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Van der Waals attraction in symmetric arrays

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Abstract. The allowed electromagnetic modes in the presence of a symmetric array of macroscopic bodies are investigated. They are systematically classified by their behaviour with respect to the different symmetry operations. In the presence of two bodies we require the modes to be even or odd, in the presence of lattices we apply Floquet's theorem. The van der Waals (vdW) energy of the array under consideration is calculated from the average quantum energy of the electromagnetic modes. Since finite boundary conditions are used, no difficulties regarding branchpoints and different Riemann surfaces are encountered. Closed expressions for the vdW energy in periodic lattices of spheres or cylinders are obtained, which can be explicitly evaluated at a reasonable rate of effort.

1. Introduction

Recently, a number of powerful methods for treating the vdW attraction between macroscopic bodies have been proposed. The integration of the average quantum energy of the allowed electromagnetic modes has been simplified by using Green function techniques (van Kampen *et al* 1968, Richmond and Ninham 1971, Gerlach 1971). Exact summations of the reaction field approach have been reported (Bade 1957, Renne *et al* 1967, 1968, Langbein 1971a, b). The overall equivalence of the two procedures has been shown (Renne *et al* 1967, 1968, Langbein 1971a). The physical difficulties originally encountered in investigations based on Green function techniques have been eliminated by assuming finite boundary conditions (Langbein 1973a, b, c). The final energy expression turns out to be more transparent than that evolving from earlier treatments, that is, the frequency integration over the susceptibilities involved runs along the total imaginary axis rather than twice along the positive imaginary half-axis (Langbein 1973a, b, c).

These drastic simplifications of the general procedure suggest a reconsideration of the vdW attraction in different geometrical structures. The successful application of the Green function technique has been reported for the case of half-spaces and multilayers (van Kampen *et al* 1968, Ninham and Parsegian 1970a, b). The reaction field approach was used for calculating the vdW energy between spheres and cylinders (Langbein 1971c, 1972, Mitchell and Ninham 1972, Parsegian 1972, Langbein 1972, Mitchell *et al* 1973a, b). Since this approach starts with fluctuations at a distinct position, it does not *a priori* account for the possible symmetry operations of the array under consideration.

In order to find the vdW energy of an array of dielectric bodies we need the frequencies of all allowed electromagnetic modes. By using Green function techniques it is possible to exploit the different symmetry operations. The number of secular equations resulting from the boundary conditions at the surfaces of the bodies investigated is reduced considerably if it is taken into account that any allowed mode remains allowed on application of any symmetry operation. If the array under consideration is invariant against inversion, as is true in the presence of two identical spheres or cylinders, the allowed modes are even or odd with respect to inversion. If we consider a tetrahedral array, we find modes having s character and others which pick up a phase factor $\exp(2n\pi i/3)$ on rotation by $2\pi/3$. When investigating a periodic lattice we conclude from the equivalence of all lattice sites that there are allowed modes gaining a phase factor $\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_j)$ on any translation $\boldsymbol{r}_j$. This fact is known as Floquet's or Bloch's theorem and has already been used in investigations on the vdW attraction between periodic multilayers (Langbein 1973c), which may be considered as one-dimensional lattices. Floquet's theorem reduces the set of secular equations between the field amplitudes in the different layers to finite order.

In the present paper we treat arrays of both spheres and cylinders. In particular, we consider pairs and periodic lattices. We emphasize the equivalence of the treatment of spheres and cylinders in all steps of the calculations. The main difference between the two cases is the fact that the modes used in the presence of spheres are not normalizable without introducing a cavity (finite boundary conditions), whereas in the presence of cylinders the cavity is not needed.

However, when integrating the change in energy of the allowed modes relative to the limit of infinite separation, we shift the frequency integration to the imaginary axis. This implies that the radial wavenumber of the spherical modes becomes imaginary, too, and the size of the cavity can be increased towards infinity without further obstacles. Now the treatment of spheres and cylinders is fully equivalent again. In both cases the dependence of the coupling parameters on the separation is given by modified Bessel functions of the second kind.

The effort involved for the investigation of the vdW attraction in periodic lattices is only slightly higher than that required in the presence of pairs. This is due to the application of Floquet's theorem, which reduces the field amplitudes at the different lattice sites to those at an individual site. If we restrict the investigations to dipole and quadrupole interactions, only a few interaction terms are left. The typical difference to the findings from a continuum approach (van Kampen *et al* 1968, Lifshitz 1955, Dzyaloshinskii *et al* 1959) is the fact that the Green function is now periodic and that the wavenumber integration is reduced to one cell of the reciprocal lattice.

2. Eigenvectors

The problem of finding the allowed electromagnetic modes for an array of dielectric bodies assumes that it is possible to solve Maxwell's equations in the presence of a single body. Complete sets of eigenvectors $\boldsymbol{D}(\boldsymbol{r}, s)$ of Maxwell's equations are available for dielectric spheres, cylinders and films (Morse and Feshbach 1953). In the case of spheres it is convenient to start with the electric and magnetic modes

$$\boldsymbol{D}_1(\boldsymbol{r}, s) = \operatorname{curl}\operatorname{curl}\boldsymbol{r} f_m(kr) Y_m^\mu(\vartheta, \varphi) \qquad (1a)$$

$$\boldsymbol{D}_2(\boldsymbol{r}, s) = k \operatorname{curl}\boldsymbol{r} f_m(kr) Y_m^\mu(\vartheta, \varphi) \qquad (2a)$$

where $f_m(kr)$ is a spherical Bessel function $j_m(kr)$, $y_m(kr)$ of the first or second kind. s

represents the triplet

$$s = (k, m, \mu) \tag{3a}$$

and k satisfies the relation

$$k^2 = \left(\frac{\omega}{c}\right)^2 \epsilon(\omega)\mu(\omega). \tag{4a}$$

In the case of cylinders we have analogously

$$\boldsymbol{D}_1(\boldsymbol{r}, s) = \operatorname{curl}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}F_m(lr)\,\mathrm{e}^{\mathrm{i}m\varphi} \tag{1b}$$

$$\boldsymbol{D}_2(\boldsymbol{r}, s) = \frac{\omega}{c}(\epsilon\mu)^{1/2}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}F_m(lr)\,\mathrm{e}^{\mathrm{i}m\varphi} \tag{2b}$$

where $F_m(lr)$ is a modified cylindrical Bessel function $I_m(lr)$, $K_m(lr)$ of the first or second kind. $\boldsymbol{n}$ is the unit vector parallel to the cylinder axis. s represents the triplet

$$s = (k, l, m) \tag{3b}$$

and k and l satisfy the relation

$$k^2 = l^2 + \left(\frac{\omega}{c}\right)^2 \epsilon(\omega)\mu(\omega). \tag{4b}$$

For films see the respective equations (1) to (4) in Langbein (1973c).

3. Boundary conditions

The allowed eigenvectors $\boldsymbol{D}(\boldsymbol{r}, s)$ of Maxwell's equations must not have singularities in finite space. The fields inside the bodies under consideration, therefore, are not allowed to contain Bessel functions of the second kind. At the boundaries we have to assume continuity of the normal components of the electric displacement and the magnetic induction and of the tangential components of the electric and the magnetic fields. These are six boundary conditions, which can be reduced to four owing to the fact that (i) the normal component of the electric displacement and the tangential components of the magnetic field, and (ii) the normal component of the magnetic induction and the tangential components of the electric field, are linearly dependent.

Satisfying these boundary conditions in the presence of a single sphere yields the exterior fields (Ruppin and Englman 1968)

$$\boldsymbol{D}_1(\boldsymbol{r}, s) = \operatorname{curl}\operatorname{curl}\boldsymbol{r}(a_{11}j_m(k_0r) + a_{12}y_m(k_0r))Y_m^\mu(\vartheta, \varphi) \tag{5a}$$

$$\boldsymbol{D}_2(\boldsymbol{r}, s) = k_0\operatorname{curl}\boldsymbol{r}(a_{21}j_m(k_0r) + a_{22}y_m(k_0r))Y_m^\mu(\vartheta, \varphi) \tag{6a}$$

where

$$\begin{vmatrix} j_m(k_1R) & a_{11}j_m(k_0R) + a_{12}y_m(k_0R) \\ \epsilon_1^{-1}(k_1Rj_m(k_1R))' & \epsilon_0^{-1}\{k_0R(a_{11}j_m(k_0R) + a_{12}y_m(k_0R))\}' \end{vmatrix} = 0 \tag{7a}$$

$$\begin{vmatrix} j_m(k_1R) & a_{21}j_m(k_0R) + a_{22}y_m(k_0R) \\ \mu_1^{-1}(k_1Rj_m(k_1R))' & \mu_0^{-1}\{k_0R(a_{21}j_m(k_0R) + a_{22}y_m(k_0R))\}' \end{vmatrix} = 0. \tag{8a}$$

Equations (7a) and (8a) relate to a sphere of radius R, electric susceptibility $\epsilon_1(\omega)$, and magnetic susceptibility $\mu_1(\omega)$ in a surrounding medium with susceptibilities $\epsilon_0(\omega)$, $\mu_0(\omega)$.

Satisfying the boundary conditions in the presence of a single cylinder requires mixing of electric and magnetic modes. We obtain the exterior field (Langbein 1972, Mitchell *et al* 1973a, b)

$$\boldsymbol{D}(\boldsymbol{r}, s) = \operatorname{curl}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}(a_{11}I_m(l_0r)+a_{12}K_m(l_0r))\,\mathrm{e}^{\mathrm{i}m\varphi}$$

$$+\frac{\omega}{c}(\epsilon_0\mu_0)^{1/2}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}(a_{21}I_m(l_0r)+a_{22}K_m(l_0r))\,\mathrm{e}^{\mathrm{i}m\varphi} \tag{5b}$$

where

$$\frac{km}{l_0l_1R}\frac{\omega}{c}\frac{\epsilon_0\mu_0-\mu_1\epsilon_1}{\epsilon_1(\epsilon_0\mu_0)^{1/2}}(a_{21}I_m(l_0R)+a_{22}K_m(l_0R))I_m(l_1R)$$

$$+\begin{vmatrix} l_1\epsilon_1^{-1}I_m(l_1R) & l_0\epsilon_0^{-1}(a_{11}I_m(l_0R)+a_{12}K_m(l_0R)) \\ (I_m(l_1R))' & (a_{11}I_m(l_0R)+a_{12}K_m(l_0R))' \end{vmatrix} = 0 \tag{7b}$$

$$\frac{km}{l_0l_1R}\frac{\omega}{c}\frac{\epsilon_0\mu_0-\epsilon_1\mu_1}{\mu_1(\epsilon_0\mu_0)^{1/2}}(a_{11}I_m(l_0R)+a_{12}K_m(l_0R))I_m(l_1R)$$

$$+\begin{vmatrix} l_1\mu_1^{-1}I_m(l_1R) & l_0\mu_0^{-1}(a_{21}I_m(l_0R)+a_{22}K_m(l_0R)) \\ (I_m(l_1R))' & (a_{21}I_m(l_0R)+a_{22}K_m(l_0R))' \end{vmatrix} = 0. \tag{8b}$$

As above, the radius of the cylinder is R, its susceptibilities are $\epsilon_1(\omega)$, $\mu_1(\omega)$, and those in the exterior are $\epsilon_0(\omega)$, $\mu_0(\omega)$.

With respect to the boundary conditions in the case of films, see equations (5) and (6) in Langbein (1973c).

4. Normalizability

The boundary conditions at the surfaces of the bodies under consideration render only two relations between the four amplitudes $a_{11}, a_{12}, a_{21}, a_{22}$. We have to look for an additional physical argument yielding two further relations. This additional argument is the normalizability of all allowed electric or magnetic modes.

From the asymptotic behaviour of the spherical Bessel functions for large arguments $j_m(kr) \simeq (kr)^{-1}\sin(kr-\frac{1}{2}m\pi)$, $y_m(kr) \simeq -(kr)^{-1}\cos(kr-\frac{1}{2}m\pi)$ we learn that the electric and magnetic modes (5*a*) and (6*a*) cannot be normalized in infinite space. We rather have to introduce finite boundaries and to normalize all modes within the resulting cavity. Consequently, the allowed modes depend on the properties and the size of the cavity. In the following calculations of the vdW energy between symmetric arrays of bodies we will eliminate the properties of the cavity by increasing its size towards infinity.

The cavity eventually turns out to be an auxiliary condition for splitting up the continuous energy spectrum of allowed electromagnetic modes during the integration.

Several types of cavities may be suggested:

(i) a perfectly conducting cavity, which requires that the tangential components of the electric field vanish at the boundaries;

(ii) a perfectly diamagnetic cavity, which requires that the tangential components of the magnetic field vanish at the boundaries;

(iii) a totally reflecting cavity, which requires that the normal components of the electric displacement and of the magnetic induction vanish at the boundaries.

All three types of cavities have been used repeatedly in investigations into normal modes of dielectric bodies. In view of the fact that the cavity only serves as an auxiliary condition in our investigations, we choose it to be totally reflecting. Then, electric and magnetic modes can be treated fully symmetrically.

When considering a single sphere with radius R it is convenient to let the cavity also be a sphere of radius S. We obtain the auxiliary boundary conditions.

$$a_{11} j_m(k_0 S) + a_{12} y_m(k_0 S) = 0 \tag{9a}$$

$$a_{21} j_m(k_0 S) + a_{22} y_m(k_0 S) = 0. \tag{10a}$$

When considering a single cylinder we do not need a cavity at all. The Bessel functions $I_m(kr)$ increase exponentially with increasing argument, that is, we know that the correct limit for infinite size of the cavity is given by

$$a_{11} = 0 \tag{9b}$$

$$a_{21} = 0. \tag{10b}$$

In the case of the films, where the possible electric and magnetic modes are mainly plane waves, we again need a cavity and choose it to be a thick plate (see Langbein 1973c). Equations (7) to (10) enable us to calculate all allowed modes in the presence of single bodies.

5. Addition theorems

The simplest example of a symmetric array of dielectric bodies is that with two identical bodies 1 and 2. In this case we build up all modes symmetrically from those centred around the individual bodies. The exterior fields in the presence of two bodies now contain eight amplitudes $a_{11}(j)$, $a_{12}(j)$, $a_{21}(j)$, $a_{22}(j)$; $j = 1, 2$. The subscripts, as in equations (5) and (6), refer to electric and magnetic modes and to Bessel functions of the first and second kind, respectively.

Between these eight amplitudes, the boundary conditions at the surfaces of the bodies 1 and 2 give rise to four relations analogous to equations (7) and (8). However, before using these relations we have to transform the fields from body 1 to body 2 and vice versa. In other words, we need the addition theorems between the eigenvectors $\boldsymbol{D}(\boldsymbol{r}-\boldsymbol{r}_j, s)$ of Maxwell's equations. The existence of such addition theorems is guaranteed by the fact that any complete set of eigenvectors of a linear differential equation can be expanded in terms of any other complete set.

In order to derive the addition theorems for the spherical fields (1a), (2a) it is appropriate to introduce inversely oriented spherical coordinates, as shown in figure 1. By

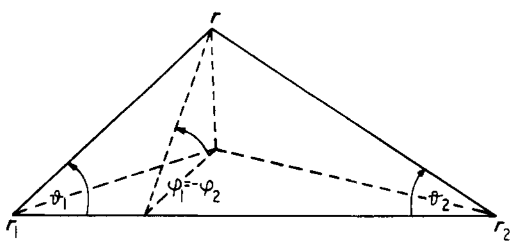

Figure 1. Inverted spherical coordinates.

repeatedly differentiating the addition theorem for spherical Bessel functions of order zero (see equations (10.1.45) and (10.1.46) in Abramowitz and Stegun 1965) with respect to distance and angle we obtain

$$f_m(k|\boldsymbol{r}-\boldsymbol{r}_2|)Y_m^\mu(\vartheta_2,\varphi_2) = \sum_{n=\mu}^{\infty}(2n+1)U_{mn}^\mu(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)j_n(k|\boldsymbol{r}-\boldsymbol{r}_1|)Y_n^{-\mu}(\vartheta_1,\varphi_1) \tag{11a}$$

where

$$U_{mn}^\mu(\zeta) = \left(\frac{2}{\zeta}\right)^\mu \sum_{\nu=0}^{m-\mu}(-1)^\nu \frac{\Gamma(m-\nu+\frac{1}{2})\Gamma(n-\nu+\frac{1}{2})\Gamma(\mu+\nu+\frac{1}{2})}{\Gamma(m+n-\mu-\nu+\frac{3}{2})\Gamma(\mu+\frac{1}{2})\Gamma(\frac{1}{2})}$$
$$\times\frac{(m+n-\nu)!}{(m-\mu-\nu)!(n-\mu-\nu)!\nu!}(m+n-\mu-2\nu+\tfrac{1}{2})f_{m+n-\mu-2\nu}(\zeta). \tag{12a}$$

From this scalar addition theorem we find that for the magnetic modes (2*a*)

$$\begin{aligned}\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_2)&f_m(k|\boldsymbol{r}-\boldsymbol{r}_2|)Y_m^\mu(\vartheta_2,\varphi_2)\\ &= \sum_{n=\mu}^{\infty}(2n+1)\{V_{mn}^\mu(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_1)j_n(k|\boldsymbol{r}-\boldsymbol{r}_1|)Y_n^{-\mu}(\vartheta_1,\varphi_1)\\ &\quad + W_{mn}^\mu(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)k^{-1}\operatorname{curl}\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_1)j_n(k|\boldsymbol{r}-\boldsymbol{r}_1|)Y_n^{-\mu}(\vartheta_1,\varphi_1)\}\end{aligned} \tag{13a}$$

where

$$V_{mn}^\mu(\zeta) = U_{mn}^\mu(\zeta) - \frac{n-\mu+1}{(n+1)(2n+1)}\zeta U_{mn+1}^\mu(\zeta) - \frac{n+\mu}{n(2n+1)}\zeta U_{mn-1}^\mu(\zeta) \tag{14a}$$

$$W_{mn}^\mu(\zeta) = \frac{\mathrm{i}\mu}{n(n+1)}\zeta U_{mn}^\mu(\zeta). \tag{15a}$$

The corresponding theorem for the electric modes (1*a*) is obtained by applying another curl operator, which mainly entails an exchange of the coefficients $V_{mn}^\mu(\zeta)$ and $W_{mn}^\mu(\zeta)$ at the right-hand side of (13*a*). We find both addition theorems to couple electric and magnetic modes. A detailed description of the derivation of relations (11*a*) to (15*a*) will be reported elsewhere.

The addition theorems for the cylindrical fields (1*b*), (2*b*) are readily available in literature. Introducing mutually inverted cylindrical coordinates as shown in figure 2, we obtain from Graf's addition theorem (see equation (9.1.79) in Abramowitz and Stegun 1965)

$$I_m(l|\boldsymbol{r}-\boldsymbol{r}_2|)\exp(\mathrm{i}m\varphi_2) = \sum_{n=-\infty}^{+\infty} I_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|)I_n(l|\boldsymbol{r}-\boldsymbol{r}_1|)\exp\{\mathrm{i}n(\varphi_1+\pi)\} \tag{11b}$$

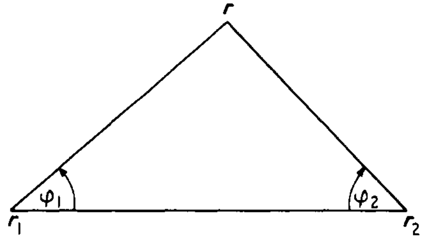

Figure 2. Inverted cylindrical coordinates.

$$K_m(l|\boldsymbol{r}-\boldsymbol{r}_2|)\exp(im\varphi_2) = \sum_{n=-\infty}^{+\infty} K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|)I_n(l|\boldsymbol{r}-\boldsymbol{r}_1|)\exp(in\varphi_1). \tag{12b}$$

These theorems apply immediately also to the vector fields (1*b*), (2*b*). In the case of spheres we find electric and magnetic mode coupling by the addition theorem, whereas in the case of cylinders this coupling is caused by the boundary conditions.

6. Pair states: spheres

Returning now to the calculation of allowed modes in the presence of two identical bodies 1 and 2 we note that the spherical addition theorem (13*a*) basically couples modes of different orders m and n. Any dipole, quadrupole, or octupole at $\boldsymbol{r}_2$ induces dipoles, quadrupoles, and octupoles at $\boldsymbol{r}_1$, and vice versa. There is no coupling of modes showing different rotational behaviour. Hence, we build up the allowed modes from

$$\begin{aligned}\boldsymbol{D}(\boldsymbol{r}, s) = \sum_{j=1,2}\sum_{m=\mu}^{\infty}\Bigg(&\operatorname{curl}\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_j)\boldsymbol{a}_1(m, j)\boldsymbol{f}_m(k|\boldsymbol{r}-\boldsymbol{r}_j|)\frac{Y_m^{\pm\mu}(\vartheta_j, \varphi_j)}{(m\pm\mu)!}\\ &+k\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_j)\boldsymbol{a}_2(m, j)\boldsymbol{f}_m(k|\boldsymbol{r}-\boldsymbol{r}_j|)\frac{Y_m^{\pm\mu}(\vartheta_j, \varphi_j)}{(m\pm\mu)!}\Bigg)\end{aligned} \tag{16a}$$

where

$$\boldsymbol{a}_i(m, j)\boldsymbol{f}_m(k|\boldsymbol{r}-\boldsymbol{r}_j|) = a_{i1}(m, j)j_m(k|\boldsymbol{r}-\boldsymbol{r}_j|)+a_{i2}(m, j)y_m(k|\boldsymbol{r}-\boldsymbol{r}_j|). \tag{17a}$$

The inversion of the order of the spherical harmonics $Y_m^{\pm\mu}(\vartheta_j, \varphi_j)$ centred around bodies 1 and 2 guarantees the same rotational behaviour according to $\varphi_2 = -\varphi_1$. Transposing the modes centred around body 2 to body 1 by means of addition theorem (13*a*), we find these terms to contain only Bessel functions $j_n(k|\boldsymbol{r}-\boldsymbol{r}_1|)$ of first kind. This is due to the condition $|\boldsymbol{r}-\boldsymbol{r}_1| < |\boldsymbol{r}_2-\boldsymbol{r}_1|$ involved in addition theorems (11*a*) and (13*a*). This condition is always satisfied at the surface of body 1, where continuity of the different components of the electromagnetic field causes boundary conditions (7*a*), (8*a*). We wind up with

$$\begin{aligned}\kappa_1(m)a_{11}(m, 1)+\kappa_2(m)a_{12}(m, 1)+\kappa_1(m)(2m+1)\sum_{n=\mu}^{\infty}\frac{(m+\mu)!}{(n-\mu)!}\\ \times\{\boldsymbol{a}_1(n, 2)\boldsymbol{V}_{nm}^{-\mu}(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)+\boldsymbol{a}_2(n, 2)\boldsymbol{W}_{nm}^{-\mu}(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)\} = 0\end{aligned} \tag{18a}$$

$$\begin{aligned}\lambda_1(m)a_{21}(m, 1)+\lambda_2(m)a_{22}(m, 1)+\lambda_1(m)(2m+1)\sum_{n=\mu}^{\infty}\frac{(m+\mu)!}{(n-\mu)!}\\ \times\{\boldsymbol{a}_2(n, 2)\boldsymbol{V}_{nm}^{-\mu}(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)+\boldsymbol{a}_1(n, 2)\boldsymbol{W}_{nm}^{-\mu}(k|\boldsymbol{r}_2-\boldsymbol{r}_1|)\} = 0\end{aligned} \tag{19a}$$

where

$$\kappa_1(m) = \begin{vmatrix} j_m(k_1R) & j_m(k_0R) \\ \epsilon_1^{-1}(k_1Rj_m(k_1R))' & \epsilon_0^{-1}(k_0Rj_m(k_0R))' \end{vmatrix} \tag{20a}$$

$$\kappa_2(m) = \begin{vmatrix} j_m(k_1R) & y_m(k_0R) \\ \epsilon_1^{-1}(k_1Rj_m(k_1R))' & \epsilon_0^{-1}(k_0Ry_m(k_0R))' \end{vmatrix} \tag{21a}$$

$$\lambda_1(m) = \begin{vmatrix} j_m(k_1R) & j_m(k_0R) \\ \mu_1^{-1}(k_1Rj_m(k_1R))' & \mu_0^{-1}(k_0Rj_m(k_0R))' \end{vmatrix} \tag{22a}$$

$$\lambda_2(m) = \begin{vmatrix} j_m(k_1R) & y_m(k_0R) \\ \mu_1^{-1}(k_1Rj_m(k_1R))' & \mu_0^{-1}(k_0Ry_m(k_0R))' \end{vmatrix}. \tag{23a}$$

To satisfy the boundary conditions at the surface of body 2 we have to transpose the modes centred at body 1 to body 2 and once more apply equations (7*a*) and (8*a*). The resulting conditions differ from equations (18*a*) and (19*a*) by the exchange of bodies 1 and 2 and by inversion of the order μ.

We know from symmetry arguments that the allowed modes must be even or odd on exchange of bodies 1 and 2; in fact both systems of boundary conditions are found to become identical by using

$$\frac{(m+\mu)!}{(n-\mu)!}V_{nm}^{-\mu}(\zeta) = \frac{(m-\mu)!}{(n+\mu)!}V_{nm}^{\mu}(\zeta) \tag{24a}$$

$$\frac{(m+\mu)!}{(n-\mu)!}W_{nm}^{-\mu}(\zeta) = -\frac{(m-\mu)!}{(n+\mu)!}W_{nm}^{\mu}(\zeta) \tag{25a}$$

and

$$\boldsymbol{a}_1(m, 2) = \pm\boldsymbol{a}_1(m, 1); \qquad \boldsymbol{a}_2(m, 2) = \mp\boldsymbol{a}_2(m, 1). \tag{26a}$$

The electric and the magnetic contributions to the allowed modes have the inverse symmetry behaviour. We obtain

$$\kappa_1(m)a_{11}(m, 1)+\kappa_2(m)a_{12}(m, 1)\pm\kappa_1(m)(2m+1)\sum_{n=\mu}^{\infty}\frac{(m-\mu)!}{(n+\mu)!}$$
$$\times(\boldsymbol{a}_1(n, 1)\boldsymbol{V}_{nm}^{\mu}+\boldsymbol{a}_2(n, 1)\boldsymbol{W}_{nm}^{\mu}) = 0 \tag{27a}$$

$$\lambda_1(m)a_{21}(m, 1)+\lambda_2(m)a_{22}(m, 1)\mp\lambda_1(m)(2m+1)\sum_{n=\mu}^{\infty}\frac{(m-\mu)!}{(n+\mu)!}$$
$$\times(\boldsymbol{a}_2(n, 1)\boldsymbol{V}_{nm}^{\mu}+\boldsymbol{a}_1(n, 1)\boldsymbol{W}_{nm}^{\mu}) = 0. \tag{28a}$$

The final boundary conditions (27*a*) and (28*a*) for the amplitudes $a_{11}(m, j)$, $a_{12}(m, j)$, $a_{21}(m, j)$ and $a_{22}(m, j)$ at body 1 and body 2 do not impose any condition on the ratios $a_{12}(m, j)/a_{11}(m, j)$ and $a_{22}(m, j)/a_{21}(m, j)$, that is, for normalizing the modes under investigation we are free to use equations (9*a*) and (10*a*). Then all amplitudes are fixed. All possible eigenfrequencies result from the secular determinant following from (9*a*), (10*a*) and (27*a*), (28*a*).

7. Pair states: cylinders

The investigation of allowed modes in the presence of two cylinders is analogous to that in the presence of two spheres. However, the calculations are mathematically simpler because the normalization conditions (9*b*), (10*b*) exclude Bessel functions of the first kind from the very beginning. Accordingly, we build up the allowed modes from

$$\boldsymbol{D}(\boldsymbol{r}, s) = \sum_{j=1,2}\sum_{m=-\infty}^{+\infty}\Big(\mathrm{curl\,curl}\,\boldsymbol{n}\,\mathrm{e}^{ikz}a_{12}(m, j)K_m(l|\boldsymbol{r}-\boldsymbol{r}_j|)\exp(\mathrm{i}m\varphi_j)$$
$$+\frac{\omega}{c}(\epsilon_0\mu_0)^{1/2}\,\mathrm{curl}\,\boldsymbol{n}\,\mathrm{e}^{ikz}a_{22}(m, j)K_m(l|\boldsymbol{r}-\boldsymbol{r}_j|)\exp(\mathrm{i}m\varphi_j)\Big). \tag{16b}$$

Transposing the modes centred at body 2 to body 1 by means of the addition theorem (12*b*), we again find the transposed terms to contain only Bessel functions $I_n(l|\boldsymbol{r}-\boldsymbol{r}_1|)$ of the first kind. Satisfying the boundary conditions (7*b*) and (8*b*) at the surface of body 1 yields

$$\kappa_1(m)a_{12}(m,1)+\lambda_1(m)\sum_{n=-\infty}^{+\infty} a_{12}(n,2)K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|)$$

$$+\kappa_2(m)\sum_{n=-\infty}^{+\infty} a_{22}(n,2)K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|) = 0 \tag{18b}$$

$$\kappa_1(m)a_{22}(m,1)+\lambda_2(m)\sum_{n=-\infty}^{+\infty} a_{22}(n,2)K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|)$$

$$+\kappa_2(m)\sum_{n=-\infty}^{+\infty} a_{12}(n,2)K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|) = 0 \tag{19b}$$

where

$$\kappa_1(m) = \begin{vmatrix} l_1\epsilon_1^{-1}I_m(l_1R) & l_0\epsilon_0^{-1}K_m(l_0R) \\ (I_m(l_1R))' & (K_m(l_0R))' \end{vmatrix}\begin{vmatrix} l_1\mu_1^{-1}I_m(l_1R) & l_0\mu_0^{-1}K_m(l_0R) \\ (I_m(l_1R))' & (K_m(l_0R))' \end{vmatrix}$$

$$-\left(\frac{km}{l_0l_1R}\,\frac{\omega}{c}(\epsilon_1\mu_1-\epsilon_0\mu_0)I_m(l_1R)\right)^2\frac{K_m^2(l_0R)}{\epsilon_0\mu_0\epsilon_1\mu_1} \tag{20b}$$

$$\kappa_2(m) = km\frac{\omega}{c}\,\frac{\epsilon_1\mu_1-\epsilon_0\mu_0}{\epsilon_1\mu_1(\epsilon_0\mu_0)^{1/2}}\left(\frac{I_m(l_1R)}{l_0R}\right)^2 \tag{21b}$$

$$\lambda_1(m) = \begin{vmatrix} l_1\epsilon_1^{-1}I_m(l_1R) & l_0\epsilon_0^{-1}I_m(l_0R) \\ (I_m(l_1R))' & (I_m(l_0R))' \end{vmatrix}\begin{vmatrix} l_1\mu_1^{-1}I_m(l_1R) & l_0\mu_0^{-1}K_m(l_0R) \\ (I_m(l_1R))' & (K_m(l_0R))' \end{vmatrix}$$

$$-\left(\frac{km}{l_0l_1R}\,\frac{\omega}{c}(\epsilon_1\mu_1-\epsilon_0\mu_0)I_m(l_1R)\right)^2\frac{I_m(l_0R)K_m(l_0R)}{\epsilon_0\mu_0\epsilon_1\mu_1} \tag{22b}$$

$$\lambda_2(m) = \begin{vmatrix} l_1\epsilon_1^{-1}I_m(l_1R) & l_0\epsilon_0^{-1}K_m(l_0R) \\ (I_m(l_1R))' & (K_m(l_0R))' \end{vmatrix}\begin{vmatrix} l_1\mu_1^{-1}I_m(l_1R) & l_0\mu_0^{-1}I_m(l_0R) \\ (I_m(l_1R))' & (I_m(l_0R))' \end{vmatrix}$$

$$-\left(\frac{km}{l_0l_1R}\,\frac{\omega}{c}(\epsilon_1\mu_1-\epsilon_0\mu_0)I_m(l_1R)\right)^2\frac{I_m(l_0R)K_m(l_0R)}{\epsilon_0\mu_0\epsilon_1\mu_1}. \tag{23b}$$

To satisfy the boundary conditions at the surface of body 2, we transpose the modes centred at body 1 to body 2 and again apply (7*b*) and (8*b*). The resulting conditions differ from equations (18*b*) and (19*b*) only by the exchange of body 2 for body 1. Thus, by the same symmetry argument as in the case of spheres we may put

$$a_{12}(m,2) = \pm a_{12}(m,1); \qquad a_{22}(m,2) = \pm a_{22}(m,1) \tag{26b}$$

and obtain

$$\kappa_1(m)a_{12}(m,1)\pm\sum_{n=-\infty}^{+\infty}(\lambda_1(m)a_{12}(n,1)+\kappa_2(n)a_{22}(n,1))K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|) = 0 \tag{27b}$$

$$\kappa_1(m)a_{22}(m,1)\pm\sum_{n=-\infty}^{+\infty}(\kappa_2(m)a_{12}(n,1)+\lambda_2(n)a_{22}(n,1))K_{m+n}(l|\boldsymbol{r}_2-\boldsymbol{r}_1|) = 0. \tag{28b}$$

Contrary to our procedure in the presence of two spheres in equation (16*b*) we did not invert the axis of rotation at body 2. This is possible because the cylindrical Bessel functions are even with respect to order and in view of the summation over all orders m. This symmetry permits a further reduction of conditions (27*b*) and (28*b*) by putting

$$a_{12}(-m, 1) = \pm a_{12}(m, 1); \qquad a_{22}(-m, 1) = \mp a_{22}(m, 1). \tag{29b}$$

It is sufficient to consider positive values of m.

The characteristic difference between the final boundary conditions (27*b*) and (28*b*) for cylinders and the respective equations (27*a*) and (28*a*) for spheres is the fact that by normalization we were able to cancel Bessel functions of the first kind. In the case of spheres we have to consider amplitude vectors $\boldsymbol{a}_1(m, 1)$, $\boldsymbol{a}_2(m, 1)$, in the case of cylinders we need only the second components $a_{12}(m, 1)$, $a_{22}(m, 1)$. This difference will disappear in the investigations into the vdW energy between bodies 1 and 2 as discussed in §§ 10 and 11.

8. Complex integration

The retarded van der Waals energy between two bodies 1 and 2 is given by the energy gain of the electromagnetic radiation field in the presence of 1 and 2. We have to provide the eigenfrequencies ω_m resulting from the final boundary conditions (27) and (28) with their average quantum energy $kT \ln \sinh(\hbar\omega_m/2kT)$ and to sum the energy change relative to the limit $|\boldsymbol{r}_2 - \boldsymbol{r}_1| = \infty$ over all allowed modes m:

$$\Delta E = \mathrm{Re} \sum_m \left[kT \ln \sinh \frac{\hbar\omega_m}{2kT} \right]_{\infty}^{|\boldsymbol{r}_2 - \boldsymbol{r}_1|}. \tag{30}$$

By restricting ourselves to the real part of the total energy gain we account for the continuous energy exchange between the electromagnetic modes (photons) and the electron transitions of the bodies under consideration. The energy dissipation from the photons to the electrons enters this semiclassical treatment via the imaginary part of the electric and magnetic susceptibilities. In thermal equilibrium it is balanced by an equivalent energy dissipation from the electrons to the photons.

The most convenient method of carrying out the summation (30) is the Green function technique introduced by van Kampen *et al* (1968) and generalized by Ninham *et al* (Ninham *et al* 1970, Richmond and Ninham 1971). It makes use of the analytical identity

$$\sum_m f(\omega_m) - \sum_n f(\omega_n) = \frac{1}{2\pi \mathrm{i}} \oint \mathrm{d}\omega f(\omega) \frac{\mathrm{d}}{\mathrm{d}\omega} \ln g(\omega) \tag{31}$$

where m runs over all zeros and n runs over all poles of $g(\omega)$ within the contour of integration. This contour must not contain poles of $f(\omega)$. If $g(\omega)$ is chosen such that its zeros and poles yield the eigenfrequencies of the allowed electromagnetic modes for separations of the bodies under consideration $|\boldsymbol{r}_2 - \boldsymbol{r}_1|$ and ∞, we can use (31) directly for summing (30). This objective is achieved if

$$f(\omega) = kT \ln \sinh \frac{\hbar\omega}{2kT} \tag{32}$$

and if $g(\omega)$ equals the ratio of the secular determinants resulting from (27) and (28) for finite and infinite separation. The contour of integration has to enclose the positive half-plane. It runs along the imaginary axis at the right-hand side of the branchpoints of ln sinh($\hbar\omega/2kT$) and is closed by an infinite semicircle. Since the integral along the semicircle vanishes with increasing radius, we are left with the integral along the imaginary axis from $-i\infty$ to $+i\infty$.

9. Imaginary frequences

It follows that we need the secular determinants resulting from boundary conditions (27) and (28) only at imaginary values of the frequency. According to (4a) we are dealing with purely imaginary arguments of the Bessel functions in the case of spheres, whereas in the case of cylinders the argument of the Bessel functions becomes strictly real (see equation (4b)). We may proceed directly to the limit of infinite cavities $S \to \infty$. The spherical normalization conditions (9a) and (10a) are thus reduced to

$$\lim_{S\to\infty} \frac{a_{12}}{a_{11}} = \lim_{S\to\infty} \frac{a_{22}}{a_{21}} = \pm i \qquad \text{for } \operatorname{Im} k \gtrless 0. \tag{33a}$$

Inserting (35a) into (17a) yields

$$\boldsymbol{a}_i(m, j)\boldsymbol{f}_m(k|\boldsymbol{r}-\boldsymbol{r}_j|) = a_{i1}(m, j)(j_m \pm i y_m) = a_{i1}(m, j)h_m^{(1,2)}(k|\boldsymbol{r}-\boldsymbol{r}_j|) \qquad \text{for } \operatorname{Im} k \gtrless 0. \tag{34a}$$

The right-hand side of (34a) decreases exponentially with increasing modules, independent of the sign of Im k. This suggests that spherical Bessel functions $h_m^{(1)}(kr)$, $h_m^{(2)}(kr)$ should be used from the very beginning. However, when doing so it is not possible to satisfy boundary conditions (7) and (8) at the surface of bodies 1 and 2. Transition to imaginary values of the radial wavenumber k is not possible before the final secular equations have been derived.

Fixing the relative amplitudes a_{i2}/a_{i1} by means of (32a) removes the last difference between the treatment of spheres and cylinders. $h_m^{(1)}(i\zeta)$ equals $i^{-(m+2)}(\frac{1}{2}\pi\zeta)^{-1/2}K_{m+1/2}(\zeta)$ (see equation (10.2.15) in Abramowitz and Stegun 1965).

It should be pointed out that the radial wavenumber l in the case of cylinders becomes imaginary for small values of the translational wavenumber k. The term $K_m(l|\boldsymbol{r}_2-\boldsymbol{r}_1|)$ then oscillates instead of decreasing exponentially. For proper treatment of this case a cavity should have been used. However, after shifting the frequency integration to the imaginary axis, l is real everywhere, and the procedure adopted is finally justified.

When considering the attraction between two films (see Langbein 1973c) it is possible to represent the allowed modes by plane waves. We need a cavity for normalization. The shift of the frequency integration to the imaginary axis again justifies the transition to infinite cavities. We are left with exponentially decreasing modes, which still satisfy the boundary conditions at the surfaces of the films. In view of this fact it has been believed that investigations of the vdW energy merely require calculation of the energy of exponentially decreasing surface modes (van Kampen *et al* 1968, Richmond and Ninham 1971, Gerlach 1971). However, the present investigations show that the surface mode hypothesis, besides causing branchpoints and different Riemann surfaces, is restricted to simple planar geometries such as half-spaces or multilayers.

10. Pair energy: spheres

The boundary conditions (27a) and (28a) in the presence of two spheres yield one secular determinant for each μ. The integer μ characterizes the rotational behaviour of the fields under investigation and runs from $-\infty$ to $+\infty$. Each determinant is dissected into two parts according to the behaviour of the fields on exchange of sphere 1 for sphere 2. The secular determinants arising for μ and $-\mu$ differ by the sign of the coupling parameters $W^{\mu}_{mn}(\zeta)$, that is, by the way of coupling electric and magnetic modes. They become identical if the sign of the amplitudes $a_2(n, 1)$ is appropriately changed. The determinant arising for $\mu = 0$, consequently, does not contain any coupling of electric and magnetic modes.

The order m of the spherical Bessel functions generally runs from $|\mu|$ to infinity. The dipole interactions merely enter the secular determinants $\mu = 0, 1$; the quadrupole interactions merely enter the secular determinants $\mu = 0, 1, 2$. Any monopole interactions are excluded by $V^{0}_{0n}(\zeta) = 0$, $W^{0}_{0n}(\zeta) = 0$, that is, there are no fields (1*a*) and (2*a*) for $m = 0$. The secular determinant arising for $\mu = 0$ starts with the dipole term $m = 1$.

Using (30) to (32) we find after partial integration with respect to frequency

$$\Delta E = \frac{\hbar}{4\pi} \int_{-\infty}^{+\infty} \mathrm{d}\omega \cot \frac{\hbar\omega}{2kT} \sum_{\mu=-\infty}^{+\infty} \sum_{+,-} \ln g(\mathrm{i}\omega; \mu, \pm) \tag{35a}$$

with the Green function $g(\mathrm{i}\omega; \mu, \pm)$ representing the ratio of secular determinants for finite and infinite separation

$$g(\mathrm{i}\omega; \mu, \pm) = \begin{vmatrix} 1 \pm \dfrac{\kappa_1(\mu)}{\kappa_1 + \mathrm{i}\kappa_2} \dfrac{2\mu+1}{(2\mu)!} V^{\mu}_{\mu\mu} & \pm \dfrac{\kappa_1(\mu)}{\kappa_1 + \mathrm{i}\kappa_2} \dfrac{2\mu+1}{(2\mu)!} W^{\mu}_{\mu\mu} & \cdots \\ \mp \dfrac{\lambda_1(\mu)}{\lambda_1 + \mathrm{i}\lambda_2} \dfrac{2\mu+1}{(2\mu)!} W^{\mu}_{\mu\mu} & 1 \mp \dfrac{\lambda_1(\mu)}{\lambda_1 + \mathrm{i}\lambda_2} \dfrac{2\mu+1}{(2\mu)!} V^{\mu}_{\mu\mu} & \cdots \\ \cdot & \cdot & \cdots \end{vmatrix} \tag{36a}$$

The coupling parameters $V^{\mu}_{mn}(\mathrm{i}\zeta)$ and $W^{\mu}_{mn}(\mathrm{i}\zeta)$ necessary for treating interactions up to octupole are summarized in table 1.

Table 1. Spherical coupling parameters

$$\mathrm{i}^{m+n+2} V^{\mu}_{mn}(\mathrm{i}\zeta) = \binom{m+1}{2} \zeta^{-1} \mathrm{e}^{-\zeta} \sum_{0}^{m+n} a_k \zeta^{-k}; \qquad \mathrm{i}^{m+n} W^{\mu}_{mn}(\mathrm{i}\zeta) = \binom{m+1}{2} \zeta^{-1} \mathrm{e}^{-\zeta} \sum_{0}^{m+n} b_k \zeta^{-k}$$

μ	m	n	a_k					b_k			
0	1	0	0	0							
		1	0	1	1						
	2	0	0	0	0						
		1	0	1	3	3					
		2	0	1	5	12	12				
	3	0	0	0	0	0					
		1	0	1	6	15	15				
1	1	1	1	1	1			1	1		
	2	1	1	3	6	6		1	3	3	
		2	1	5	21	48	48	1	5	12	12
	3	1	1	6	21	45	45	1	6	15	15
2	2	2	0	8	24	48	48	0	8	24	24

If we restrict ourselves to dipole interactions, use a perturbation expansion for $g(\mathrm{i}\omega, \mu, \pm)$, and carry out the summations over $\mu = -1, 0, +1$ and over $\pm$, we end up with

$$\Delta E = -\frac{9\hbar}{8\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega \cot\frac{\hbar\omega}{2kT}\frac{\mathrm{e}^{-2\zeta}}{\zeta^2}\left[\left\{\left(\frac{\kappa_1(1)}{\kappa_1+\mathrm{i}\kappa_2}\right)^2+\left(\frac{\lambda_1(1)}{\lambda_1+\mathrm{i}\lambda_2}\right)^2\right\}\right.$$
$$\left.\times\left(1+\frac{2}{\zeta}+\frac{5}{\zeta^2}+\frac{6}{\zeta^3}+\frac{3}{\zeta^4}\right)-2\frac{\kappa_1(1)}{\kappa_1+\mathrm{i}\kappa_1}\frac{\lambda_1(1)}{\lambda_1+\mathrm{i}\lambda_2}\left(1+\frac{2}{\zeta}+\frac{1}{\zeta^2}\right)\right] \qquad (38a)$$

with $\zeta = k|\boldsymbol{r}_2-\boldsymbol{r}_1|$. We obtain an electric, a magnetic and a mixed contribution. Taking the limit $R \to 0$ we find the electric term to agree with the findings reported by Casimir and Polder (1948) for the retarded vdW energy between atoms. These authors use quantum electrodynamics and fourth-order perturbation theory. An equivalent result has been obtained by Mitchell *et al* (1972) who considered the interaction of retarded dipoles. Their calculations are based on the perturbation approach together with the surface mode hypothesis, that is, they represent the dipoles by spherical Bessel functions $h_1^{(1)}(kr)$. The first derivation of the electric term for macroscopic spheres was reported on the basis of the perturbation approach together with finite boundary conditions and a plane-wave expansion for the electromagnetic fields (Langbein 1970).

The fact that all these earlier findings are re-obtained in spite of numerous simplifications of the final expressions (35*a*) and (36*a*) shows the strength and generality of the present method. The theory is now complete and rigorous. It accounts correctly for all spatial symmetries of the system under consideration and includes both electric and magnetic interactions. Equations (35*a*) and (36*a*) are valid also for spin–spin interactions between two molecules.

11. Pair energy: cylinders

In the presence of two spheres we classified the electromagnetic fields by their rotational behaviour. In the presence of two cylinders we classify them by their translational behaviour. The boundary conditions (27*b*) and (28*b*) yield one secular determinant for each translational wavenumber k; k is continuous and runs from $-\infty$ to $+\infty$. The secular determinants arising for k and $-k$ are identical. Each determinant is dissected into two according to the behaviour of the fields on exchange of cylinder 1 for cylinder 2.

The order m of the cylindrical Bessel functions runs generally from $-\infty$ to $+\infty$. However, by using the different behaviour of electric and magnetic modes on inversion, we were able to find relations (29*b*) between the field amplitudes for inverse order m and to dissect each determinant a second time. We thus have electric and magnetic secular determinants with m running from 0 to ∞. (In view of the different behaviour of the fields on inversion the secular determinants arising in the presence of spheres likewise no longer depend on the sign of μ.)

From (30) to (32) we find

$$\Delta E = \frac{\hbar}{4\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega \cot\frac{\hbar\omega}{2kT}\frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}k \sum_{+,-}\sum_{\kappa,\lambda} \ln g_{\kappa,\lambda}(\mathrm{i}\omega; k, \pm) \qquad (35b)$$

with the Green function $g_{\kappa,\lambda}(\mathrm{i}\omega; k, \pm)$ being the ratio of secular determinants resulting from (27*b*) and (28*b*) for finite and infinite separations

$$g_\kappa(\mathrm{i}\omega; k, \pm) = \begin{vmatrix} 1 \pm \frac{\lambda_1(0)}{\kappa_1(0)} K_0 & \pm \frac{\lambda_1(0)}{\kappa_1(0)} 2K_1 & 0 & \cdots \\ \pm \frac{\lambda_1(1)}{\kappa_1(1)} K_1 & 1 \pm \frac{\lambda_1(1)}{\kappa_1(1)} (K_2 + K_0) & \pm \frac{\kappa_2(1)}{\kappa_1(1)} (K_2 - K_0) & \cdots \\ \pm \frac{\kappa_2(1)}{\kappa_1(1)} K_1 & \pm \frac{\kappa_2(1)}{\kappa_1(1)} (K_2 + K_0) & 1 \pm \frac{\lambda_2(1)}{\kappa_1(1)} (K_2 - K_0) & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{vmatrix} \qquad (36b)$$

$$g_\lambda(\mathrm{i}\omega; k, \pm) = \begin{vmatrix} 1 \pm \frac{\lambda_2(0)}{\kappa_1(0)} K_0 & 0 & \pm \frac{\lambda_2(0)}{\kappa_1(0)} 2K_1 & \cdots \\ \pm \frac{\kappa_2(1)}{\kappa_1(1)} K_1 & 1 \pm \frac{\lambda_1(1)}{\kappa_1(1)} (K_2 - K_0) & \pm \frac{\kappa_2(1)}{\kappa_1(1)} (K_2 + K_0) & \cdots \\ \pm \frac{\lambda_2(1)}{\kappa_1(1)} K_1 & \pm \frac{\kappa_2(1)}{\kappa_1(1)} (K_2 - K_0) & 1 \pm \frac{\lambda_2(1)}{\kappa_1(1)} (K_2 + K_0) & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{vmatrix}. \qquad (37b)$$

Comparison of equations (35*a*) and (36*a*) with equations (35*b*) to (37*b*) shows the close agreement of the final results in the cases of spheres and cylinders. In both cases we end up with coupling parameters proportional to $K_m(\zeta)$. m is half an integer and ζ equals $k|\boldsymbol{r}_2 - \boldsymbol{r}_1|$ for spheres, whereas m is an integer and ζ equals $l|\boldsymbol{r}_2 - \boldsymbol{r}_1|$ for cylinders. The decrease of the susceptibility factor in the coupling parameters with increasing order m makes it possible to cut off the determinants $g(\mathrm{i}\omega; \mu, \pm)$ and $g_{\kappa,\lambda}(\mathrm{i}\omega; k, \pm)$ after a few terms.

If we restrict ourselves to a second-order perturbation treatment of the secular determinants $g_{\kappa,\lambda}(\mathrm{i}\omega; k, \pm)$ and carry out the summation over $+,-$ and κ, λ we obtain

$$\Delta E = -\frac{\hbar}{4\pi} \int_{-\infty}^{+\infty} \mathrm{d}\omega \cot \frac{\hbar\omega}{2kT} \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}k \sum_{m,n} \left(\frac{\lambda_1(m)}{\kappa_1(m)} \frac{\lambda_1(n)}{\kappa_1(n)} + 2 \frac{\kappa_2(m)}{\kappa_1(m)} \frac{\kappa_2(n)}{\kappa_1(n)} \right.$$
$$\left. + \frac{\lambda_2(m)}{\kappa_1(m)} \frac{\lambda_2(n)}{\kappa_1(n)} \right) K_{m+n}^2(\zeta) \qquad (38b)$$

with $\zeta = l|\boldsymbol{r}_2 - \boldsymbol{r}_1|$. By using the asymptotic behaviour of $K_m(\zeta)$ for large arguments (equation (9.7.2) in Abramowitz and Stegun 1965) we find the integrand in (38*b*) to be proportional to $\mathrm{e}^{-2\zeta}/\zeta$, that is, one inverse power of ζ less than in the presence of spheres, (equation (38*a*)). This entails that the retarded vdW energy between cylinders obeys a $|\boldsymbol{r}_2 - \boldsymbol{r}_1|^{-6}$ law at large separations rather than the $|\boldsymbol{r}_2 - \boldsymbol{r}_1|^{-7}$ law found for spheres. This result was first derived by Mitchell *et al* (1973a, b) on the basis of the perturbation approach. Equation (28*b*) again contains an electric, a magnetic and a mixed contribution to the total vdW energy.

12. Rotation theorem

When calculating the vdW energy of a symmetric cluster of macroscopic bodies, it is possible to classify the allowed electromagnetic modes according to the symmetry group of the cluster. In the case of two spheres or cylinders inversion has been used. In the presence of a tetrahedral array of spheres there exist electromagnetic modes of s character and others which are multiplied by the phase factor $\exp(2\pi i n/3)$ on rotation by $2\pi/3$. In the case of infinite lattices, eventually, we know that the allowed electromagnetic modes obey Floquet's theorem.

However, before we are able to exploit the latter symmetry operation, we need a rotation theorem for the spherical modes (1*a*) and (2*a*). When applying the addition theorem (13*a*), inversely oriented spherical coordinates have been used at positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. This choice of coordinates is obviously restricted to two bodies. If we consider more than two bodies and want to classify the allowed modes by the possible symmetry operations, we have to start with parallel coordinate systems of all bodies. To satisfy the boundary conditions at the surface of an individual body i, we have to rotate the coordinates at j to the connecting line $\boldsymbol{r}_i - \boldsymbol{r}_j$, to apply the addition theorem (13*a*), and to rotate the coordinates back in their former direction.

Let us now consider the geometric situation shown in figure 3. The standard direction of all coordinates is $\boldsymbol{n}$. We want to rotate the coordinates at position $\boldsymbol{r}_j$ to the

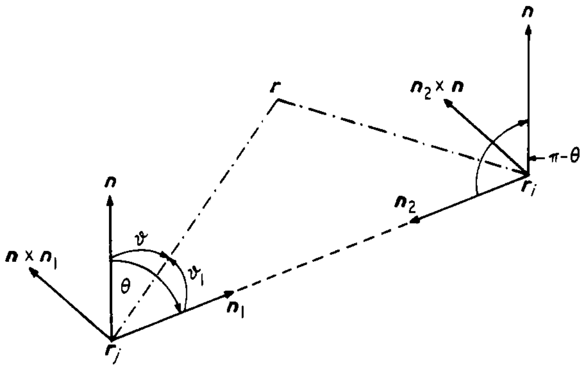

Figure 3. Rotation to $\boldsymbol{n}_1 = \boldsymbol{r}_i - \boldsymbol{r}_j$.

connecting line $\boldsymbol{n}_1 = (\boldsymbol{r}_i - \boldsymbol{r}_j)/|\boldsymbol{r}_i - \boldsymbol{r}_j|$ and denote the polar angle of $\boldsymbol{n}_1$ in the system $\boldsymbol{n}$ by θ, $\boldsymbol{n} \cdot \boldsymbol{n}_1 = \cos\theta$, and the azimuth of $\boldsymbol{n} \times \boldsymbol{n}_1$ by ϕ. The polar angle and the azimuth of an arbitrary vector $\boldsymbol{r} - \boldsymbol{r}_j$ in systems $\boldsymbol{n}$ and $\boldsymbol{n}_1$ is denoted by ϑ, φ and ϑ_1, φ_1 respectively, the azimuth being counted relative to $\boldsymbol{n} \times \boldsymbol{n}_1$ in both systems. Then, from figure 4 we find

$$
\begin{aligned}
\cos\vartheta &= \cos\theta\cos\vartheta_1 + \sin\theta\sin\vartheta_1\sin\varphi_1 \\
\sin\vartheta\sin\varphi &= -\sin\theta\cos\vartheta_1 + \cos\theta\sin\vartheta_1\sin\varphi_1 \\
\sin\vartheta\cos\varphi &= \sin\vartheta_1\cos\varphi_1
\end{aligned}
\tag{39a}
$$

and

$$
\begin{pmatrix} \frac{1}{0!} Y_1^{-1} \\ \frac{1}{1!} Y_1^0 \\ \frac{1}{2!} Y_1^1 \end{pmatrix}_{\vartheta,\varphi}
=
\begin{pmatrix}
\cos^2\frac{1}{2}\theta & \mathrm{i}\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta & \sin^2\frac{1}{2}\theta \\
2\mathrm{i}\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta & 1-2\sin^2\frac{1}{2}\theta & -2\mathrm{i}\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta \\
\sin^2\frac{1}{2}\theta & -\mathrm{i}\sin\frac{1}{2}\theta\cos\frac{1}{2}\theta & \cos^2\frac{1}{2}\theta
\end{pmatrix}
\begin{pmatrix} \frac{1}{0!} Y_1^{-1} \\ \frac{1}{1!} Y_1^0 \\ \frac{1}{2!} Y_1^1 \end{pmatrix}_{\vartheta_1,\varphi_1}
\tag{40a}
$$

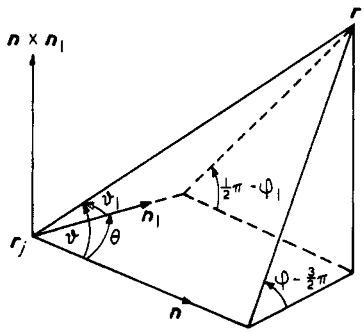

Figure 4. Rotation theorem.

The rotation changes the order μ, but not the degree m of the spherical harmonics $Y_m^\mu(\vartheta, \varphi)$. We obtain generally

$$\frac{1}{(m+\mu)!} Y_m^\mu(\vartheta, \varphi) = \sum_{\lambda=-m}^{+m} C(m, \mu, \lambda, \theta) \frac{1}{(m+\lambda)!} Y_m^\lambda(\vartheta_1, \varphi_1) \tag{41a}$$

where $C(m, \mu, \lambda, \theta)$ may be represented by a Jacobi polynomial of argument $\sin^2 \frac{1}{2}\theta$.

After transposing the modes centred at position $\boldsymbol{r}_j$ to position $\boldsymbol{r}_i$ by means of addition theorem (13a), we find spherical coordinates in the inverse direction $\boldsymbol{n}_2 = -\boldsymbol{n}_1$ (see figure 3). To satisfy the boundary conditions at the surface of body i, we have to rotate the coordinates back to the standard system $\boldsymbol{n}$. The polar angle for the transformation from $\boldsymbol{n}_2$ to $\boldsymbol{n}$ is $\pi - \theta$. The φ axis $\boldsymbol{n}_2 \times \boldsymbol{n}$ equals the axis $\boldsymbol{n} \times \boldsymbol{n}_1$ used before. Hence

$$\frac{1}{(n+\lambda)!} Y_n^\lambda(\vartheta_2, \varphi_2) = \sum_{\mu=-n}^{+n} C(n, \lambda, \mu, \pi-\theta) \frac{1}{(n+\mu)!} Y_n^\mu(\vartheta, \varphi). \tag{42a}$$

The coefficients $C(n, \lambda, \mu, \theta)$ for complementary angles θ and $\pi - \theta$ and inverse degrees λ, μ and $-\lambda, -\mu$ satisfy the relations

$$C(n, \lambda, \mu, \pi-\theta) = (-1)^{n+\lambda} C(n, \lambda, -\mu, \theta) \tag{43a}$$

and

$$C(n, -\lambda, -\mu, \theta) = C^*(n, \lambda, \mu, \theta). \tag{44a}$$

13. Lattice states

We are now well prepared to treat the allowed electromagnetic modes and the vdW energy in lattices. Let us consider a lattice with basis vectors $\boldsymbol{c}_i$, $i = 1, 2, 3$ (or $i = 1, 2$ in the case of cylinders). We construct the allowed modes in lattices analogous to (16), but with j running over all lattice sites $\boldsymbol{r}_j$ and all coordinates being oriented in a standard direction $\boldsymbol{n}$. The translational invariance of the lattice entails that any allowed mode is allowed even after any translation, that is, we can classify all modes according to Floquet's theorem and put

$$\boldsymbol{a}_i(m, j) = \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}_j)\boldsymbol{a}_i(m). \tag{45}$$

Equation (45) holds for bodies of arbitrary shape. Hence, in the case of spheres we start with

$$\boldsymbol{D}(\boldsymbol{r}, \boldsymbol{q}) = \sum_j \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}_j)\{\operatorname{curl}\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_j)\boldsymbol{a}_1(m, \mu)+k\operatorname{curl}(\boldsymbol{r}-\boldsymbol{r}_j)\boldsymbol{a}_2(m, \mu)\}$$

$$\times \boldsymbol{f}_m(k|\boldsymbol{r}-\boldsymbol{r}_j|)\frac{Y_m^\mu(\vartheta_j, \varphi_j)}{(m+\mu)!} \tag{46a}$$

whereas in the case of cylinders we use

$$\boldsymbol{D}(\boldsymbol{r}, \boldsymbol{q}) = \sum_j \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}_j)\{\operatorname{curl}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}a_{12}(m)$$

$$+\frac{\omega}{c}(\epsilon_0\mu_0)^{1/2}\operatorname{curl}\boldsymbol{n}\,\mathrm{e}^{\mathrm{i}kz}a_{22}(m)\}K_m(l|\boldsymbol{r}-\boldsymbol{r}_j|)\exp(\mathrm{i}m\varphi_j). \tag{46b}$$

The second argument of the amplitudes $\boldsymbol{a}_i(m, \mu)$ in the case of spheres is no longer the lattice site j, but the rotational wavenumber μ. In the case of cylinders it is still possible to classify the allowed modes by the translation wavenumber k.

Continuity of the different components of the electromagnetic fields across the surfaces of bodies j gives rise to conditions (7) and (8). In order to satisfy these conditions, we have to transform all fields to an individual body i. In the case of spheres this implies that we have to rotate the coordinates at $\boldsymbol{r}_j$ to the direction $\boldsymbol{r}_i-\boldsymbol{r}_j$ by using rotation theorem (41*a*), to transpose the fields from $\boldsymbol{r}_j$ to $\boldsymbol{r}_i$ by using addition theorem (13*a*), and to rotate the coordinates back to the standard direction $\boldsymbol{n}$ by using rotation theorem (42*a*). We finish with fields centred only at $\boldsymbol{r}_i$ and by satisfying (7) and (8) we obtain

$$\varkappa_1(m)a_{11}(m, \mu)+\varkappa_2(m)a_{12}(m, \mu)$$

$$+\varkappa_1(m)(2m+1)\sum_{j\neq i}\exp\{\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{r}_j-\boldsymbol{r}_i)\}\sum_{n,\nu,\lambda}\exp(\mathrm{i}\nu\phi_j)C(n, \nu, \lambda, \theta_j)(-1)^{m-\lambda}$$

$$\times\frac{(m-\lambda)!}{(n+\lambda)!}(\boldsymbol{a}_1(n, \nu)\boldsymbol{V}_{nm}^\lambda+\boldsymbol{a}_2(n, \nu)\boldsymbol{W}_{nm}^\lambda)\exp(-\mathrm{i}\mu\phi_j)C^*(m, \lambda, \mu, \theta_j) = 0 \tag{47a}$$

and

$$\lambda_1(m)a_{21}(m, \mu)+\lambda_2(m)a_{22}(m, \mu)$$

$$+\lambda_1(m)(2m+1)\sum_{j\neq i}\exp\{\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{r}_j-\boldsymbol{r}_i)\}\sum_{n,\nu,\lambda}\exp(\mathrm{i}\nu\phi_j)C(n, \nu, \lambda, \theta_j)(-1)^{m-\lambda}$$

$$\times\frac{(m-\lambda)!}{(n+\lambda)!}(\boldsymbol{a}_1(n, \nu)\boldsymbol{W}_{nm}^\lambda+\boldsymbol{a}_2(n, \nu)\boldsymbol{V}_{nm}^\lambda)\exp(-\mathrm{i}\mu\phi_j)C^*(m, \lambda, \mu, \theta_j) = 0. \tag{48a}$$

The different sums and factors in (47*a*) and (48*a*) can clearly be attributed to the sequence rotation–translation–rotation. By changing the sign of μ we find equations (47*a*) and (48*a*) turn into their complex conjugates. The secular determinant resulting from (47*a*) and (48*a*) is hermitic and its eigenfrequencies are real, if the susceptibilities involved are real. The different behaviour of electric and magnetic modes on inversion implies

$$\boldsymbol{a}_1(m, -\mu) = \pm\boldsymbol{a}_1^*(m, \mu); \qquad \boldsymbol{a}_2(m, -\mu) = \mp\boldsymbol{a}_2^*(m, \mu). \tag{49a}$$

Equations (47*a*) and (48*a*) permit an exact calculation of the spectrum of a lattice of spheres from that of single spheres. Each single line is split into a band. Modes belonging to the same band differ only by the wavenumber $\boldsymbol{q}$.

Satisfying the boundary conditions in the case of cylinders involves much less effort than in the case of spheres. The respective rotation theorem is easy to handle. Similar to our procedure in the case of spheres we denote by ϕ the azimuth of $\boldsymbol{n}\times\boldsymbol{n}_1$, where $\boldsymbol{n}$ is parallel to the cylinder axis and $\boldsymbol{n}_1 = (\boldsymbol{r}_i-\boldsymbol{r}_j)/|\boldsymbol{r}_i-\boldsymbol{r}_j|$. Then, by using the addition theorem (12*b*) and applying boundary conditions (7) and (8), we find

$$\begin{aligned}\varkappa_1(m)a_{12}(m)+\sum_{j\neq i}\exp\{\mathrm{i}\boldsymbol{q}\,.\,(\boldsymbol{r}_j-\boldsymbol{r}_i)\}\sum_n(\lambda_1(m)a_{12}(n)+\varkappa_2(m)a_{22}(n))\\ \times\exp\{\mathrm{i}n(\phi_j-\tfrac{1}{2}\pi)\}K_{n-m}(l|\boldsymbol{r}_j-\boldsymbol{r}_i|)\exp\{-\mathrm{i}m(\phi_j+\tfrac{1}{2}\pi)\} = 0\end{aligned} \tag{47b}$$

and

$$\begin{aligned}\varkappa_1(m)a_{22}(m)+\sum_{j\neq i}\exp\{\mathrm{i}\boldsymbol{q}\,.\,(\boldsymbol{r}_j-\boldsymbol{r}_i)\}\sum_n(\varkappa_2(m)a_{12}(n)+\lambda_2(m)a_{22}(n))\\ \times\exp\{\mathrm{i}n(\phi_j-\tfrac{1}{2}\pi)\}K_{n-m}(l|\boldsymbol{r}_j-\boldsymbol{r}_i|)\exp\{-\mathrm{i}m(\phi_j+\tfrac{1}{2}\pi)\} = 0,\end{aligned} \tag{48b}$$

where $\varkappa_1(m)$, $\varkappa_2(m)$, $\lambda_1(m)$, $\lambda_2(m)$ are given by equations (20*b*) to (23*b*).

Equations (47*b*) and (48*b*) differ from the respective equations (27*b*) and (28*b*) in the presence of only two cylinders mainly by the generalized phase factor $\exp\{\mathrm{i}\boldsymbol{q}\,.\,(\boldsymbol{r}_j-\boldsymbol{r}_i)\}$. By changing the sign of m we find equations (47*b*) and (48*b*) turn into their complex conjugates. We end up with a hermitic secular determinant and real eigenfrequencies so that

$$a_{12}(-m) = \pm a_{12}^*(m); \qquad a_{22}(-m) = \mp a_{22}^*(m). \tag{49b}$$

14. Lattice energies

To calculate the vdW energy between bodies in a lattice, we again apply the complex integration technique described in §§ 8 and 9. We need the secular determinant resulting from (47), (48) only at imaginary frequencies. By turning to the limit of infinite cavities we may simplify equations (47*a*) and (48*a*) by using (33*a*) and (34*a*). $V^{\mu}_{mn}(\mathrm{i}\zeta)$ and $W^{\mu}_{mn}(\mathrm{i}\zeta)$ are obtained if the addition theorem (13*a*) is applied to Bessel functions $h^{(1)}_m(\mathrm{i}\zeta)$ of the third kind. Both coupling parameters decrease exponentially with increasing $\mathrm{i}\zeta$ (see table 1).

In the presence of two spheres one secular determinant has been obtained for each rotational wavenumber μ. In a lattice of spheres a classification of modes according to their rotational behaviour is in general no longer possible. Equations (47*a*) and (48*a*) couple all multipoles $m = 1, 2, \ldots$ and $-m \leqslant \mu \leqslant +m$. Only the monopole $m = 0$ is excluded owing to $V^0_{0n}(\zeta) = W^0_{0n}(\zeta) = 0$. When considering two spheres we found even and odd states in the case of inversion. A lattice of spheres is classified by Floquet's theorem, that is, the summation over $+$, $-$ in (35*a*) is now replaced by an integration over $\boldsymbol{q}$. The integration includes all $\boldsymbol{q}$ values yielding different modes and thus runs over one cell of the reciprocal lattice $\boldsymbol{b}_i$, where $\boldsymbol{b}_i\,.\,\boldsymbol{c}_j = 2\pi\delta_{ij}$; $i, j = 1, 2, 3$. Hence,

$$\Delta E = \frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}\mathrm{d}\omega\cot\frac{\hbar\omega}{2kT}\frac{1}{(2\pi)^3}\int\mathrm{d}\boldsymbol{q}\ln g(\mathrm{i}\omega;\boldsymbol{q}). \tag{50}$$

The Green function $g(\mathrm{i}\omega;\boldsymbol{q})$ represents the ratio of secular determinants resulting from (47*a*) and (48*a*) for finite and infinite separations.

If we consider dipole interactions alone, $g(i\omega; \boldsymbol{q})$ is found to be given by a secular determinant of order six. It contains the terms $m = 1$, $\mu = -1, 0, +1$ and electric and magnetic contributions. Then, the evaluation of (50) needs very little effort.

In the presence of two cylinders we were able to distinguish between secular determinants for electric and magnetic modes. In a lattice of cylinders, where equation (29*b*) is replaced by equation (49*b*), we find electric and magnetic mode coupling. The summation over the symmetry characters $+, -$ in (35*b*) is again replaced by an integration over the wavenumber $\boldsymbol{q}$, which extends over one cell of the reciprocal lattice $\boldsymbol{b}_i$. Since in the case of cylinders the lattice and the reciprocal lattice are two dimensional, it is logical to account for the translational invariance in the direction of the cylinder axis by a third lattice vector $\boldsymbol{c}_3$ of zero length. The reciprocal vector $\boldsymbol{b}_3$ then has length infinity, that is, the k integration in (35*b*) is the integration over the missing third component of $\boldsymbol{q}$, and we once more end up with equation (50).

15. Conclusions

The use of finite boundary conditions permits the application of the Green function technique without encountering any difficulties related to branch points and different Riemann surfaces. The systematic classification of all electromagnetic modes according to the symmetry operations of the array under consideration leads to a considerable reduction of the secular determinant involved. The simultaneous use of these two principles results in an analytic representation of the vdW energy, which involves a secular determinant of order six if we restrict ourselves to dipole interactions, and a secular determinant of order sixteen if the problem is restricted to dipole and quadrupole interactions.

This enables us to tackle the topical problem of the structure of rare gas crystals. It is in these lattices where the conventional perturbation approach to vdW attraction appears to be most unsatisfactory. Ever since the first investigations into triplet vdW interactions by Axilrod and Teller (1943) attempts have been made to explain the energy gain of the face-centred cubic structure relative to the hexagonal close-packed structure on the basis of multiplet contributions (Jansen 1964, Jansen and Lombardi 1965, Fowler and Graben 1972). However, the multiplet and higher-order perturbation terms converge but slowly. None of these interactions favours the face-centred cubic structure to such an extent that the next higher terms might not inverse the result. The present theory, which by taking the limit $R \to 0$ includes atoms, avoids all multiplet expansions by making use of Floquet's theorem.

Knowledge of the vdW energy of two-dimensional arrays of cylinders is required, for example, for an understanding of viral self-assembly, in models of muscle energetics and in investigations of crystalline polymers.

In view of the effort involved in transposing and rotating electromagnetic modes one may be tempted to utilize the expansion in terms of plane waves reported earlier (Langbein 1970). This treatment offers the advantage that all symmetry operations (inversion, translation) are taken into account from the very beginning and that the addition theorem becomes particularly easy. However, there is no physically relevant method of reducing the resulting secular determinant to finite order except for the restriction to dipole and quadrupole interactions. This is possible only on the basis of the spherical and cylindrical modes used here.

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