Limiting Optical Frequencies in Alkali Halide Crystals

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It recently has been pointed out by Rosenstock on the basis of symmetry arguments that the frequencies of the three optical branches of an ionic crystal in the limit of infinite wavelengths are all equal. This result is in contrast with the relation $(\omega_l/\omega_t)=(\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}$ due to Lyddane, Sachs, and Teller, where ω_l and ω_t are the limiting longitudinal and transverse frequencies and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively. By use of Kellermann's model for NaCl we have obtained the small-$\mathbf{k}$ expansions of the elements of the dynamical matrix for a finite spherical crystal of radius R. It is found that, if the limit $\mathbf{k}\rightarrow 0$ is taken before the limit $R\rightarrow\infty$, the three optical frequencies are all equal, while if the order of taking limits is reversed the result of Lyddane, Sachs, and Teller is obtained. These conclusions are in agreement with Rosenstock's result, and with remarks of Fröhlich, and provide an explicit expression for the infrared frequency in the finite-crystal case. A similar calculation for Wigner's low-density electron crystal yields the result that in a finite spherical crystal the limiting frequencies of the two transverse branches and the one "longitudinal" branch are all equal. The possibility of the experimental observation of these effects is discussed.

I. INTRODUCTION

IN a recent paper Rosenstock[1] pointed out on the basis of symmetry arguments that at $\mathbf{k}=0$ (i.e., the infinite-wavelength limit) the distinction between longitudinal and transverse lattice waves in a crystal breaks down, and that in particular the limiting values of the so-called longitudinal optical and transverse optical frequencies in an ionic crystal should be equal. This conclusion contradicts the well-known Lyddane, Sachs, Teller relation,[2]

$$\omega_l/\omega_t=(\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}\neq 1, \tag{1.1}$$

where ω_l and ω_t are the limiting (as $\mathbf{k}\rightarrow 0$) longitudinal and transverse optical frequencies, and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively. Furthermore, Kellermann[3] in his study of the vibrations of the sodium chloride lattice obtained different limiting frequencies as $\mathbf{k}\rightarrow 0$ for the longitudinal and transverse optical modes. Kellermann's numerical results for ω_l and ω_t do not quite satisfy the relation (1.1), presumably largely due to his neglect of the polarizability of the ions.[4] Rosenstock in his discussion has also neglected the polarizability of the ions. However, as Rosenstock points out,[1] neglect of the ionic polarizability means setting $\epsilon_\infty=1$, but since ϵ_0 is still unequal to unity in the general case, so is the left-hand side of Eq. (1.1).[5] Rosenstock's conclusion that $(\omega_l/\omega_t)=1$ cannot therefore be due to his neglect of ionic polarizabilities. On the other hand, Fröhlich[6] has pointed out that in a spherical specimen of an ionic crystal whose radius is large compared with the lattice parameter but small compared with the wavelength of the lattice waves propagating through it, there is no difference between longitudinal and transverse waves, and that the frequency of these long-wavelength waves in a sphere is different from those in a specimen which is large compared with the wavelength. It is of some interest, therefore, to see under what conditions the ordinary theory of lattice dynamics leads to Rosenstock's result, and under what conditions it predicts Kellermann's result.

We have, accordingly, used Kellermann's model to evaluate the normal mode frequencies of a finite, spherical ionic crystal of radius R in the limit as $\mathbf{k}\rightarrow 0$. Our results, briefly summarized, are that if the passage to the limit $\mathbf{k}\rightarrow 0$ is carried out for fixed, finite R, the limiting optical frequencies are all equal, while if the passage to the limit $R\rightarrow\infty$ is carried out first, and then the limit $\mathbf{k}\rightarrow 0$ is taken, Kellermann's result is recovered. In the former case an explicit expression for the infrared frequency in the finite-crystal case is obtained.

Before proceeding to a study of the limiting optical frequencies in ionic crystals, however, we first discuss the analogous problem for Wigner's low-density electron crystal.[7] Essentially the same questions arise here, but the discussion is simplified somewhat by the fact that there is only one particle in a unit cell. Also, some of the results obtained in this case can be carried over directly to the study of ionic crystals.

[1] H. B. Rosenstock, Phys. Rev. **121**, 416 (1961).
[2] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).
[3] E. W. Kellermann, Phil. Trans. Roy. Soc. London **A238**, 513 (1940).
[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 87.
[5] However, Kellermann's results for ω_l and ω_t agree reasonably well with Eq. (1.1) if ϵ_∞ is set equal to unity and the experimental value of ϵ_0 is used.
[6] H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1958), 2nd ed., p. 149 ff.
[7] E. P. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

II. THE ELECTRON CRYSTAL

Wigner's model of the low-density electron gas is that it consists of a body-centered cubic array of electrons immersed in a uniform background of positive charge. The elements of the dynamical matrix for the vibrations of the electron crystal have been found to be[8]

$$D_{xy}(\mathbf{k})=\tfrac{1}{3}\omega_p^2\delta_{xy}-\frac{e^2}{M}\sum_l{}'\frac{3x_ly_l-\delta_{xy}r_l^2}{r_l^5}(e^{i\mathbf{k}\cdot\mathbf{r}_l}-\delta_{xy}), \quad (2.1)$$

where ω_p^2 is the square of the classical plasma frequency, and $\mathbf{r}_l$ is the position vector of the lth electron in the crystal. The prime on the sum excludes the point $r_l=0$. In the present case

$$\omega_p^2=4\pi ne^2/M, \quad (2.2)$$

where n is the number density of electrons and equals $2/a_0^3$ in terms of the lattice parameter a_0.

The last sum on the right-hand side of Eq. (2.1), viz.,

$$\sum_l{}'\frac{3x_l^2-r_l^2}{r_l^5},$$

will be shown below to vanish for a finite lattice of cubic symmetry. It also vanishes, as can be seen from symmetry arguments,[9] in the case of an infinite lattice having cubic symmetry. Since these are the only cases we will consider in this paper, we simplify the following discussion by omitting this term from discussion and using as the elements of the dynamical matrix

$$D_{xy}(\mathbf{k})=\tfrac{1}{3}\omega_p^2-\frac{e^2}{M}\sum_l{}'\frac{3x_ly_l-\delta_{xy}r_l^2}{r_l^5}e^{i\mathbf{k}\cdot\mathbf{r}_l}. \quad (2.3)$$

The limiting behavior as $\mathbf{k}\to 0$ of the lattice sum in Eq. (2.3) has been found by Cohen and Keffer[10] in the case of an infinite crystal to be

$$\frac{4\pi n}{3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right), \quad (2.4)$$

and we see that the limiting value at $\mathbf{k}=0$ depends on the direction along which the origin in $\mathbf{k}$ space is approached. They have also evaluated the limiting behavior of this sum when the crystal is taken to be a sphere of radius R centered at the reference ion. In this case they obtain

$$\sum_l{}'\frac{3x_ly_l-\delta_{xy}r_l^2}{r_l^5}e^{i\mathbf{k}\cdot\mathbf{r}_l}\xrightarrow[\mathbf{k}\to 0]{}\frac{4\pi n}{3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\times\left(1-\frac{3j_1(kR)}{kR}\right), \quad (2.5)$$

where $j_l(\rho)$ is the lth spherical Bessel function,[11] and we see that the sum vanishes at $\mathbf{k}=0$ in a finite spherical crystal as we would expect from symmetry arguments. The elements of the dynamical matrix for a finite spherical crystal can thus be expressed in the small $\mathbf{k}$ limit as

$$D_{xy}(\mathbf{k})\xrightarrow[\mathbf{k}\to 0]{}\tfrac{1}{3}\omega_p^2\delta_{xy}-\tfrac{1}{3}\omega_p^2\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\times\left(1-\frac{3j_1(kR)}{kR}\right). \quad (2.6)$$

With the result given by Eq. (2.6) we find that

$$\mathrm{Tr}\mathbf{D}=\sum_{j=1}^{3}\omega_j^2(\mathbf{k})=\omega_p^2,$$

so that Kohn's sum rule[12] is still satisfied in a finite spherical crystal, at least in the long wavelength limit.

We denote the factor $[1-3j_1(kR)/kR]$ by Δ. The secular determinant constructed from the elements (2.6) when expanded yields the following equation for the determination of the eigenfrequencies

$$\lambda^3-3\lambda^2+3(1-\Delta)(1+\Delta)\lambda-(1-\Delta)^2(1+2\Delta)=0, \quad (2.7)$$

independent of the direction cosines of $\mathbf{k}$, where $\lambda=3\omega^2/\omega_p^2$. The roots of Eq. (2.7) are readily determined to be

$$\lambda=1-\Delta\ \text{(twice)};\quad \lambda=1+2\Delta; \quad (2.8)$$

or in terms of frequencies,

$$\omega^2=\frac{j_1(kR)}{kR}\omega_p^2\ \text{(twice)}$$
$$\omega^2=\left[1-2\frac{j_1(kR)}{kR}\right]\omega_p^2. \quad (2.9)$$

Now, the function $j_1(\rho)/\rho$ approaches the limit $\frac{1}{3}$ as $\rho\to 0$, and goes to zero in the limit as $\rho\to\infty$. From Eq. (2.9) we see therefore that if we keep R finite and pass to the limit as $\mathbf{k}\to 0$, we find that all three frequencies approach the same limit

$$\omega^2\xrightarrow[R\text{ fixed},\ \mathbf{k}\to 0]{}\tfrac{1}{3}\omega_p^2. \quad (2.10)$$

On the other hand, if we carry out the passages to the limits in the order in which they are usually done, first letting R become infinite and then letting $\mathbf{k}$ go to zero, we obtain the previously derived results[13]:

$$\omega^2\xrightarrow[R\to\infty,\ \mathbf{k}\to 0]{}\begin{cases}\omega_p^2\\ 0\ \text{(twice)}\end{cases}. \quad (2.11)$$

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[8] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. **1**, 395 (1960).

[9] See, for example, C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1953), p. 92.

[10] M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

[11] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 77.

[12] W. Kohn (unpublished work); see J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

[13] C. B. Clark, Phys. Rev. **109**, 1133 (1958).

The pathological behavior of $\omega_j(\mathbf{k})$ in the limit as $\mathbf{k}\to 0$ described by Eqs. (2.10) and (2.11) has previously been commented on by Carr.[14]

In obtaining the results expressed by Eq. (2.9) we have made the assumption that the reference ion is at the center of the sphere. This assumption arises in obtaining the expression (2.5). It is of some interest to see what are the effects of displacing the reference ion from the center of the sphere by a translation vector of the lattice. We denote this translation vector by $\mathbf{a}$. The required lattice sum becomes

$$S=\sum_l{}' \frac{3(x_l-a_x)(y_l-a_y)-(\mathbf{r}_l-\mathbf{a})^2\delta_{xy}}{|\mathbf{r}_l-\mathbf{a}|^5}\times\exp[i\mathbf{k}\cdot(\mathbf{r}_l-\mathbf{a})]. \quad (2.12)$$

Since $\mathbf{a}$ is a translation vector of the lattice, the infinite lattice result for the small $\mathbf{k}$ limit of this sum, Eq. (2.4) still holds. The value of the sum appropriate to a spherical crystal of radius R is given by

$$S_R=S_\infty-S_{\infty-R}, \quad (2.13)$$

where $S_{\infty-R}$ is the contribution to this sum from points $\mathbf{r}_l$ lying outside the sphere. Following Cohen and Keffer, we evaluate this latter contribution by replacing the sum by an integral:

$$S_{\infty-R}=n\int_R^\infty\int_0^{2\pi}\int_0^\pi \frac{3(x-a_x)(y-a_y)-\delta_{xy}(\mathbf{r}-\mathbf{a})^2}{|\mathbf{r}-\mathbf{a}|^5}\times\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{a})]d^3\mathbf{r}. \quad (2.14)$$

This replacement is valid in the small-$\mathbf{k}$ limit. For our purposes this integral is most conveniently written as

$$S_{\infty-R}=n\exp(-i\mathbf{k}\cdot\mathbf{a})\frac{\partial^2}{\partial a_x\partial a_y}\times\int_R^\infty\int_0^\pi\int_0^{2\pi}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{a}|}d^3\mathbf{r} \quad (2.15)$$

$$=n\exp(-i\mathbf{k}\cdot\mathbf{a})\frac{\partial^2}{\partial a_x\partial a_y}I(\mathbf{a};\mathbf{k}). \quad (2.16)$$

Since we have that $|\mathbf{r}|\geqslant R>|\mathbf{a}|$, we expand the denominator of the integrand in powers of (a/r):

$$|\mathbf{r}-\mathbf{a}|^{-1}=\frac{1}{r}+\frac{a}{r^2}P_1(\cos\gamma)+\frac{a^2}{r^3}P_2(\cos\gamma)+\cdots, \quad (2.17)$$

where γ is the angle between $\mathbf{a}$ and $\mathbf{r}$. The integral $I(\mathbf{a};\mathbf{k})$ becomes

$$I(\mathbf{a};\mathbf{k})=\sum_{l=0}^\infty a^l\int_R^\infty\int_0^\pi\int_0^{2\pi}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r^{l+1}}\times P_l(\cos\gamma)r^2\sin\theta drd\theta d\phi. \quad (2.18)$$

[14] W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).

The integrals are evaluated in Appendix A with the result that

$$I(\mathbf{a};\mathbf{k})=\frac{4\pi}{k^2}\sum_{l=0}^\infty i^l(ak)^lP_l(\cos\delta)\frac{j_{l-1}(kR)}{(kR)^{l-1}}, \quad (2.19)$$

where δ is the angle between the vectors $\mathbf{a}$ and $\mathbf{k}$. Since we want the second mixed partial derivative of this function with respect to a_x and a_y we need consider only the terms with $l\geqslant 2$.

As a check on the calculation we consider the $l=2$ term in this expansion:

$$I^{(2)}(\mathbf{a};\mathbf{k})=-\frac{4\pi}{k^2}\frac{j_1(kR)}{kR}\frac{1}{2}[3(\mathbf{a}\cdot\mathbf{k})^2-a^2k^2]. \quad (2.20)$$

We thus obtain

$$\frac{\partial^2 I^{(2)}(\mathbf{a};\mathbf{k})}{\partial a_x\partial a_y}=\frac{4\pi}{k^2}\frac{j_1(kR)}{kR}(\delta_{xy}k^2-3k_xk_y). \quad (2.21)$$

From Eqs. (2.13), (2.15), and (2.21) we finally obtain the result that in the case $\mathbf{a}\to 0$,

$$S_R=\frac{4\pi n}{3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)-\frac{4\pi n}{3}\frac{3j_1(kR)}{kR}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right),$$

which is identical with the result given in Eq. (2.5).

It is clear from Eq. (2.19) and the fact that

$$\lim_{\rho\to 0}\frac{j_l(\rho)}{\rho^l}=\frac{1}{1\times 3\times 5\cdots\times(2l+1)}, \quad (2.22)$$

that all terms in the expansion for $I(\mathbf{a};\mathbf{k})$ with $l\geqslant 3$ are of $O(k^{l-2})$ as $\mathbf{k}\to 0$ and are well behaved, i.e., show no pathological behavior in the small $\mathbf{k}$ limit. The result obtained by taking the second mixed partial derivatives of $I(\mathbf{a};\mathbf{k})$ with respect to $\mathbf{k}$ is also well behaved in the limit as $\mathbf{k}\to 0$. Since for large ρ

$$j_l(\rho)\sim\frac{1}{\rho}\cos[\rho-\tfrac{1}{2}(l+1)\pi], \quad \rho\gtrsim l$$

the terms with $l\geqslant 3$ in the expansion of the second derivative will show a strong $\mathbf{a}$ dependence only for values of $\mathbf{a}$ comparable with R, provided kR is large. However, if we pass to the limit $\mathbf{k}\to 0$, the terms with $l\geqslant 3$ go to zero and we are left with the contribution from only the $l=2$ term, which is independent of $\mathbf{a}$. Therefore, as long as we are only interested in the limiting values of the frequencies in the limit as $\mathbf{k}\to 0$ for fixed R, we can assert that the results given by Eq. (2.10) are independent of the location of the reference lattice point.

III. LIMITING OPTICAL FREQUENCIES IN NaCl-TYPE CRYSTALS

The dynamical matrix for the NaCl crystal has been given by Kellermann[3]:

$$\left\{\begin{matrix}
\begin{Bmatrix}1&1\\x&x\end{Bmatrix}-\omega^2 & \begin{Bmatrix}1&2\\x&x\end{Bmatrix} & \begin{Bmatrix}1&1\\x&y\end{Bmatrix} & \begin{Bmatrix}1&2\\x&y\end{Bmatrix} & \begin{Bmatrix}1&1\\x&z\end{Bmatrix} & \begin{Bmatrix}1&2\\x&z\end{Bmatrix}\\
\begin{Bmatrix}2&1\\x&x\end{Bmatrix} & \begin{Bmatrix}2&2\\x&x\end{Bmatrix}-\omega^2 & \begin{Bmatrix}2&1\\x&y\end{Bmatrix} & \begin{Bmatrix}2&2\\x&y\end{Bmatrix} & \begin{Bmatrix}2&1\\x&z\end{Bmatrix} & \begin{Bmatrix}2&2\\x&z\end{Bmatrix}\\
\begin{Bmatrix}1&1\\y&x\end{Bmatrix} & \begin{Bmatrix}1&2\\y&x\end{Bmatrix} & \begin{Bmatrix}1&1\\y&y\end{Bmatrix}-\omega^2 & \begin{Bmatrix}1&2\\y&y\end{Bmatrix} & \begin{Bmatrix}1&1\\y&z\end{Bmatrix} & \begin{Bmatrix}1&2\\y&z\end{Bmatrix}\\
\begin{Bmatrix}2&1\\y&x\end{Bmatrix} & \begin{Bmatrix}2&2\\y&x\end{Bmatrix} & \begin{Bmatrix}2&1\\y&y\end{Bmatrix} & \begin{Bmatrix}2&2\\y&y\end{Bmatrix}-\omega^2 & \begin{Bmatrix}2&1\\y&z\end{Bmatrix} & \begin{Bmatrix}2&2\\y&z\end{Bmatrix}\\
\begin{Bmatrix}1&1\\z&x\end{Bmatrix} & \begin{Bmatrix}1&2\\z&x\end{Bmatrix} & \begin{Bmatrix}1&1\\z&y\end{Bmatrix} & \begin{Bmatrix}1&2\\z&y\end{Bmatrix} & \begin{Bmatrix}1&1\\z&z\end{Bmatrix}-\omega^2 & \begin{Bmatrix}1&2\\z&z\end{Bmatrix}\\
\begin{Bmatrix}2&1\\z&x\end{Bmatrix} & \begin{Bmatrix}2&2\\z&x\end{Bmatrix} & \begin{Bmatrix}2&1\\z&y\end{Bmatrix} & \begin{Bmatrix}2&2\\z&y\end{Bmatrix} & \begin{Bmatrix}2&1\\z&z\end{Bmatrix} & \begin{Bmatrix}2&2\\z&z\end{Bmatrix}-\omega^2
\end{matrix}\right\}, \qquad (3.1)$$

where

$$\begin{Bmatrix}k&k'\\x&y\end{Bmatrix}=-\frac{1}{(M_kM_{k'})^{\frac{1}{2}}}e_ke_{k'}\sum_l\left[\frac{\partial^2}{\partial x\partial y}\frac{1}{|\mathbf{r}-\mathbf{a}^l|}\right]_{r=r_{kk'}}\times\exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]-\frac{1}{(M_kM_{k'})^{\frac{1}{2}}}\delta_{xy}\frac{e^2}{V_a}[A\cos2\pi r_0k_x+B(\cos2\pi r_0k_y+\cos2\pi r_0k_z)], \qquad (3.2a)$$

$$\begin{Bmatrix}k&k\\x&y\end{Bmatrix}=-\frac{1}{M_k}e_k^2\lim_{r\to0}\left[\sum_l\frac{\partial^2}{\partial x\partial y}\frac{1}{|\mathbf{r}-\mathbf{a}^l|}\exp(2\pi i\mathbf{k}\cdot\mathbf{a}^l)-\frac{\partial^2}{\partial x\partial y}\frac{1}{|\mathbf{r}|}\right]+\frac{1}{M_k}\delta_{xy}\frac{e^2}{V_a}(A+2B). \qquad (3.2b)$$

In these expressions k and k' label the two ions in a unit cell, M_k and $M_{k'}$ are the corresponding ionic masses, $\mathbf{r}_{kk'}$ is the vector joining the two ions in a unit cell, $\mathbf{a}^l$ is a lattice translation vector, and r_0 is the distance between nearest-neighbor ions. The constants B and A are proportional to the first and second derivatives of the repulsive interaction between ions, which is assumed to act between nearest-neighbor ions only. They are related to the coefficient of compressibility β by[3]

$$\frac{1}{\beta}=\frac{1}{6r_0}\frac{e^2}{V_a}(A+2B). \qquad (3.3)$$

The lattice generated by the $\{\mathbf{a}^l\}$ is a face-centered cubic lattice, and the $\{\mathbf{a}^l\}$ can be written explicitly as

$$\mathbf{a}^l=r_0(l_x,l_y,l_z), \qquad (3.4)$$

where l_x, l_y, l_z are three integers whose sum is even. V_a, the volume of a unit cell of the lattice, is $2r_0^3$.

The sum in square brackets in Eq. (3.2b) can be written as

$$S\begin{pmatrix}k&k\\x&y\end{pmatrix}={\sum_l}'\frac{3a_x^la_y^l-\delta_{xy}(a^l)^2}{(a^l)^5}\exp(2\pi i\mathbf{k}\cdot\mathbf{a}^l). \qquad (3.5)$$

This sum differs from that given in Eq. (2.3) only in the replacement of $\mathbf{k}$ by $2\pi\mathbf{k}$, and in the fact that it is carried out over a face-centered rather than a body-centered cubic lattice. Noting these changes we can use Eq. (2.4) to give us the small-$\mathbf{k}$ behavior of

$$S\begin{pmatrix}k&k\\x&y\end{pmatrix}$$

for the case of a finite spherical crystal of radius R centered at the reference ion:

$$S_R\begin{pmatrix}k&k\\x&y\end{pmatrix}\underset{k\to0}{\longrightarrow}\frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\times\left(1-\frac{3j_1(2\pi kR)}{2\pi kR}\right). \qquad (3.6)$$

Combining this result with Eq. (3.2b) we obtain for

$$\begin{Bmatrix}k&k\\x&y\end{Bmatrix}$$

in the small $\mathbf{k}$ limit

$$\begin{Bmatrix}k&k\\x&y\end{Bmatrix}=-\frac{e^2}{M_k}\frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\left(1-\frac{3j_1(2\pi kR)}{2\pi kR}\right)+\delta_{xy}\frac{e^2}{M_k}\frac{1}{2r_0^3}(A+2B). \qquad (3.7)$$

Turning now to the lattice sum appearing in Eq. (3.2a), we see that it can be written explicitly as

$$S\begin{pmatrix}k&k'\\x&y\end{pmatrix}=\sum_l\frac{3(x_{kk'}-a_x^l)(y_{kk'}-a_y^l)-\delta_{xy}|\mathbf{r}_{kk'}-a^l|^2}{|\mathbf{r}_{kk'}-a^l|^5}\times\exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]. \qquad (3.8)$$

The small-$\mathbf{k}$ limiting behavior of this sum for an infinite lattice,

$$S_\infty\begin{pmatrix}k&k'\\x&y\end{pmatrix}$$

is obtained in Appendix B, with the result that

$$S_\infty\begin{pmatrix} k & k' \\ x & y \end{pmatrix}_{\mathbf{k}\to 0}=\frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right). \tag{3.9}$$

The contribution to this sum coming from values of $\mathbf{a}^l$ lying outside a sphere of radius R centered at the point $\mathbf{a}^l=0$ is again approximated by an integral:

$$S_{\infty-R}\begin{pmatrix} k & k' \\ x & y \end{pmatrix}_{\mathbf{k}\to 0}=\frac{1}{2r_0^3}\int_R^\infty\int_0^\pi\int_0^{2\pi}\frac{3(x-x_{kk'})(y-y_{kk'})-\delta_{xy}(\mathbf{r}-\mathbf{r}_{kk'})^2}{|\mathbf{r}-\mathbf{r}_{kk'}|^5}\times e^{2\pi i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_{kk'})}d^3\mathbf{r}. \tag{3.10}$$

This is just the integral appearing in Eq. (2.14) and we can make use of the results of Appendix A to write

$$S_{\infty-R}\begin{pmatrix} k & k' \\ x & y \end{pmatrix}_{\mathbf{k}\to 0}=\frac{e^{-2\pi i\mathbf{k}\cdot\mathbf{r}_{kk'}}}{2r_0^3}4\pi\frac{j_1(2\pi kR)}{2\pi kR}\times\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right). \tag{3.11}$$

Combining the results expressed by Eqs. (3.9) and (3.11) we have that

$$S_R\begin{pmatrix} k & k' \\ x & y \end{pmatrix}=\frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\times\left(1-3\frac{j_1(2\pi kR)}{2\pi kR}\right). \tag{3.12}$$

This result is not too surprising in view of the independence of such sums to the choice of origin in the limit as $\mathbf{k}\to 0$. The corresponding element of the dynamical matrix becomes

$$\begin{Bmatrix} k & k \\ x & y \end{Bmatrix}=\frac{e^2}{(M_kM_{k'})^{\frac{1}{2}}}\frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy}-\frac{3k_xk_y}{k^2}\right)\times\left(1-3\frac{j_1(2\pi kR)}{2\pi kR}\right)-\delta_{xy}\frac{e^2}{(M_kM_{k'})^{\frac{1}{2}}}\times\frac{1}{2r_0^3}[A+2B]. \tag{3.13}$$

With the result of Eq. (3.7) we see that the trace of the dynamical matrix in the limit as $\mathbf{k}\to 0$ is given by

$$\mathrm{Tr}\mathbf{D}(\mathbf{k})=3\left(\frac{1}{M_+}+\frac{1}{M_-}\right)\frac{e^2}{2r_0^3}(A+2B)=\frac{18r_0}{\beta}\left(\frac{1}{M_+}+\frac{1}{M_-}\right), \tag{3.14}$$

where we have used Eq. (3.3). Thus, as expected, the Liebfried-Brout sum rule[15] is satisfied in the long wavelength limit for a finite crystal.

The 6×6 secular determinant is inconvenient to expand and we have solved it only for waves propagating along the [100], [110] and [111] directions. Setting the factor $[1-3J_1(2\pi kR)/2\pi kR]$ equal to Δ as before, we find in each case the following six solutions:

$$\omega^2=0,\ \text{(three solutions)}$$

$$\omega^2=\frac{e^2}{V_a}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)\times\left[(A+2B)-\frac{4\pi}{3}\Delta\right],\ \text{(two solutions)} \tag{3.15}$$

$$\omega^2=\frac{e^2}{V_a}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)\left[(A+2B)-\frac{8\pi}{3}\Delta\right].$$

In view of the results of the preceding section we can assert with confidence that these six frequencies are the eigenvalues of the dynamical matrix in the small-$\mathbf{k}$ limit, and are independent of the direction along which the origin in $\mathbf{k}$ space is approached.

The first three roots clearly correspond to the acoustic modes, and we do not discuss them further here. The next two frequencies are those associated with the "transverse" optical mode. We see that if we pass to the limit $\mathbf{k}\to 0$ keeping R fixed and finite, the three optical frequencies approach the common value

$$\omega_0^2=\frac{e^2}{V_a}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)(A+2B). \tag{3.16}$$

On the other hand, if, in the usual way, we pass to the limit $R\to\infty$ first and then pass to the limit $\mathbf{k}\to 0$, the two "transverse" optical frequencies approach

$$\omega_t^2=\frac{e^2}{V_a}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)(A+2B-4\pi/3), \tag{3.17a}$$

while the "longitudinal" optical frequency approaches

$$\omega_l^2=\frac{e^2}{V_a}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)(A+2B+8\pi/3). \tag{3.17b}$$

The results expressed by Eq. (3.17) are, apart from an obvious misprint in his paper, the limiting values of the optical frequencies found by Kellermann.

Equation (3.16) rewritten with the aid of Eq. (3.3),

$$\omega_0^2=\frac{6r_0}{\beta}\left(\frac{1}{M_+}+\frac{1}{M_-}\right), \tag{3.18}$$

[15] G. Leibfried, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part 1, p. 247; R. Brout, Phys. Rev. **113**, 43 (1959).

gives an explicit expression for the single infrared frequency in the finite-crystal case discussed by Fröhlich.[6]

IV. DISCUSSION

In this note we have established the result that the values of the longitudinal and transverse optical frequencies in an ionic crystal of the sodium chloride type in the infinite-wavelength limit depend on whether the crystal is assumed to be of infinite extent or of finite size.[16] In the former case the results of Kellermann have been recovered which show that the two kinds of modes have different limiting frequencies. In the latter case, it is found that the longitudinal optical and transverse optical modes have the same frequency in the infinite-wavelength limit, in agreement with Rosenstock's contention.

The mathematical explanation for this difference is based on the nonuniform convergence of the electrostatic lattice sums in Eqs. (2.3) and (3.2), as functions of $\mathbf{k}$ in the limit as $\mathbf{k}\rightarrow 0$. That the qualitative behavior of a function described by an expansion in trigonometric functions should be different, when only a finite number of terms is retained, from the result of extending the sum to infinity is familiar from the expansion in Fourier series of functions which are discontinuous or have discontinuous derivatives. The sum of any finite number of terms, no matter how large, can lead to only a continuous, analytic function. It is the passage to an infinite sum which introduces the discontinuities.

The question we must try to answer now is this: Are the results we have obtained purely mathematical and devoid of physical content in that they may be incapable of experimental verification, or is the degeneracy of the longitudinal and transverse modes at $\mathbf{k}=0$ a physical effect which under the proper conditions can be observed?

Since no crystal occurring in nature is infinite in extent, it may be argued that our result of degenerate optical frequencies in a finite crystal is the physically correct one. Unfortunately, the situation is not quite so simple.

The results we have obtained for the optical frequencies are rigorous only at $\mathbf{k}=0$ itself. When we proceed to finite values of $\mathbf{k}$ the evaluation of the frequencies as functions of $\mathbf{k}$ is beset by two related difficulties. The first is associated with the determination of the higher order terms in the expansion of the electrostatic lattice sums in powers of $\mathbf{k}$. The terms of $O(k^2)$ in the expansion of the sum in Eq. (2.3) have been obtained in the infinite lattice case by Cohen and Keffer. To obtain the corresponding terms in the finite lattice case, we would have to proceed somewhat more carefully than we have in this paper. The replacement of the sums over all lattice points outside the sphere of radius R by integrals corresponds to using the leading term in the three-dimensional form of Poisson's summation formula. The omission of the terms past the integral in this summation formula is justified in obtaining the leading $\mathbf{k}$-dependent terms, but it would have to be rectified in a calculation of the higher order terms. The second difficulty has to do with the dependence of the values of the electrostatic lattice sums on the choice of the position of the reference ion relative to the center of the sphere. We can expect this dependence to be small for reference ions whose vector distance $\mathbf{a}$ from the center is small, particularly when kR is large. However, these conditions are not satisfied for all of the ions in the spherical sample. An approximate way of taking account of the a dependence of the lattice sums and hence of the frequencies is to evaluate the latter for a particular choice of the displacement vector $\mathbf{a}$ and then to average the result over all values of $\mathbf{a}$, assuming the spherically symmetric distribution function

$$\begin{aligned} P(a)da &= \frac{4\pi a^2}{\frac{4}{3}\pi R^3}da, \quad 0<a<R \\ &= 0, \qquad R<a \end{aligned} \tag{4.1}$$

for the probability of finding an ion in the shell defined by the interval $(a, a+da)$.

Rather than carrying out the rather elaborate calculations outlined above, we have preferred to reason in the following somewhat simpler way in drawing physical conclusions from the results of the analysis of the preceding sections. In the small-$\mathbf{k}$ limit, no matter what the correction terms to $\omega_j^2(\mathbf{k})$ are, they will be of higher order in $\mathbf{k}$ than are the results expressed by Eqs. (3.15). This means that for small enough $\mathbf{k}$ we should be able to obtain meaningful results from a discussion of Eqs. (3.15) alone. We see that the small-$\mathbf{k}$ values of ω^2 are determined by the terms containing $\Delta=1-3j_1(2\pi kR)/2\pi kR$. An explicit expression for $j_1(\rho)/\rho$ is

$$\frac{j_1(\rho)}{\rho}=\sin\rho/\rho^3-\cos\rho/\rho^2. \tag{4.2}$$

As we have remarked in previous sections, if ρ is sufficiently small this quantity approaches $\frac{1}{3}$, while it goes to zero for large ρ. However, Δ does not reach its limiting values very rapidly. When $2\pi kR=1$, $\Delta=0.0964$ which is small, but not zero, while at $2\pi kR=3\pi$, $\Delta=0.966$, which is not very close to unity. Thus, if by some technique it is possible to measure the dispersion curves for the optical branches of the frequency spectrum for values of $\mathbf{k}$ such that $0<2\pi kR<3\pi$, the oscillation of the longitudinal and transverse optical branches should be observable.

The usual techniques for determining dispersion curves, viz., x-ray diffuse scattering measurements, and the inelastic, coherent scattering of low-energy neutrons,

[16] Although we speak here of crystals of infinite size, it is clear that these remarks apply as well to calculations based on the cyclic boundary condition, since in the latter case every ion is considered as equivalent to every other ion, and the lattice sums are extended to infinity.

do not give very accurate results for very small values of $\mathbf{k}$. There is, however, another method for determining the value of the frequency of the transverse optical mode for very small values of $\mathbf{k}$. This is by measuring the so-called "reststrahl" frequency, which is usually defined as the limiting value of the frequency of a transverse optical branch as $\mathbf{k}\to 0$. However, strictly speaking, the value of the reststrahl frequency is not that of the transverse optical branch at $\mathbf{k}=0$, but corresponds to a very small, but finite value of $\mathbf{k}$, which can be determined in the following way.[17] If $\mathbf{q}$ is the wave vector of the incident photon, the energy conservation condition on its interaction with phonons leads to the equation

$$2\pi cq=\omega_j(\mathbf{k}), \qquad (4.3)$$

where $q=|\mathbf{q}|$, c is the speed of light, and j denotes the transverse optical branch. The "momentum" conservation condition requires

$$\mathbf{q}=\mathbf{k}. \qquad (4.4)$$

Combining Eqs. (4.3) and (4.4), we have for the equation determining $\mathbf{k}$

$$2\pi ck=\omega_j(\mathbf{k}). \qquad (4.5)$$

A typical value for a frequency in the transverse optical branch is 3×10^{13} sec^{-1}, so that the value of k obtained from Eq. (4.5) is

$$k\sim1.6\times10^2\ \text{cm}^{-1}. \qquad (4.6)$$

From studies of the dynamics of simple models of crystals[18] it is known that the values of the wave vector $\mathbf{k}$ are discrete, whether the ionic displacements satisfy the cyclic boundary condition, clamped boundary conditions, or natural boundary conditions. The minimum (nonzero) value of $\mathbf{k}$ in each of these cases is of the order of the reciprocal of the linear dimensions of the crystal. In the present case of a spherical crystal of radius R this criterion implies

$$k_{\min}\sim1/2R. \qquad (4.7)$$

For this value of $k_{\min}$, $2\pi k_{\min}R\sim\pi$, for which $\Delta=0.696$. This value of Δ is intermediate between its two limiting values, implying a similar statement about the longitudinal and transverse frequencies. Since Eq. (4.7) expresses the minimum value that k can have in a crystal, combining Eqs. (4.6) and (4.7) we find that in order for the photons to be able to interact with the optical mode phonons, we must have

$$k\sim1.6\times10^2\ \text{cm}^{-1}>k_{\min}\sim1/2R. \qquad (4.8)$$

This means that if reflectance studies to determine the reststrahl frequency were carried out on powder samples of (say) NaCl whose particles are of the order of, or greater than, 6×10^{-3} cm in diameter, then if the present theory is correct away from $\mathbf{k}=0$, a decrease in the value of the reststrahl frequency would be observed as the particle size increases. To the authors' knowledge, no such experiments have as yet been carried out, but they appear to be feasible.

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APPENDIX A. EVALUATION OF $I(a;k)$ DEFINED BY EQ. (2.16)

In this Appendix we evaluate the integral $I(\mathbf{a};\mathbf{k})$ defined by

$$I(\mathbf{a};\mathbf{k})=\sum_{n=0}^{\infty}a^n\int_R^\infty r^2dr\int_0^\pi \sin\theta d\theta \times\int_0^{2\pi}d\varphi\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r^{n+1}}P_n(\cos\theta), \qquad (A.1)$$

where we have chosen $\mathbf{a}$ to be the polar axis in writing the term $P_n(\cos\theta)$. Writing $\mathbf{k}=(k_x,k_y,k_z)$ we evaluate the φ integral to find

$$\int_0^{2\pi}\exp[ir(k_x\sin\theta\cos\varphi+k_y\sin\theta\sin\varphi+k_z\cos\theta)]d\varphi =2\pi J_0[r(k_x^2+k_y^2)^{\frac{1}{2}}\sin\theta]\exp[irk_z\cos\theta]. \qquad (A.2)$$

We can simplify this result by noting that

$$k_z=k\cos\delta,\quad (k_x^2+k_y^2)^{\frac{1}{2}}=k\sin\delta, \qquad (A.3)$$

where δ is the angle between $\mathbf{k}$ and $\mathbf{a}$. The θ integral is then evaluated by using an identity given by Stratton[19]:

$$j_n(kr)P_n(\cos\delta) =\frac{i^{-n}}{2}\int_0^\pi e^{ikr\cos\delta\cos\theta} \times J_0(kr\sin\delta\sin\theta)P_n(\cos\theta)\sin\theta d\theta, \qquad (A.4)$$

where $j_n(x)$ is a spherical Bessel function of order n. Thus we are finally left with the r integral

$$4\pi i^nP_n(\cos\delta)\int_R^\infty\frac{j_n(kr)}{r^{n-1}}dr =4\pi i^nk^{n-2}\frac{j_{n-1}(kR)}{(kR)^{n-1}}P_n(\cos\delta), \qquad (A.5)$$

which leads to the expression for $I(\mathbf{a};\mathbf{k})$:

$$I(\mathbf{a};\mathbf{k})=\frac{4\pi}{k^2}\sum_{n=0}^{\infty}i^n(ak)^nP_n(\cos\delta)\frac{j_{n-1}(kR)}{(kR)^{n-1}}. \qquad (A.6)$$

[17] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 56.

[18] See, for example, E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

[19] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), p. 411

APPENDIX B

We work out here the behavior of the lattice sum

$$S_\infty\begin{pmatrix}k & k'\\ x & y\end{pmatrix}=\sum_l \frac{3(x_{kk'}-a_x{}^l)(y_{kk'}-a_y{}^l)-\delta_{xy}|\mathbf{a}^l-\mathbf{r}_{kk'}|^2}{|\mathbf{a}^l-\mathbf{r}_{kk'}|^5}\exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})] \tag{B.1}$$

in the limit as $\mathbf{k}\to 0$. In fact, what we will actually do is to evaluate the sum

$$\Sigma=\sum_l \frac{\exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]}{|\mathbf{a}^l-\mathbf{r}_{kk'}|^5}, \tag{B.2}$$

and take mixed partial derivatives with respect to k_x and k_y.

We begin by rewriting Eq. (B.2) as

$$\Sigma=\frac{1}{\Gamma(5/2)}\sum_l\int_0^\infty t^{\frac{3}{2}}\exp[-t|\mathbf{a}^l-\mathbf{r}_{kk'}|^2+2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]dt, \tag{B.3}$$

$$=\frac{1}{\Gamma(5/2)}\sum_l \exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]\int_\epsilon^\infty t^{\frac{3}{2}}\exp(-t|\mathbf{a}^l-\mathbf{r}_{kk'}|^2) +\frac{1}{\Gamma(5/2)}\int_0^\epsilon t^{\frac{3}{2}}dt\sum_l \exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})-t|\mathbf{a}^l-\mathbf{r}_{kk'}|^2]$$

$$=\Sigma^{(1)}+\Sigma^{(2)}. \tag{B.4}$$

The sum $\Sigma^{(1)}$ can be transformed into

$$\Sigma^{(1)}=\frac{\epsilon^{\frac{5}{2}}}{\Gamma(5/2)}\sum_l \exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]\phi_{\frac{3}{2}}(\epsilon|\mathbf{a}^l-\mathbf{r}_{kk'}|^2), \tag{B.5}$$

where we have introduced the auxiliary integrals

$$\phi_m(x)=\int_1^\infty t^m e^{-xt}dt, \tag{B.6a}$$

$$=\frac{e^{-x}}{x}+\frac{m}{x}\phi_{m-1}(x). \tag{B.6b}$$

We transform the sum $\Sigma^{(2)}$ with the aid of Ewald's generalized theta-function transformation[20]

$$\frac{2}{\sqrt{\pi}}\sum_l \exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})-t|\mathbf{a}^l-\mathbf{r}_{kk'}|^2]=\frac{2\pi}{V_a}\sum_h\frac{1}{t^{\frac{3}{2}}}\exp\left[-\frac{\pi^2}{t}|\mathbf{y}(h)+\mathbf{k}|^2+2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}\right], \tag{B.7}$$

where $\mathbf{y}(h)$ is a translation vector of the reciprocal lattice. Thus, $\Sigma^{(2)}$ becomes

$$\Sigma^{(2)}=\frac{\sqrt{\pi}}{2}\frac{1}{\Gamma(5/2)}\int_0^\epsilon t^{\frac{3}{2}}dt\frac{2\pi}{V_a}\sum_h\frac{1}{t^{\frac{3}{2}}}\exp\left[-\frac{\pi}{t}|\mathbf{y}(h)+\mathbf{k}|^2+2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}\right]$$

$$=\frac{\sqrt{\pi}}{2}\frac{1}{\Gamma(5/2)}\frac{2\pi}{V_a}\epsilon\int_1^\infty\frac{du}{u^2}\sum_h\exp\left[-\pi^2\frac{u}{\epsilon}|\mathbf{y}(h)+\mathbf{k}|^2+2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}\right]$$

$$=\frac{\epsilon\pi^{\frac{3}{2}}}{\Gamma(5/2)V_a}\sum_h e^{2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}}\varphi_{-2}\left(\frac{\pi^2}{\epsilon}|\mathbf{y}(h)+\mathbf{k}|^2\right). \tag{B.8}$$

To ensure equal rates of convergence in the sums $\Sigma^{(1)}$ and $\Sigma^{(2)}$ we pick ϵ to equal π/r_0^2, and obtain

$$\Sigma=\frac{\pi^{\frac{5}{2}}}{\Gamma(5/2)r_0^5}\sum_l \exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l-\mathbf{r}_{kk'})]\varphi_{\frac{3}{2}}\left(\frac{\pi}{r_0^2}|\mathbf{a}^l-\mathbf{r}_{kk'}|^2\right)+\frac{\pi^{\frac{5}{2}}}{2\Gamma(5/2)r_0^5}\sum_h e^{2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}}\varphi_{-2}(\pi r_0^2|\mathbf{y}(h)+\mathbf{k}|^2). \tag{B.9}$$

[20] Reference 4, p. 251.

We need the nonvanishing terms in $(\partial^2/\partial k_x\partial k_y)\sum$ in the limit as $\mathbf{k}\to 0$. Differentiating, we obtain

$$S_\infty\begin{pmatrix} k & k' \\ x & y \end{pmatrix} = \frac{\pi^{\frac{5}{2}}}{\Gamma(5/2)r_0^5}\sum_l \{3(a_x^l - x_{kk'})(a_y^l - y_{kk'}) - \delta_{xy}(\mathbf{a}^l - \mathbf{r}_{kk'})^2\}\varphi_{\frac{3}{2}}\left(\frac{\pi}{r_0^2}|\mathbf{a}^l - \mathbf{r}_{kk'}|^2\right)\exp[2\pi i\mathbf{k}\cdot(\mathbf{a}^l - \mathbf{r}_{kk'})]$$
$$-\frac{1}{4\pi^2}\frac{\pi^{\frac{5}{2}}}{2\Gamma(5/2)r_0^5}\sum_h \exp[2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}]\exp\{-\pi r_0^2[\mathbf{y}(h)+\mathbf{k}]^2\}$$
$$\times 4\pi r_0^2\left\{\frac{3[y_x(h)+h_x][y_y(h)+k_y] - \delta_{xy}[\mathbf{y}(h)+\mathbf{k}]^2}{[\mathbf{y}(h)+\mathbf{k}]^2}\right\}. \quad \text{(B.10)}$$

In the limit as $\mathbf{k}\to 0$ this expression becomes

$$S_\infty\begin{pmatrix} k & k' \\ x & y \end{pmatrix}_{\mathbf{k}\to 0} = \frac{\pi^{\frac{5}{2}}}{\Gamma(5/2)r_0^5}\sum_l \{3(a_x^l - x_{kk'})(a_y^l - y_{kk'}) - \delta_{xy}(\mathbf{a}^l - \mathbf{r}_{kk'})^2\}\varphi_{\frac{3}{2}}\left(\frac{\pi}{r_0^2}|\mathbf{a}^l - \mathbf{r}_{kk'}|^2\right)$$
$$-\frac{\pi^{\frac{3}{2}}}{2\Gamma(5/2)r_0^3}\exp(-\pi r_0^2 k^2)\left[\frac{3k_x k_y}{k^2} - \delta_{xy}\right]$$
$$-\frac{\pi^{\frac{3}{2}}}{2\Gamma(5/2)r_0^3}\sum_h{}' \exp[2\pi i\mathbf{y}(h)\cdot\mathbf{r}_{kk'}]\exp[-\pi r_0^2 y^2(h)]\frac{3y_x(h)y_y(h) - \delta_{xy}y^2(h)}{y^2(h)}. \quad \text{(B.11)}$$

The sums over l and h vanish identically, and we are left with

$$S_\infty\begin{pmatrix} k & k' \\ x & y \end{pmatrix} \underset{\mathbf{k}\to 0}{\longrightarrow} \frac{4\pi}{3}\frac{1}{2r_0^3}\left(\delta_{xy} - \frac{3k_x k_y}{k^2}\right). \quad \text{(B.12)}$$