{\vec{A}})^{-1}\cdot\vec{\vec{f}}_{\ell} \tag{3.26}$$

and

$$\vec{\vec{g}}'_{\ell} \equiv (1-\vec{\vec{\chi}}^{ext}\cdot\vec{\vec{A}})^{-1}\cdot\vec{\vec{g}}_{\ell} \tag{3.27}$$

and multiply eqs. (3.25) and (3.15) on the left with $(1-\vec{\vec{\chi}}^{ext}\cdot\vec{\vec{A}})^{-1}$ we get

$$\sum_{\ell=1}^{N} \vec{\vec{f}}'_{\ell}\cdot\{\delta_{\ell m}+\vec{\vec{a}}_{\ell}\cdot\vec{\vec{Q}}_{\ell,m}-\vec{\vec{D}}_{\ell,m}\} + \sum_{\ell=1}^{N}\vec{\vec{g}}'_{\ell}\cdot\vec{\vec{Q}}_{\ell,m} = 1 \tag{3.28}$$

and

$$\sum_{\ell=1}^{N} \vec{\vec{f}}'_{\ell}\cdot\{\vec{\vec{a}}_{\ell}\cdot\vec{\vec{D}}'_{\ell,m}+\vec{\vec{E}}_{\ell,m}\} + \sum_{\ell=1}^{N}\vec{\vec{g}}'_{\ell}\cdot\{\delta_{\ell m}+\vec{\vec{D}}'_{\ell,m}\} = 0. \tag{3.29}$$

On the other hand from eqs. (3.18), (3.20), (3.26) and (3.27) it follows that

$$\vec{\vec{\mathcal{A}}} = (1-\vec{\vec{\chi}}^{ext}\cdot\vec{\vec{A}})^{-1}\cdot\sum_{\ell=1}^{N}(\vec{\vec{f}}_{\ell}\cdot\vec{\vec{a}}_{\ell}+\vec{\vec{g}}_{\ell}) = \sum_{\ell=1}^{N}(\vec{\vec{f}}'_{\ell}\cdot\vec{\vec{a}}_{\ell}+\vec{\vec{g}}'_{\ell}). \tag{3.30}$$

So by solving the sets of equations (3.28) and (3.29), instead of the sets (3.11) and (3.15) we directly obtain the quantity $\vec{\vec{\mathcal{A}}}$, eq. (3.30), which appears in the expression (3.19) for the susceptibility tensor $\vec{\vec{\chi}}$. Note that for N=1 we can easily obtain from eqs. (3.28) - (3.30) the result in paper II: eq. (II.3.28) where $\vec{\vec{D}} = \vec{\vec{D}}_{\ell,\ell}$, $\vec{\vec{D}}' = \vec{\vec{D}}'_{\ell,\ell}$ and $\vec{\vec{E}} = \vec{\vec{E}}_{\ell,\ell}$. (From eqs. (3.21) and (3.24) follows that $\vec{\vec{Q}}_{\ell,\ell} = 0$).

In a similar way as we obtained a set of equations determining $\vec{\vec{\mathcal{F}}}$ instead of $\vec{\vec{\chi}}^{ext}$ we can also find a set of equations determining $\vec{\vec{\chi}}$ directly. In order to do this we rewrite eq. (3.11) as follows

$$\sum_{\ell=1}^{N} \vec{\vec{f}}_\ell \cdot \{\delta_{\ell m} + \vec{\vec{a}}_\ell \cdot \vec{\vec{R}}_{\ell,m} - \vec{\vec{D}}_{\ell,m}\} + \sum_{\ell=1}^{N} \vec{\vec{g}}_\ell \cdot \vec{\vec{R}}_{\ell,m}$$

$$= 1 - \sum_{\ell=1}^{N} (\vec{\vec{f}}_\ell \cdot \vec{\vec{a}}_\ell + \vec{\vec{g}}_\ell) \cdot \vec{\vec{F}} = 1 - \vec{\vec{\chi}}^{ext} \cdot \vec{\vec{F}}, \tag{3.31}$$

where

$$\vec{\vec{R}}_{\ell,m} \equiv \vec{\vec{A}}_{\ell,m} - \vec{\vec{F}} \ (= \vec{\vec{Q}}_{\ell,m} + \vec{\vec{A}} - \vec{\vec{F}} = \vec{\vec{Q}}_{\ell,m} + \vec{\vec{M}} - \tfrac{1}{3}). \tag{3.32}$$

Defining

$$\vec{\vec{f}}''_\ell \equiv (1 - \vec{\vec{\chi}}^{ext} \cdot \vec{\vec{F}})^{-1} \cdot \vec{\vec{f}}_\ell \tag{3.33}$$

and

$$\vec{\vec{g}}''_\ell \equiv (1 - \vec{\vec{\chi}}^{ext} \cdot \vec{\vec{F}})^{-1} \cdot \vec{\vec{g}}_\ell \tag{3.34}$$

and multiplying eqs. (3.31) and (3.15) on the left with $(1 - \vec{\vec{\chi}}^{ext} \cdot \vec{\vec{F}})^{-1}$ we get

$$\sum_{\ell=1}^{N} \vec{\vec{f}}''_\ell \cdot \{\delta_{\ell m} + \vec{\vec{a}}_\ell \cdot \vec{\vec{R}}_{\ell,m} - \vec{\vec{D}}_{\ell,m}\} + \sum_{\ell=1}^{N} \vec{\vec{g}}''_\ell \cdot \vec{\vec{R}}_{\ell,m} = 1 \tag{3.35}$$

and

$$\sum_{\ell=1}^{N} \vec{\vec{f}}''_\ell \cdot \{\vec{\vec{a}}_\ell \cdot \vec{\vec{D}}'_{\ell,m} + \vec{\vec{E}}_{\ell,m}\} + \sum_{\ell=1}^{N} \vec{\vec{g}}''_\ell \cdot \{\delta_{\ell m} + \vec{\vec{D}}'_{\ell m}\} = 0. \tag{3.36}$$

Now we have

$$\vec{\vec{X}} = (1-\vec{\vec{X}}^{ext}\cdot\vec{\vec{F}})^{-1}\cdot\vec{\vec{X}}^{ext} = (1-\vec{\vec{X}}^{ext}\cdot\vec{\vec{F}})^{-1}\cdot\sum_{\ell=1}^{N}(\vec{\vec{f}}_\ell\cdot\vec{\vec{a}}_\ell+\vec{\vec{g}}_\ell)$$

$$= \sum_{\ell=1}^{N}(\vec{\vec{f}}''_\ell\cdot\vec{\vec{a}}_\ell+\vec{\vec{g}}''_\ell). \tag{3.37}$$

The advantage of the evaluation of $\vec{\vec{\mathcal{A}}}$ in eq. (3.22) is that $\vec{\vec{\mathcal{A}}}$ is somewhat easier to calculate since the diagonal elements $\vec{\vec{Q}}_{\ell,\ell}=0$. Furthermore the form (3.22) is the same as the form of the susceptibility of a simple point dipole lattice where $\vec{\vec{\mathcal{A}}}=\rho\vec{\vec{\alpha}}^0$, which results in the Clausius Mosotti relation. We shall, however, determine the susceptibility tensor here directly from the sets of equations (3.35) - (3.37). We can write the formal solution of eqs. (3.35) and (3.36) as follows:

define

$$\vec{\vec{X}}_\ell \equiv \vec{\vec{f}}''_\ell\cdot\vec{\vec{a}}_\ell+\vec{\vec{g}}''_\ell \tag{3.38}$$

so that

$$\vec{\vec{X}} = \sum_{\ell=1}^{N}\vec{\vec{X}}_\ell. \tag{3.39}$$

Equations (3.35) and (3.36) then become

$$\sum_{\ell=1}^{N}\{\vec{\vec{X}}_\ell\cdot\vec{\vec{R}}_{\ell,m}+\vec{\vec{f}}''_\ell\cdot(\delta_{\ell m}-\vec{\vec{D}}_{\ell,m})\} = 1 \tag{3.40}$$

and

$$\sum_{\ell=1}^{N}\{\vec{\vec{X}}_\ell\cdot(\delta_{\ell m}+\vec{\vec{D}}'_{\ell,m}) + \vec{\vec{f}}''_\ell\cdot(\vec{\vec{E}}_{\ell,m}-\vec{\vec{a}}_\ell\delta_{\ell m})\} = 0. \tag{3.41}$$

From these equations $\vec{\vec{f}}''_\ell$ can be eliminated.

Before we do so we first introduce a matrix notation:

$\vec{\vec{R}}_{\ell,m}$ is represented by a 3Nx3N matrix $\underline{\underline{\vec{\vec{R}}}}$; $\vec{\vec{X}}_{\ell}$ is represented by a row of tensors: $\underline{\vec{\vec{X}}}$ and is thus a 3x3N matrix. The row of unit tensors is denoted by $\underline{\vec{\vec{e}}}$. The other quantities in eqs. (3.40) and (3.41) are represented by matrices in a similar way. For a term like $\sum_{\ell=1}^{N} \vec{\vec{X}}_{\ell}\cdot\vec{\vec{R}}_{\ell,m}$ we then write $\underline{\vec{\vec{X}}}\cdot\underline{\underline{\vec{\vec{R}}}}$. So eqs. (3.40) and (3.41) become

$$\underline{\vec{\vec{X}}}\cdot\underline{\underline{\vec{\vec{R}}}} + \underline{\vec{\vec{f}}}''\cdot(\underline{\underline{\vec{\vec{I}}}}-\underline{\underline{\vec{\vec{D}}}}) = \underline{\vec{\vec{e}}}, \tag{3.42}$$

$$\underline{\vec{\vec{X}}}\cdot(\underline{\underline{\vec{\vec{I}}}}+\underline{\underline{\vec{\vec{D}}}}')+\underline{\vec{\vec{f}}}''\cdot(\underline{\underline{\vec{\vec{E}}}}-\underline{\underline{\vec{\vec{a}}}}) = 0. \tag{3.43}$$

Here $\underline{\underline{\vec{\vec{I}}}}$ is the 3Nx3N unit matrix and

$$(\underline{\underline{\vec{\vec{a}}}})_{\ell,m} = \vec{\vec{a}}_{\ell}\delta_{\ell m}. \tag{3.44}$$

Furthermore we denote a column of tensors $\vec{\vec{c}}_{\ell}$ by $\underline{\tilde{\vec{\vec{c}}}}$ so that

$$\underline{\vec{\vec{b}}}\cdot\underline{\tilde{\vec{\vec{c}}}} = \sum_{\ell=1}^{N} \vec{\vec{b}}_{\ell}\cdot\vec{\vec{c}}_{\ell}. \tag{3.45}$$

The solution of eqs. (3.42) and (3.43) is now given by

$$\underline{\vec{\vec{X}}} = \underline{\vec{\vec{e}}}\cdot\{\underline{\underline{\vec{\vec{R}}}}-(\underline{\underline{\vec{\vec{I}}}}+\underline{\underline{\vec{\vec{D}}}}')\cdot(\underline{\underline{\vec{\vec{E}}}}-\underline{\underline{\vec{\vec{a}}}})^{-1}\cdot(\underline{\underline{\vec{\vec{I}}}}-\underline{\underline{\vec{\vec{D}}}})\}^{-1}, \tag{3.46}$$

where $(\underline{\underline{\vec{\vec{M}}}})^{-1}$ is the inverse matrix of $\underline{\underline{\vec{\vec{M}}}}$, not to be confused with the matrix of inverse tensors $\underline{\underline{\vec{\vec{M}}^{-1}}}$. From eq. (3.45), choosing $\underline{\vec{\vec{b}}} = \underline{\vec{\vec{X}}}$ and $\underline{\vec{\vec{c}}} = \underline{\vec{\vec{e}}}$, together with eqs. (3.39) and (3.46) we finally obtain

$$\vec{\vec{X}} = \underline{\vec{\vec{e}}}\cdot\{\underline{\underline{\vec{\vec{R}}}}-(\underline{\underline{\vec{\vec{I}}}}+\underline{\underline{\vec{\vec{D}}}}')\cdot(\underline{\underline{\vec{\vec{E}}}}-\underline{\underline{\vec{\vec{a}}}})^{-1}\cdot(\underline{\underline{\vec{\vec{I}}}}-\underline{\underline{\vec{\vec{D}}}})\}^{-1}\cdot\underline{\tilde{\vec{\vec{e}}}}\ . \tag{3.47}$$

The result of paper II (eq. (II.3.24)) for one molecule in a unit cell can easily be obtained from eq. (3.47) by taking N=1 and using $\vec{\vec{R}}_{1,1} = \vec{\vec{A}}-\vec{\vec{F}}$, $\vec{\vec{D}}_{1,1} = \vec{\vec{D}}$, $\vec{\vec{D}}'_{1,1} = \vec{\vec{D}}'$ and $\vec{\vec{E}}_{1,1} = \vec{\vec{E}}$, where $\vec{\vec{A}}$, $\vec{\vec{D}}$, $\vec{\vec{D}}'$ and $\vec{\vec{E}}$ are defined by eqs. (II.3.15) – (II.3.18).

Finally we remark that the lattice sums in the various quantities can be expressed in rapidly converging lattice sums as we did in papers I and II. These lattice sums are: $\vec{\vec{A}}_{\ell,m}(\vec{k},\omega)$, defined by eq. (3.12),

$$\vec{\vec{\vec{B}}}_{\ell,m}(\vec{k},\omega) \equiv \sum_{\lambda}\vec{k}_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}}, \tag{3.48}$$

contained in $\vec{D}_{\ell,m}$ and $\vec{D}'_{\ell,m}$, and

$$\vec{\vec{\vec{\vec{C}}}}_{\ell,m}(\vec{k},\omega) \equiv \sum_{\lambda}\vec{k}_{\lambda}\vec{k}_{\lambda}\vec{\vec{H}}(\vec{k}-\vec{k}_{\lambda},\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}}, \tag{3.49}$$

contained in $\vec{E}_{\ell,m}$. Just as in paper II we can write (cf. eqs. (II.3.26), (II.3.31) and (II.3.34)):

$$\vec{\vec{A}}_{\ell,m}(\vec{k},\omega) = \vec{\vec{M}}_{\ell,m}(\vec{k},\omega)+\vec{\vec{F}}(\vec{k},\omega)-\frac{1}{3}, \tag{3.50}$$

$$\vec{\vec{\vec{B}}}_{\ell,m}(\vec{k},\omega) = \vec{k}\vec{\vec{M}}_{\ell,m}(\vec{k},\omega)-\frac{1}{3}\vec{k}\vec{\vec{U}}+i\vec{\vec{\vec{N}}}_{\ell,m}(\vec{k},\omega) \tag{3.51}$$

and

$$\left[\vec{\vec{\vec{\vec{C}}}}_{\ell,m}(\vec{k},\omega)\right]_{\alpha\beta\gamma\delta} = k_{\alpha}k_{\beta}\left[\vec{\vec{M}}_{\ell,m}(\vec{k},\omega)\right]_{\gamma\delta}-\frac{1}{3}k_{\alpha}k_{\beta}\delta_{\gamma\delta}+ik_{\alpha}\left[\vec{\vec{\vec{N}}}_{\ell,m}(\vec{k},\omega)\right]_{\beta\gamma\delta}$$

$$+ ik_{\beta}\left[\vec{\vec{\vec{N}}}_{\ell,m}(\vec{k},\omega)\right]_{\alpha\gamma\delta}+\left[\vec{\vec{\vec{\vec{O}}}}_{\ell,m}(\vec{k},\omega)\right]_{\alpha\beta\gamma\delta}. \tag{3.52}$$

In an almost analogous way as in the previous papers we derive that for $\ell \neq m$:

$$\vec{\vec{M}}_{\ell,m}(\vec{k},\omega) = -\rho^{-1}\sum_{i}\left[(\vec{\nabla}\vec{\nabla}+\omega^{2})\{\mathrm{erfc}(\sqrt{\pi}\frac{R}{a})\frac{\cos\ \omega R}{4\pi R}\}e^{-i\vec{k}\cdot\vec{R}}\right]_{\vec{R}_i+\vec{r}_{\ell m}}$$

$$+ \sum_{\lambda}{}' \frac{(\vec{k}-\vec{k}_{\lambda})(\vec{k}-\vec{k}_{\lambda})-\omega^{2}}{|\vec{k}-\vec{k}_{\lambda}|^{2}-\omega^{2}}\mathscr{L}(|\vec{k}-\vec{k}_{\lambda}|,\omega)e^{-i\vec{k}_{\lambda}\cdot\vec{r}_{\ell m}} \qquad +$$

$$+\frac{\vec{k}\vec{k}-\omega^2}{k^2-\omega^2}\left[\mathcal{L}(k,\omega)-1\right]+\frac{1}{3}\ , \tag{3.53}$$

$$\vec{\vec{N}}_{\ell,m}(\vec{k},\omega) = -\rho^{-1}\sum_i\left[\vec{\nabla}(\vec{\nabla}\vec{\nabla}+\omega^2)\{\mathrm{erfc}(\sqrt{\pi}\tfrac{R}{a})\frac{\cos\,\omega R}{4\pi R}\}e^{-i\vec{k}\cdot\vec{R}}\right]_{\vec{R}_i+\vec{r}_{\ell m}}$$

$$+\ i{\sum_\lambda}'(\vec{k}-\vec{k}_\lambda)\frac{(\vec{k}-\vec{k}_\lambda)(\vec{k}-\vec{k}_\lambda)-\omega^2}{|\vec{k}-\vec{k}_\lambda|^2-\omega^2}\mathcal{L}(|\vec{k}-\vec{k}_\lambda|,\omega)e^{-i\vec{k}_\lambda\cdot\vec{r}_{\ell m}}$$

$$+\ i\vec{k}\,\frac{\vec{k}\vec{k}-\omega^2}{k^2-\omega^2}\left[\mathcal{L}(k,\omega)-1\right] \tag{3.54}$$

and

$$\vec{\vec{\vec{O}}}_{\ell,m}(\vec{k},\omega) = \rho^{-1}\sum_i\left[\vec{\nabla}\vec{\nabla}(\vec{\nabla}\vec{\nabla}+\omega^2)\{\mathrm{erfc}(\sqrt{\pi}\tfrac{R}{a})\frac{\cos\,\omega R}{4\pi R}\}e^{-i\vec{k}\cdot\vec{R}}\right]_{\vec{R}_i+\vec{r}_{\ell m}}$$

$$+\ {\sum_\lambda}'(\vec{k}-\vec{k}_\lambda)(\vec{k}-\vec{k}_\lambda)\frac{(\vec{k}-\vec{k}_\lambda)(\vec{k}-\vec{k}_\lambda)-\omega^2}{|\vec{k}-\vec{k}_\lambda|^2-\omega^2}\mathcal{L}(|\vec{k}-\vec{k}_\lambda|,\omega)e^{-i\vec{k}_\lambda\cdot\vec{r}_{\ell m}}$$

$$+\ \vec{k}\vec{k}\,\frac{\vec{k}\vec{k}-\omega^2}{k^2-\omega^2}\left[\mathcal{L}(k,\omega)-1\right]. \tag{3.55}$$

The function $\mathcal{L}(k,\omega)$ is defined by eq. (A.14) of paper II.

The cut off parameter <u>a</u> is some length of order of the lattice parameters or the intermolecular distances. (See II, page 31). Note that in the sums over $\vec{R}$-space the origin $\vec{R}_i=0$ is included. In the derivation of eqs. (3.53) - (3.55) we have used $\ell\neq m$ viz. by putting $\vec{\vec{H}}(\vec{R}_i+\vec{r}_{\ell m}) = \vec{\vec{F}}(\vec{R}_i+\vec{r}_{\ell m})$ for $\ell\neq m$. This is not true for $\ell=m$. In that case we must use the derivations of papers I and II yielding $\vec{\vec{M}}$, $\vec{\vec{N}}$ and $\vec{\vec{\vec{O}}}$: eqs. (I.3.27), (II.3.32) and (II.3.35). As already remarked at the end of the appendix of paper II we have used in eq. (I.3.27) a different cut off function.

4. First order spatial dispersion and optical activity

In section 3 we gave an expression (3.47) for the $\vec{k}$-dependent dielectric susceptibility tensor for a lattice with N point dipoles and quadrupoles in a unit cell. Under the assumption that this $\vec{k}$-dependence (spatial dispersion) is small we shall give in this section the result in 0th and 1st order.

According to eq. (3.46) we can write for the row of tensors $\underline{\vec{\vec{X}}}$:

$$\underline{\vec{\vec{X}}} = \underline{\vec{\vec{e}}}\cdot(\underline{\underline{\vec{\vec{T}}}})^{-1}, \tag{4.1}$$

with

$$\underline{\underline{\vec{\vec{T}}}} \equiv \underline{\underline{\vec{\vec{R}}}}-(\underline{\underline{\vec{\vec{I}}}}+\underline{\underline{\vec{\vec{D}}}}')\cdot(\underline{\underline{\vec{\vec{E}}}}-\underline{\underline{\vec{\vec{a}}}})^{-1}\cdot(\underline{\underline{\vec{\vec{I}}}}-\underline{\underline{\vec{\vec{D}}}}). \tag{4.2}$$

As can be seen from their definitons, together with eqs. (3.48) - (3.55), the elements of the various quantities appearing in $\underline{\underline{\vec{\vec{T}}}}$ can be expanded in powers of ak where $\underline{a}$ is the cut off parameter of order of the lattice parameters or the intermolecular distances. For values of k such that ak is small we can break off the expansion after the first order term. For the first two terms of e.g. $\underline{\underline{\vec{\vec{D}}}}$ we shall write:

$$\underline{\underline{\vec{\vec{D}}}} = \underline{\underline{\vec{\vec{D}}}}^{(0)}+\underline{\underline{\vec{\vec{D}}}}^{(1)}, \tag{4.3}$$

Thus we have up to first order:

$$(\underline{\underline{\vec{\vec{T}}}})^{-1} = (\underline{\underline{\vec{\vec{T}}}}^{(0)}+\underline{\underline{\vec{\vec{T}}}}^{(1)})^{-1} = (\underline{\underline{\vec{\vec{T}}}}^{(0)})^{-1}-(\underline{\underline{\vec{\vec{T}}}}^{(0)})^{-1}\cdot\underline{\underline{\vec{\vec{T}}}}^{(1)}\cdot(\underline{\underline{\vec{\vec{T}}}}^{(0)})^{-1}, \tag{4.4}$$

with

$$\underline{\underline{\vec{\vec{T}}}}^{(0)} = \underline{\underline{\vec{\vec{R}}}}^{(0)}-(\underline{\underline{\vec{\vec{I}}}}+\underline{\underline{\vec{\vec{D}}}}'^{(0)})\cdot(\underline{\underline{\vec{\vec{E}}}}^{(0)}-\underline{\underline{\vec{\vec{a}}}}^{(0)})^{-1}\cdot(\underline{\underline{\vec{\vec{I}}}}-\underline{\underline{\vec{\vec{D}}}}^{(0)}) \tag{4.5}$$

and

$$\underline{\underline{\overset{\rightrightarrows}{T}}}^{(1)} = \underline{\underline{\overset{\rightrightarrows}{R}}}^{(1)} + (\underline{\underline{\overset{\rightrightarrows}{I}}} + \underline{\underline{\overset{\rightrightarrows}{D}}}'^{(0)}) \cdot (\underline{\underline{\overset{\rightrightarrows}{E}}}^{(0)} - \underline{\underline{\overset{\rightrightarrows}{a}}}^{(0)})^{-1} \cdot \underline{\underline{\overset{\rightrightarrows}{D}}}^{(1)}$$

$$+ (\underline{\underline{\overset{\rightrightarrows}{I}}} + \underline{\underline{\overset{\rightrightarrows}{D}}}'^{(0)}) \cdot (\underline{\underline{\overset{\rightrightarrows}{E}}}^{(0)} - \underline{\underline{\overset{\rightrightarrows}{a}}}^{(0)})^{-1} \cdot (\underline{\underline{\overset{\rightrightarrows}{E}}}^{(1)} - \underline{\underline{\overset{\rightrightarrows}{a}}}^{(1)}) \cdot (\underline{\underline{\overset{\rightrightarrows}{E}}}^{(0)} - \underline{\underline{\overset{\rightrightarrows}{a}}}^{(0)})^{-1} \cdot (\underline{\underline{\overset{\rightrightarrows}{I}}} - \underline{\underline{\overset{\rightrightarrows}{D}}}^{(0)})$$

$$- \underline{\underline{\overset{\rightrightarrows}{D}}}'^{(1)} \cdot (\underline{\underline{\overset{\rightrightarrows}{E}}}^{(0)} - \underline{\underline{\overset{\rightrightarrows}{a}}}^{(0)})^{-1} \cdot (\underline{\underline{\overset{\rightrightarrows}{I}}} - \underline{\underline{\overset{\rightrightarrows}{D}}}^{(0)}). \tag{4.6}$$

For the expansion of $\underline{\overset{\rightrightarrows}{X}}$, eq. (4.1), we then have

$$\underline{\overset{\rightrightarrows}{X}} = \underline{\overset{\rightrightarrows}{X}}^{(0)} + \underline{\overset{\rightrightarrows}{X}}^{(1)} = \underline{\overset{\rightrightarrows}{e}} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} - \underline{\overset{\rightrightarrows}{e}} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} \cdot \underline{\underline{\overset{\rightrightarrows}{T}}}^{(1)} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} \tag{4.7}$$

and for the susceptibility $\overset{\rightrightarrows}{\chi}$:

$$\overset{\rightrightarrows}{\chi} = \overset{\rightrightarrows}{\chi}^{(0)} + \overset{\rightrightarrows}{\chi}^{(1)}, \tag{4.8}$$

with

$$\overset{\rightrightarrows}{\chi}^{(0)} = \underline{\overset{\rightrightarrows}{e}} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} \cdot \underline{\tilde{\overset{\rightrightarrows}{e}}} = \sum_{\ell,m=1}^{N} (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1}_{\ell,m} \tag{4,9}$$

and

$$\overset{\rightrightarrows}{\chi}^{(1)} = -\underline{\overset{\rightrightarrows}{e}} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} \cdot \underline{\underline{\overset{\rightrightarrows}{T}}}^{(1)} \cdot (\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)})^{-1} \cdot \underline{\tilde{\overset{\rightrightarrows}{e}}}. \tag{4.10}$$

Using eq. (4.7) and the fact that $\underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)} = \underline{\underline{\tilde{\overset{\rightrightarrows}{T}}}}^{(0)^{T}}$ (see below) we can write for $\overset{\rightrightarrows}{\chi}^{(1)}$ (eq. (4.10))

$$\overset{\rightrightarrows}{\chi}^{(1)} = -\underline{\overset{\rightrightarrows}{X}}^{(0)} \cdot \underline{\underline{\overset{\rightrightarrows}{T}}}^{(1)} \cdot \underline{\tilde{\overset{\rightrightarrows}{X}}}^{(0)^{T}} = -\sum_{\ell,m=1}^{N} \overset{\rightrightarrows}{X}_{\ell}^{(0)} \cdot \overset{\rightrightarrows}{T}_{\ell,m}^{(1)} \cdot \overset{\rightrightarrows}{X}_{m}^{(0)^{T}}. \tag{4.11}$$

The superscript T stands for transposition of the (3-dimensional) tensors. The meaning of the tilda is:

$$(\underline{\underline{\tilde{\overset{\rightrightarrows}{A}}}})_{\ell,m} = \overset{\rightrightarrows}{A}_{m,\ell}. \tag{4.12}$$

So, for a product of two of such matrices:

$$\widetilde{(\underline{\underline{\overset{\rightrightarrows}{A}}} \cdot \underline{\underline{\overset{\rightrightarrows}{B}}})}^{T} = \underline{\underline{\tilde{\overset{\rightrightarrows}{B}}}}^{T} \cdot \underline{\underline{\tilde{\overset{\rightrightarrows}{A}}}}^{T}. \tag{4.13}$$

The fact that $\underline{\underline{\tilde{\overset{\rightrightarrows}{T}}}}^{(0)^{T}} = \underline{\underline{\overset{\rightrightarrows}{T}}}^{(0)}$ can be seen as follows. In the expression

(4.5) for $\underline{\underline{\vec{\vec{T}}}}^{(0)}$ is $\underline{\underline{\vec{\vec{R}}}}^{(0)} = \tilde{\underline{\underline{\vec{\vec{R}}}}}^{(0)^T}$ which can be seen from the definitions (3.32) and (3.12). It is a consequence of the fact that the tensor $\vec{\vec{H}}(\vec{k}_\lambda)$ is symmetric and an even function of $\vec{k}_\lambda$ so that only the even terms of the exponent in eq. (3.12) contribute. In the same way only the even terms of the exponent in def. (3.17) contribute for $\vec{k}=0$. Moreover $\beta'_{\alpha\beta\gamma} = \beta_{\beta\alpha\gamma}$ which follows from the symmetry of the molecular polarizability tensor $\vec{\vec{\alpha}}_\ell$ so that $\tilde{\underline{\underline{\vec{\vec{E}}}}}^{(0)^T} = \underline{\underline{\vec{\vec{E}}}}^{(0)}$. From the (see paper II page 33) symmetry property of $\vec{\vec{\alpha}}_\ell$ follows also that $\rho\vec{\vec{\alpha}}^{0}_\ell$ is symmetric so that $\tilde{\underline{\vec{\vec{a}}}}^{(0)^T} = \underline{\vec{\vec{a}}}^{(0)}$. Finally we have $\tilde{\vec{\vec{D}}}'^{(0)^T} = -\vec{\vec{D}}^{(0)}$ which is a consequence of the symmetry relation between $\vec{\vec{\vec{\beta}}}'$ and $\vec{\vec{\vec{\beta}}}$ and of the fact that in the 0th order term of (3.16) only the odd terms of the exponent contribute. In a similar way as we can derive the symmetry of $\underline{\vec{\vec{T}}}^{(0)}$ we find from eq. (4.6) that

$$\tilde{\underline{\vec{\vec{T}}}}^{(1)^T} = -\underline{\vec{\vec{T}}}^{(1)}. \qquad (4.14)$$

so that

$$\vec{\vec{T}}^{(1)^T}_{\ell,m} = -\vec{\vec{T}}^{(1)}_{m,\ell} \text{ and } \vec{\vec{T}}^{(1)}_{\ell,\ell} = 0. \qquad (4.15)$$

Applying this property to eq. (4.11) we obtain for $\vec{\vec{X}}^{(1)}$:

$$\vec{\vec{X}}^{(1)} = \vec{\vec{\Phi}} - \vec{\vec{\Phi}}^T, \qquad (4.16)$$

with

$$\vec{\vec{\Phi}} = -\sum_{\substack{m,\ell=1\\ m<\ell}}^{N} \vec{\vec{X}}^{(0)}_m \cdot \vec{\vec{T}}^{(1)}_{m,\ell} \cdot \vec{\vec{X}}^{(0)^T}_\ell . \qquad (4.17)$$

Because $\vec{\vec{T}}^{(1)}_{m,\ell}$ is of first order in $\vec{k}$ we can write for $\vec{\vec{\Phi}}$

(in cartesian components):

$$\phi_{\alpha\beta} = i\psi_{\alpha\beta\gamma}k_{\gamma}\,, \tag{4.18}$$

from which we arrive at the gyration tensor in the same way as in section 4 of paper II (cf. eqs. (II.4.28)-(II.4.35)):

$$g_{\gamma\delta} = \delta_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\,, \tag{4.19}$$

where $\delta_{\alpha\beta\gamma}$ is the permutation tensor or Levi-Civita tensor.

Now the first order spatial dispersion of the dielectric susceptibility and therefore the optical activity is known if the positions of the N molecules in the unit cell, the structure of the lattice and the values of $\vec{\vec{\alpha}}_\ell$ and $\vec{\vec{\vec{\beta}}}_\ell$ of each of the N molecules are known. The computation of the 0th and 1st order of the lattice sums and the matrix operations have to be carried out numerically. The calculations above are simplified by the fact that the lattice sums (3.53) - (3.55) are even functions in $a\omega$. Since terms of order $a^2\omega^2$ and higher can be neglected in this first order theory one may put $\omega=0$ in those lattice sums.

In the next section we shall finally show how the expressions reduce in the case of N point dipoles in a unit cell.

5. The susceptibility of a composite point dipole lattice

We obtain the susceptibility for the case of N point dipoles in a unit cell from the results of the foregoing sections by setting $\vec{\vec{\vec{\beta}}}_\ell$ and $\vec{\vec{\vec{\beta}}}'_\ell$ equal to zero. This means that $\vec{\vec{D}}_{\ell,m}$, $\vec{\vec{D}}'_{\ell,m}$ and

$\vec{E}_{\ell,m}$ (eqs. (3.13), (3.16) and (3.17)) become zero and $\vec{\vec{a}}_{\ell}$ reduces to $\rho\vec{\vec{\alpha}}^{0}_{\ell}$ (eq. (3.7)). The expression (3.47) for the susceptibility then reduces to

$$\vec{\vec{\chi}} = \underline{\vec{e}}\cdot\left[\,\underline{\underline{\vec{\vec{R}}}}+(\underline{\underline{\vec{\vec{a}}}})^{-1}\right]^{-1}\cdot\tilde{\underline{\vec{\vec{e}}}} = \sum_{\ell,m=1}^{N}\left[\,\underline{\underline{\vec{\vec{R}}}}+(\underline{\underline{\vec{\vec{a}}}})^{-1}\right]^{-1}_{\ell,m}, \tag{5.1}$$

where now (cf. eq. (3.44))

$$\vec{\vec{a}}_{\ell,m} = \rho\vec{\vec{\alpha}}^{0}_{\ell}\delta_{\ell m}, \tag{5.2}$$

so that

$$(\underline{\underline{\vec{\vec{a}}}})^{-1}_{\ell,m} = (\rho\vec{\vec{\alpha}}^{0}_{\ell})^{-1}\delta_{\ell m}. \tag{5.3}$$

Here $(\rho\vec{\vec{\alpha}}^{0}_{\ell})^{-1}$ is the inverse tensor of $\rho\vec{\vec{\alpha}}^{0}_{\ell}$. If we restrict ourselves again to 0th and 1st order spatial dispersion we get for the 0th and 1st order susceptibility:

$$\vec{\vec{\chi}}^{(0)} = \sum_{\ell=1}^{N}\vec{\vec{\chi}}^{(0)}_{\ell} = \sum_{\ell,m=1}^{N}\left[\,\underline{\underline{\vec{\vec{R}}}}^{(0)}+(\underline{\underline{\vec{\vec{a}}}})^{-1}\right]^{-1}_{\ell,m} \tag{5.4}$$

and

$$\vec{\vec{\chi}}^{(1)} = -\sum_{\ell,m=1}^{N}\vec{\vec{\chi}}^{(0)}_{\ell}\cdot\vec{\vec{R}}^{(1)}_{\ell,m}\cdot\vec{\vec{\chi}}^{(0)T}_{m} \tag{5.5}$$

For $\vec{\vec{R}}^{(0)}_{\ell,m}$ and $\vec{\vec{R}}^{(1)}_{\ell,m}$ we have with eqs. (3.32) and (3.50)

$$\vec{\vec{R}}^{(0)}_{\ell,m} = \vec{\vec{M}}^{(0)}_{\ell,m}-\frac{1}{3} \tag{5.6}$$

and

$$\vec{\vec{R}}^{(1)}_{\ell,m} = \vec{\vec{M}}^{(1)}_{\ell,m}. \tag{5.7}$$

Here $\vec{\vec{M}}^{(0)}_{\ell,m}$ and $\vec{\vec{M}}^{(1)}_{\ell,m}$ are the 0th and 1st order terms of the lattice sum $\vec{\vec{M}}_{\ell,m}$ (eq. (3.53)). In these two sums we can neglect the ω-dependence which is of order $a^2\omega^2$ and higher. The result is then for $\ell \neq m$

$$\vec{\vec{M}}^{(0)}_{\ell,m} = \frac{\rho^{-1}}{4\pi} \sum_i \left[\frac{1-3\hat{\vec{R}}\hat{\vec{R}}}{R^3} \{ \mathrm{erfc}(\sqrt{\pi}\frac{R}{a}) + \frac{2R}{a} e^{-\frac{\pi R^2}{a^2}} \} - \hat{\vec{R}}\hat{\vec{R}} \frac{4\pi}{a^3} e^{-\frac{\pi R^2}{a^2}} \right]_{\vec{R}_i+\vec{r}_{\ell m}}$$

$$+ \sum_\lambda{}' \vec{k}_\lambda \vec{k}_\lambda e^{-\frac{a^2 k_\lambda^2}{4\pi}} \cos(\vec{k}_\lambda \cdot \vec{r}_{\ell m}) + \frac{1}{3} \tag{5.8}$$

and

$$\vec{\vec{M}}^{(1)}_{\ell,m} = -i\vec{k}\cdot \left[\frac{\rho^{-1}}{4\pi} \sum_i \left[\frac{\hat{\vec{R}}-3\hat{\vec{R}}\hat{\vec{R}}\hat{\vec{R}}}{R^2} \{ \mathrm{erfc}(\sqrt{\pi}\frac{R}{a}) + \frac{2R}{a} e^{-\frac{\pi R^2}{a^2}} \} \right.\right.$$

$$\left. - \hat{\vec{R}}\hat{\vec{R}}\hat{\vec{R}} \frac{4\pi R}{a^3} e^{-\frac{\pi R^2}{a^2}} \right]_{\vec{R}_i+\vec{r}_{\ell m}} + \sum_\lambda{}' \{ \hat{\vec{k}}_\lambda \hat{\vec{k}}_\lambda \hat{\vec{k}}_\lambda (\frac{a^2}{2\pi} + \frac{2}{k_\lambda^2}) k_\lambda e^{-\frac{a^2 k_\lambda^2}{4\pi}}$$

$$\left. - (\vec{\vec{U}}\hat{\vec{k}}_\lambda + \hat{\vec{k}}_\lambda \vec{\vec{U}}) \frac{1}{k_\lambda} e^{-\frac{a^2 k_\lambda^2}{4\pi}} \} \sin(\vec{k}_\lambda \cdot \vec{r}_{\ell m}) \right]. \tag{5.9}$$

Here $\hat{\vec{R}} \equiv \vec{R}/R$ and $\hat{\vec{k}}_\lambda \equiv \vec{k}_\lambda / k_\lambda$.

This result forms in fact the basis of the numerical calculations of Endeman.$^{4)}$

Finally we give here the 0th and 1st order susceptibility for a lattice with two point dipoles in a unit cell (N=2) for which case the explicit forms of $\vec{\vec{\chi}}^{(0)}_1$ and $\vec{\vec{\chi}}^{(0)}_2$ can easily be calculated. For this simple case we have the following properties of the lattice sums:

$$\vec{\vec{R}}^{(0)}_{1,1} = \vec{\vec{R}}^{(0)}_{2,2} = \vec{\vec{M}}^{(0)} - \frac{1}{3}, \tag{5.10}$$

where $\vec{\vec{M}}^{(0)}$ is given by eq. (I.4.7),

$$\vec{\vec{R}}_{1,2}^{(0)} = \vec{\vec{R}}_{2,1}^{(0)} = \vec{\vec{M}}_{1,2}^{(0)} - \frac{1}{3} \equiv \vec{\vec{R}}^{(0)}, \tag{5.11}$$

$$\vec{\vec{R}}_{1,1}^{(1)} = \vec{\vec{R}}_{2,2}^{(1)} = 0 \tag{5.12}$$

and

$$\vec{\vec{R}}_{1,2}^{(1)} = -\vec{\vec{R}}_{2,1}^{(1)} \equiv \vec{\vec{R}}^{(1)}. \tag{5.13}$$

We then have for $\vec{\vec{X}}^{(0)}$ and $\vec{\vec{X}}^{(1)}$:

$$\vec{\vec{X}}^{(0)} = \vec{\vec{X}}_1^{(0)} + \vec{\vec{X}}_2^{(0)} \tag{5.14}$$

and

$$\vec{\vec{X}}^{(1)} = \vec{\vec{X}}_2^{(0)} \cdot \vec{\vec{R}}^{(1)} \cdot \vec{\vec{X}}_1^{(0)\,T} - \vec{\vec{X}}_1^{(0)} \cdot \vec{\vec{R}}^{(1)} \cdot \vec{\vec{X}}_2^{(0)\,T}. \tag{5.15}$$

For $\vec{\vec{X}}_1^{(0)}$ amd $\vec{\vec{X}}_2^{(0)}$ we have

$$\underset{(2)}{\vec{\vec{X}}_1^{(0)}} = \{1 - \vec{\vec{R}}^{(0)} \cdot (\vec{\vec{M}}^{(0)} - \frac{1}{3} + \underset{(2)}{\vec{\vec{a}}_1^{\,-1}})^{-1}\} \cdot \{\vec{\vec{R}}^{(0)} - (\vec{\vec{M}}^{(0)} - \frac{1}{3} + \underset{(2)}{\vec{\vec{a}}_1^{\,-1}})$$

$$\cdot \vec{\vec{R}}^{(0)\,-1} \cdot (\vec{\vec{M}}^{(0)} - \frac{1}{3} - \underset{(1)}{\vec{\vec{a}}_2^{\,-1}})\}^{-1}, \tag{5.16}$$

in which $\vec{\vec{a}}_1 = \rho\vec{\vec{\alpha}}_1^{0}$ and $\vec{\vec{a}}_2 = \rho\vec{\vec{\alpha}}_2^{0}$ are the polarizabilities of the two molecules.

References

1) Hafkenscheid, L.M. and Vlieger, J., Physica <u>75</u> (1974) 57.

2) Hafkenscheid, L.M. and Vlieger, J., Physica <u>79A</u> (1975) 517.

3) Maaskant, W.J.A. and Oosterhoff, L.J., Molecular Phys. <u>8</u> (1964) 319.

4) Endeman, H.J., Thesis Utrecht, (1965).

Samenvatting

De macroscopische diëlectrische eigenschappen van een systeem worden gekarakteriseerd door de diëlectrische susceptibiliteit. In het algemeen is deze grootheid een tensor die (in de lineaire theorie) het polarisatieveld lineair verbindt met het electrische Maxwell veld. Van ruimtelijke dispersie spreekt men als de polarisatie in een bepaald punt niet alleen afhankelijk is van het electrische Maxwell veld in hetzelfde punt, maar ook van dat veld in alle andere punten door middel van een integraalrelatie. Heeft men te maken met een homogeen oneindig medium dan komt dit tot uitdrukking in het feit dat, na Fourier transformatie, de polarisatie in een punt in de golfgetalruimte lineair afhangt van het electrische veld in hetzelfde punt middels een golfgetalafhankelijke complexe diëlectrische susceptibiliteit.

Ons doel is nu deze golfgetalafhankelijke diëlectrische susceptibiliteit af te leiden uit de microscopische eigenschappen van het systeem, in dit geval een moleculair kristal. In een afzonderlijk molecuul wordt door het daarop werkende (effectieve) electrische veld een dipool moment verdeling geïnduceerd die men lineair afhankelijk veronderstelt (ook met ruimtelijke dispersie) van het electrische veld door middel van een moleculaire polariseerbaarheidstensor. Deze moleculaire polariseerbaarheidstensor kan kwantummechanisch berekend worden. Wij beschouwen deze grootheid als gegeven. Als op het moleculaire kristal een tijdsafhankelijk uitwendig electrisch veld werkt dan bestaat het effectieve veld dat op een molecuul werkt uit dit uitwendige veld en de stralingsvelden van alle moleculen. De totale microscopische polarisatie van het kristal die daar het gevolg van is, kan in de golfgetalruimte geschreven worden als een reciproke-roostersom waarvan iedere term het produkt is van een uitwendige susceptibiliteit en het uitwendige veld, beide afhankelijk van de reciproke roosterpunten. Voor een macroscopische beschrijving van het systeem beschouwt men slechts die Fouriercomponenten van de polarisatie en het uitwendige veld, waarvoor het golfgetal in de eerste Brillouinzone ligt. Het gevolg is dat van bovengenoemde reciproke roostersom slechts één term overblijft die de polarisatie lineair verbindt met het uitwendige veld voor hetzelfde golfgetal. Dit geeft de golfgetal-afhankelijke uitwendige susceptibiliteit van het kristal, dat verder als homogeen (zij het in het algemeen anisotroop) beschouwd kan worden. De fenomenologische Maxwell theorie levert de relatie tussen deze uitwendige susceptibiliteit en de diëlectrische susceptibiliteit waaruit een uitdrukking voor de laatste afgeleid kan worden in termen van reciproke-roostersommen. In deze afleiding van de diëlectrische susceptibiliteit hebben we slechts verondersteld dat het uitwendige veld langzaam varieert over een rooster afstand. Voor de moleculaire stralingsvelden zijn geen veronderstellingen gemaakt. De (formele) uitdrukking voor de diëlectrische susceptibiliteit kan verder uitgewerkt worden door een multipoolontwikkeling te maken van de geïnduceerde moleculaire dipoolmomentverdeling. Wij zijn nagegaan in hoeverre het afbreken van deze reeksontwikkeling is toegestaan.

De orde van grootte van de ruimtelijke dispersie (golfgetal-afhankelijkheid) van de diëlectrische susceptibiliteit wordt bepaald door de verhouding tussen de moleculaire afmetingen of de moleculaire afstanden en de golflengte van het macroscopische veld. Voor optische golflengtes is deze verhouding klein en is ruimtelijke dispersie een kwantitatief klein effect, dat kwalitatief echter tot nieuwe effecten aanleiding kan geven. Zo wordt bijvoorbeeld het bekende effect van optische activiteit (dat is de draaiing van de polarisatierichting van lineair gepolariseerd licht dat zich voortplant door een medium) bepaald door de ruimtelijke dispersie in eerste orde, dus door de eerste orde term in de ontwikkeling van de susceptibiliteit naar machten van de bovengenoemde verhouding.

Men kan onderscheid maken tussen ruimtelijke dispersie die het gevolg is van de eindige moleculaire afstanden (ruimtelijke dispersie met betrekking tot het rooster) en ruimtelijke dispersie die het gevolg is van de eindige moleculaire afmetingen (moleculaire ruimtelijke dispersie). Heeft men te maken met enkelvoudige Bravais roosters (hoofdstuk I en II) dan volgt uit symmetriebeschouwingen dat er voor wat het rooster betreft geen ruimtelijke dispersie van oneven orde kan zijn. Voor dat geval kan optische activiteit slechts het gevolg zijn van moleculaire ruimtelijke dispersie. Voor enkelvoudige punt dipool roosters hebben we het effect van de tweede orde ruimtelijke dispersie (met betrekking tot het rooster) berekend. Dit effect leidt bijvoorbeeld tot optische anisotropie van kubische punt dipool roosters. In hoofdstuk II hebben wij de moleculaire ruimtelijke dispersie in eerste orde in rekening gebracht. Dat wil zeggen dat wij naast het electrische dipool moment ook het electrische quadrupool moment en het magnetische dipool moment van de moleculen in rekening hebben gebracht. Dit leidt tot optische activiteit, maar blijkt bovendien ook van invloed te zijn op de susceptibiliteit voor golfgetal gelijk aan nul. In hoofdstuk III worden samengestelde roosters beschouwd, in het bijzonder samengestelde punt dipool en quadrupool roosters. In tegenstelling tot het enkelvoudige rooster kan het samengestelde rooster ook eerste orde ruimtelijke dispersie vertonen wanneer de moleculen slechts beschouwd worden als punt dipolen.

De uitdrukkingen voor de susceptibiliteit in de verschillende gevallen bevatten roostersommen die langzaam convergent zijn. Volgens een methode, ontwikkeld voor Ewald en later gegeneraliseerd door Nijboer en De Wette, worden deze sommen elk omgezet in twee snel convergerende sommen, één over het rooster en één over het reciproke rooster. Deze snel convergerende rooster sommen kunnen voor elk kristal type gemakkelijk numeriek berekend worden. Wij hebben de berekeningen uitgevoerd voor een paar eenvoudige voorbeelden.

Studiegegevens

In 1963 legde ik het eindexamen H.B.S.-B af aan het St. Jans-College te Den Haag en begon ik mijn studie aan de Rijksuniversiteit te Leiden.

Het candidaatsexamen natuur- en wiskunde met bijvak sterrekunde legde ik af in februari 1968, het doctoraalexamen theoretische natuurkunde met bijvakken numerieke wiskunde en mechanica in september 1971. Gedurende mijn studie verrichtte ik experimenteel werk op het gebied van het Faraday effect in de groep van Dr. D. de Klerk op het Kamerlingh Onnes Laboratorium.

Van september 1971 tot december 1974 was ik werkzaam op het Instituut-Lorentz voor theoretische natuurkunde te Leiden. Het onderzoek dat ik daar verrichtte onder leiding van Dr. J. Vlieger leidde tot dit proefschrift. Hierbij waren ook de discussies met Dr. D. Bedeaux zeer nuttig.

Sinds januari 1975 ben ik als wetenschappelijk medewerker verbonden aan het Koninklijk Nederlands Meteorologisch Instituut te De Bilt.

STELLINGEN

I. In de nulde-orde diëlectrische tensor van een niet-isotroop moleculair kristal komen bijdragen voor die afkomstig zijn van de hogere-orde multipolen van de moleculen. Voor de bijdragen van de eerste- en tweede-orde multipolen kan worden aangetoond dat de vorm van de Lorentz-Lorenzformule daarbij in essentie behouden blijft.

Hoofdstuk II van dit proefschrift.

II. Bij de afleiding van de algemene formule voor de diëlectrische susceptibiliteit van een moleculair kristal behoeft slechts verondersteld te worden dat het uitwendige electrische veld langzaam varieert over de eenheidscel van het kristal.

Hoofdstuk I en III van dit proefschrift.

III. Een oneindig puntdipool-quadrupoolrooster verstrooit geen licht met golfvector in de eerste Brillouinzone.

Hoofdstuk II van dit proefschrift.

IV. Voor het numeriek "oplossen" van een overbepaald stelsel lineaire vergelijkingen volgens de discrete Chebyshev-approximatie bestaat een adekwaat computerprogramma.

V. De door Ruelle afgeleide noodzakelijke voorwaarde voor het bestaan van een faseovergang in een ééndimensionale Ising-ferromagneet waarvan de interactie afneemt met de afstand heeft een analogon in het percolatiemodel.

Ruelle, D., Commun. Math. Phys. 9 (1968) 153.

VI. Een aanzienlijke verfijning van het meteorologisch meetnet leidt niet tot een belangrijke verlenging van de termijn waarover de atmosfeer voorspelbaar is.

Lorenz, E.N., Bull. Amer. Meteor. Soc. 50 (1969) 345.
Smagorinsky, J.S., Bull. Amer. Meteor. Soc. 50 (1969) 286.

VII. In de theorie van Peterson en Fixman over de viscositeit van polymeeroplossingen wordt ten onrechte de variatie van het snelheidsveld van de vloeistof over de afmetingen van het polymeer verwaarloosd.

Peterson, J.M. en Fixman, M., J. Chem. Phys. 39 (1963) 2516.

VIII. Bij de beschrijving van molecuulvorming bij kathodeverstuiving door middel van recombinatie van onafhankelijk verstoven atomen dient men uit te gaan van de energieverdeling van de atomen binnen het rooster en niet van de experimenteel gemeten verdeling buiten het rooster.

Können, G.P., Tip, A. en de Vries, A.E., Rad. Effects 26 (1975) 23.

IX. Er zijn bezwaren aan te voeren tegen de in onderstaande artikelen gebruikte methode van ruimtelijke middeling.

Vlieger, J., Can. J. Phys. 49 (1971) 1384.
Sipe, J.E. en van Kranendonk, J., Phys. Rev. A9 (1974) 1806.

L.M. Hafkenscheid Leiden, 2 juni 1976