Chapter 9
Dielectrics and Ferroelectrics

Despite the fact that the concept of the dielectric constant is often taught in introductory physics—because, e.g., of its applications to capacitors—the concept involves subtle physics. The purpose of this chapter is to review the important dielectric properties of solids without glossing over the intrinsic difficulties.

Dielectric properties are important for insulators and semiconductors. When a dielectric insulator is placed in an external field, the field (if weak) induces a polarization that varies linearly with the field. The constant of proportionality determines the dielectric constant. Both static and time-varying external fields are of interest, and the dielectric constant may depend on the frequency of the external field. For typical dielectrics at optical frequencies, there is a simple relation between the index of refraction and the dielectric constant. Thus, there is a close relation between optical and dielectric properties. This will be discussed in more detail in the next chapter.

In some solids, below a critical temperature, the polarization may "freeze in." This is the phenomena of ferroelectricity, which we will also discuss in this chapter. In some ways ferroelectric and ferromagnetic behavior are analogous.

Dielectric behavior also relates to metals particularly by the idea of "dielectric screening" in a quasifree-electron gas. In metals, a generalized definition of the dielectric constant allows us to discuss important aspects of the many-body properties of conduction electrons. We will discuss this in some detail.

Thus, we wish to describe the ways that solids exhibit dielectric behavior. This has practical as well as intrinsic interest and is needed as a basis for the next chapter on optical properties.

9.1 The Four Types of Dielectric Behavior (B)

1. *The polarization of the electronic cloud around the atoms*: When an external electric field is applied, the electronic charge clouds are distorted. The resulting polarization is directly related to the dielectric constant. There are "anomalies"

J. D. Patterson and B. C. Bailey, *Solid-State Physics*,
https://doi.org/10.1007/978-3-319-75322-5_9

in the dielectric constant or refractive index at frequencies in which the atoms can absorb energies (resonance frequencies, or in the case of solids, interband frequencies). These often occur in the visible or ultraviolet. At lower frequencies, the dielectric constant is practically independent of frequency.

2. *The motion of the charged ions*: This effect is primarily of interest in ionic crystals in which the positive and negative ions can move with respect to one another and thus polarize the crystal. In an ionic crystal, the resonant frequencies associated with the relative motion of the positive and negative ions are in the infrared and will be discussed in the optics chapter in connection with the restrahlen effect.
3. *The rotation of molecules with permanent dipole moments*: This is perhaps the easiest type of dielectric behavior to understand. In an electric field, the dipoles tend to line up with the electric fields, while thermal effects tend to oppose this alignment, and so, the phenomenon is temperature dependent. This type of dielectric behavior is mostly relevant for liquids and gases.
4. *The dielectric screening of a quasifree electron gas*: This is a many-body problem of a gas of electrons interacting via the Coulomb interaction. The technique of using the dielectric constant with frequency and wave-vector dependence will be discussed. This phenomena is of interest for metals.

Perhaps we should mention *electrets* here as a fifth type of dielectric behavior in which the polarization may remain, at least for a very long time after the removal of an electric field. In some ways an electret is analogous to a magnet. The behavior of electrets appears to be complex and as yet they have not found wide applications. Electrets occur in organic waxes due to frozen in disorder that is long lived but probably metastable.[1]

J. D. Stranathan—"Benevolent Director"

b. Missouri, USA (1898–1981).

Book, *Particles of Modern Physics*; Electrets and Dielectric Properties of Liquids and Solids; Administration.

Perhaps some would disagree with our including him here. However, J. D. was dedicated to the University of Kansas for 44 years, and was head of the physics department there for a good portion of that time. He rode out the bad and the good times of physics funding and attracted for the most part good professors (e.g. Max Dresden) and students (e.g. Martin Gutzwiller) who were active and knowledgeable in physics and research. He can represent one strength of USA physics in that it can occur in places that are not so famous

---

[1] See Gutmann [9.9]. See also Bauer et al. [9.1].

or as well known as for example, Harvard and Berkeley. Among areas of his research was that of electrets, which are, in some ways, electrical analogs of magnets. He was best known for his book, which was a good summary of many active areas in physics before WW II.

9.2 Electronic Polarization and the Dielectric Constant (B)

The ideas in this Section link up closely with optical properties of solids. In the chapter on the optical properties of solids, we will relate the complex index of refraction to the absorption and reflection of electromagnetic radiation. Now, we remind the reader of a simple picture, which relates the complex index of refraction to the dynamics of electron motion. We will include damping.

Our model considers matters only from a classical point of view. We limit discussion to electrons in bound states, but for some solids we may want to consider quasifree electrons or both bound and quasifree electrons. For electrons bound by Hooke's law forces, the equation describing their motion in an alternating electric field $E = E_0\exp(-\mathrm{i}\omega t)$ may be written ($e > 0$)

$$m\frac{\mathrm{d}^2x}{\mathrm{d}x^2} + \frac{m}{\tau}\frac{\mathrm{d}x}{\mathrm{d}t} + m\,\omega_0^2 x = -eE_0\exp(-\mathrm{i}\omega t). \tag{9.1}$$

The term containing τ is the damping term, which can be due to the emission of radiation or the other frictional processes. ω_0 is the natural oscillation frequency of the elastically bound electron of charge $-e$ and mass m. The steady-state solution is

$$x(t) = -\frac{e}{m}\frac{E_0\exp(-\mathrm{i}\omega t)}{\omega_0^2 - \omega^2 - \mathrm{i}\omega/\tau}. \tag{9.2}$$

Below, we will assume that the field at the electronic site is the same as the average internal field. This completely neglects local field effects. However, we will follow this discussion with a discussion of local field effects, and in any case, much of the basic physics can be done without them. In effect, we are looking at atomic effects while excluding some interactions.

If N is the number of charges per unit volume, with the above assumptions, we write:

$$P = -Nex = \left(\frac{\varepsilon}{\varepsilon_0} - 1\right)\varepsilon_0 E = N\alpha E, \tag{9.3}$$

where ε is the dielectric constant and α is the polarizability. Using $E = E_0\exp(-\mathrm{i}\omega t)$,

$$\alpha = -\frac{ex}{E} = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 - \mathrm{i}\omega/\tau}. \tag{9.4}$$

The complex dielectric constant is then given by

$$\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{N}{\varepsilon_0}\frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 - \mathrm{i}\omega/\tau} \equiv \varepsilon_r + \mathrm{i}\varepsilon_i, \tag{9.5}$$

where we have absorbed the ε_0 into ε_r and ε_i for convenience. The real and the imaginary parts of the dielectric constant are then given by:

$$\varepsilon_r = 1 + \frac{Ne^2}{m\,\varepsilon_0}\frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2/\tau^2}, \tag{9.6}$$

$$\varepsilon_i = \frac{Ne^2}{m\varepsilon_0}\frac{\omega/\tau}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2/\tau^2}. \tag{9.7}$$

In the chapter on optical properties, we will note that the connection (10.8) between the complex refractive index and the complex dielectric constant is:

$$n_c^2 = (n + \mathrm{i}\,n_i)^2 = (\varepsilon_r + \mathrm{i}\varepsilon_i). \tag{9.8}$$

Therefore,

$$n^2 - n_i^2 = \varepsilon_r, \tag{9.9}$$

$$2nn_i = \varepsilon_i. \tag{9.10}$$

Thus, explicit equations for fundamental optical constants n and n_i are:

$$n^2 - n_i^2 = 1 + \frac{Ne^2}{m\varepsilon_0}\frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2/\tau^2} \tag{9.11}$$

$$2nn_i = \frac{Ne^2}{m\varepsilon_0}\frac{\omega/\tau}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2/\tau^2}. \tag{9.12}$$

Quantum mechanics produces very similar equations. The results as given by Moss[2] are

---

[2] See Moss [9.13]. Note n_i refers to the imaginary part of the dielectric constant on the left of these equations and in f_{ij}, i refers to the initial state, while j refers to the final state.

$$n^2 - n_i^2 = 1 + \sum_j \frac{\left(Ne^2 f_{ij}/m\varepsilon_0\right)\left(\omega_{ij}^2 - \omega^2\right)}{\left(\omega_{ij}^2 - \omega^2\right)^2 + \omega^2/\tau_j^2}, \tag{9.13}$$

$$2nn_i = \sum_j \frac{\left(Ne^2 f_{ij}/m\varepsilon_0\right)\omega/\tau_j}{\left(\omega_{ij}^2 - \omega^2\right)^2 + \omega^2/\tau_j^2}, \tag{9.14}$$

where the f_{ij} are called oscillator strengths and are defined by

$$f_{ij} = 2\omega_{ji}\frac{m\left|\langle\psi_i|x|\psi_j\rangle\right|^2}{\hbar}, \tag{9.15}$$

where

$$\omega_{ij} = \frac{E_i - E_j}{\hbar}, \tag{9.16}$$

with E_i and E_j being the energies corresponding to the wave functions ψ_i and ψ_j. In a solid, because of the presence of neighboring dipoles, the local electric field does not equal the applied electric field.

Clearly, dielectric and optical properties are not easy to separate. Further discussion of optical-related dielectric properties comes in the next chapter.

We now want to examine some consequences of local fields. We also want to keep in mind that we will be talking about total dielectric constants and total polarizability. Thus in an ionic crystal, there are contributions to the polarizabilities and dielectric constants from both electronic and ionic motion.

The first question we must answer is, "If an external field, E, is applied to a crystal, what electric field acts on an atom in the crystal?" See Fig. 9.1. The slab is maintained between two plates that are connected to a battery of constant voltage V. Fringing fields are neglected. Thus, the electric field, E_0, between the plates before the slab is inserted, is the same as the electric field in the solid-state after insertion (so, $E_0 d = V$). This is also the same as the electric field in a needle-shaped cavity in the slab. The electric field acting on the atom is

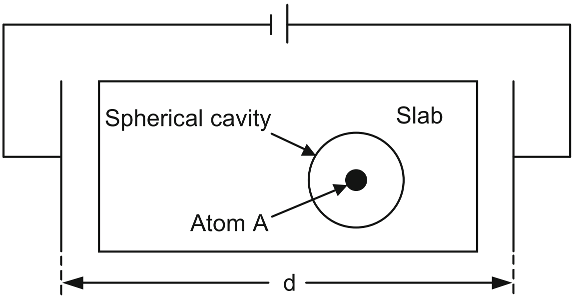

Fig. 9.1 Geometry for local field. (The external electric field in the dielectric is from right to left.)

$$E_{\text{loc}} = E_0' + E_a + E_b + E_c, \tag{9.17}$$

where, E_0' is the electric field due to charge on the plates after the slab is inserted, E_a is the electric field due to the polarization charges on the faces of the slab, and E_b is the electric field due to polarization charges on the surface of the spherical cavity (which exists in our imagination), and E_c is the polarization due to charges interior to the cavity that we assume (in total) sums to zero.

It is, of course, an approximation to write E_{loc} in the above form. Strictly speaking, to find the field at any particular atom, we should sum over the contributions to this field from all other atoms. Since this is an impossible task, we treat macroscopically all atoms that are sufficiently far from A (and outside the cavity).

By Gauss' law, we know the electric field due to two plates with a uniform charge density ($\pm\sigma$) is $E = \sigma/\varepsilon$. Further, σ due to P ending on the boundary of a slab is $\sigma = P$ (from electrostatics). Since the polarization charges on the surface of the slabs will oppose the electric field of the plate and since charge will flow to maintain constant voltage.

$$\varepsilon_0 E_0 = \varepsilon_0 E_0' - P, \tag{9.18}$$

or

$$E_0' = E_0 + \frac{P}{\varepsilon_0}. \tag{9.19}$$

Clearly, $E_a = -P/\varepsilon_0$ (see Fig. 9.2), and for all cubic crystals, $E_c = 0$. So,

$$E_{\text{loc}} = E_0 + E_b. \tag{9.20}$$

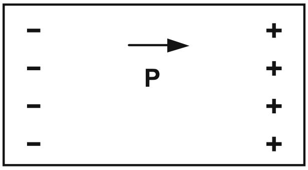

Fig. 9.2 The polarized slab. (Here the external electric field in the dielectric is from left to right.)

Using Fig. 9.3, since $\sigma_p = \boldsymbol{P} \cdot \boldsymbol{n}$ ($\boldsymbol{n}$ is outward normal), the charge on an annular region of the surface of the cavity is

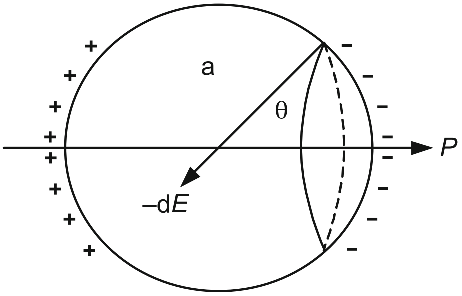

Fig. 9.3 Polarized charges around the cavity

$$\mathrm{d}q = -P\cos\theta \cdot 2\pi a \sin\theta \cdot a\mathrm{d}\theta, \tag{9.21}$$

$$\mathrm{d}E_b = \frac{1}{4\pi\varepsilon_0}\frac{\mathrm{d}q}{a^2}\cdot\cos\theta, \tag{9.22}$$

$$E_b = -\frac{P}{2\varepsilon_0}\int_0^\pi \cos^2\theta \cdot \mathrm{d}\cos\theta. \tag{9.23}$$

Thus $E_b = P/3\varepsilon_0$, and so we find

$$E_{\mathrm{loc}} = E_0 + \frac{P}{3\varepsilon_0}. \tag{9.24}$$

Since E_0 is also the average electric field in the solid, the dielectric constant is defined as

$$\varepsilon = \frac{D}{E_0} = \frac{\varepsilon_0 E_0 + P}{E_0} = \varepsilon_0 + \frac{P}{E_0}. \tag{9.25}$$

The polarization is the dipole moment per unit volume, and so, it is given by

$$P = \sum_{i(\mathrm{atoms})} E^i_{\mathrm{loc}} N_i \alpha_i, \tag{9.26}$$

where N_i is the number of atoms per unit volume of type i, and α_i is the appropriate polarizability (which can include ionic, as well as electronic motions). Thus,

$$P = \left(E_0 + \frac{P}{3\varepsilon_0}\right)\sum_i N_i\alpha_i, \tag{9.27}$$

or

$$\frac{P}{E_0} = \frac{\sum_i N_i\alpha_i}{1 - \frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i}, \tag{9.28}$$

or

$$\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{1}{\varepsilon_0}\frac{\sum_i N_i\alpha_i}{\left(1 - \frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i\right)}, \tag{9.29}$$

which can be arranged to give the Clausius–Mossotti equation

$$\frac{(\varepsilon/\varepsilon_0)-1}{(\varepsilon/\varepsilon_0)+2}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i. \tag{9.30}$$

In the optical range of frequencies (the order of but less than 10^{15} cps), $n^2 = \varepsilon/\varepsilon_0$, and the equation becomes the Lorentz–Lorenz equation

$$\frac{n^2-1}{n^2+2}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_i. \tag{9.31}$$

Finally, we show that when one resonant peak dominates, the only effect of the local field is to shift the dormant resonant (natural) frequency. From

$$\frac{\varepsilon}{\varepsilon_0}=1+\frac{1}{\varepsilon_0}\frac{N\alpha}{(1-N\alpha/3\varepsilon_0)}, \tag{9.32}$$

and

$$\alpha=\frac{e^2}{m}\frac{1}{\omega_0^2-\omega^2-\mathrm{i}\omega/\tau}, \tag{9.33}$$

we have

$$\frac{(\varepsilon/\varepsilon_0)-1}{(\varepsilon/\varepsilon_0)+2}=\frac{N\alpha}{3\varepsilon_0}=\frac{\omega_p^2}{3}\frac{1}{\omega_0^2-\omega^2-\mathrm{i}\omega/\tau}, \tag{9.34}$$

where

$$\omega_p=\sqrt{Ne^2/m\varepsilon_0} \tag{9.35}$$

is the plasma frequency. From this, we easily show

$$\frac{\varepsilon}{\varepsilon_0}=1+\frac{\omega_p^2}{\omega_0'^2-\omega^2-\mathrm{i}\omega/\tau}, \tag{9.36}$$

where

$$\omega_0'^2=\omega_0^2-\frac{1}{3}\omega_p^2, \tag{9.37}$$

which is exactly what we would have obtained in the beginning [from (9.32) and (9.33)] if $\omega_0 \to \omega_0'$, and if the term $N\alpha/3\varepsilon_0$ had been neglected.

9.3 Ferroelectric Crystals (B)

All ferroelectric crystals are polar crystals.[3] Because of their structure, polar crystals have a permanent electric dipole moment. If $\rho(\mathbf{r})$ is the total charge density, we know for polar crystals

$$\int \mathbf{r}\rho(\mathbf{r})\mathrm{d}V \neq 0. \tag{9.38}$$

Pyroelectric crystals have a polarization that changes with temperature. All polar crystals are pyroelectric, but not all polar crystals are ferroelectric. Ferroelectric crystals are polar crystals whose polarization can be reversed by an electric field. All ferroelectric crystals are also piezoelectric, in which stress changes the polarization. Piezoelectric crystals are suited for making electromechanical transducers with a variety of applications.

Ferroelectric crystals often have unusual properties. Rochelle salt $NaKC_4H_4O_6 \cdot 4H_2O$, which was the first ferroelectric crystal discovered, has both an upper and lower transition temperature. The crystal is only polarized between the two transition temperatures. The "TGS" type of ferroelectric, including triglycine sulfate and triglycine selenate, is another common class of ferroelectrics and has found application to IR detectors due to its pyroelectric properties. Ferroelectric crystals with hydrogen bonds (e.g. KH_2PO_4, which was the second ferroelectric crystal discovered) undergo an appreciable change in transition temperature when the crystal is deuterated (with deuterons replacing the H nuclei). $BaTiO_3$ was the first mechanically hard ferroelectric crystal that was discovered. Ferroelectric crystals are often classified as *displacive,* involving a lattice distortion (i.e. barium titinate, $BaTiO_3$, see Fig. 9.4), or *order–disorder* (i.e. potassium dihydrogen phosphate, KH_2PO_4, which involves the ordering of protons).

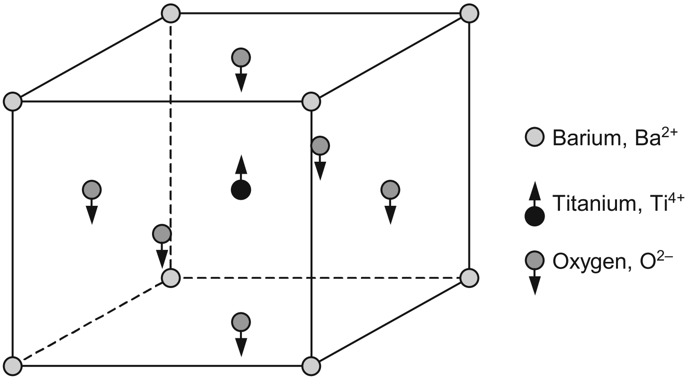

Fig. 9.4 Unit cell of barium titanate. The displacive transition is indicated by the direction of the arrows

---

[3] Ferroelectrics: The term ferro is used but iron has nothing to do with it. Low symmetry causes spontaneous polarization.

In a little more detail, displacive ferroelectrics involve transitions associated with the displacement of a whole sublattice. How this could arises is discussed in Sect. 9.3.3 where we talk about the soft mode model. The soft mode theory, introduced in 1960, has turned out to be a unifying principle in ferroelectricity (see Lines and Glass [9.12]). Order–disorder ferroelectrics have transitions associated with the ordering of ions. We have mentioned in this regard KH_2PO_4 as a crystal with hydrogen bonds in which the motion of protons is important. Ferroelectrics have found application as memories, their high dielectric constant is exploited in making capacitors, and ferroelectric cooling is another area of application.

Other examples include ferroelectric cubic perovskite (PZT) $PbZr_{(x)}Ti_{(1-x)}O_3$, $T_c = 670$ K. The ferroelectric $BaMgF_4$ (BMF) does not show a Curie T even up to melting. These are other familiar ferroelectrics as given below.

The central problem of ferroelectricity is to be able to describe the onset of spontaneous polarization. Spontaneous polarization is said to exist if, in the absence of an electric field, the free energy is minimum for a finite value of the polarization. There may be some ordering involved in a ferroelectric transition, as in a ferromagnetic transition, but the two differ by the fact that the ferroelectric transition in a solid always involves the creation of dipoles.

Just as for ferromagnets, a ferroelectric crystal undergoes a phase transition from the paraelectric phase to the ferroelectric phase, typically, as the temperature is lowered. The transition can be either first order (with a latent heat, i.e. $BaTiO_3$) or second order (without latent heat, i.e. $LiTaO_3$). Just as for ferromagnets, the ferroelectric will typically split into domains of varying size and orientation of polarization. The domain structure forms to reduce the energy. Ferroelectrics show hysteresis effects just like ferromagnets. Although we will not discuss it here, it is also possible to have antiferroelectrics that one can think of as arising from anti-parallel orientation of neighboring unit cells. A simple model of spontaneous polarization is obtained if we use the Clausius–Mossotti equation and assume (unrealistically for solids) that polarization arises from orientation effects. This is discussed briefly in a later section.

Another similar crystal to barium titanate is strontium titanate. Both have perovskite structure. $SrTiO_3$ (STO) was originally synthesized and then found in nature. For a while STO enjoyed popularity as a diamond like material in jewelry, but not being as hard as diamond it scratched much easier. It has been described as showing a quantum like (due to quantum fluctuations) paraelectric behavior at low temperature. It also shows a transition at 110 K due to soft phonon mode behavior. It becomes superconductive when electron doped and in certain cases has been shown to be useful as a substrate material. A very interesting material which bares watching. For a start see for example; Lev P. Gor'kov, "Back to mechanisms of superconductivity in low-doped strontium titanate," arXiv:1610.02062 [cond-mat.supr-con].

9.3.1 Thermodynamics of Ferroelectricity by Landau Theory (B)

For both first-order ($\gamma < 0$, latent heat, G continuous) and second-order ($\gamma > 0$, no latent heat, G' (first derivatives) are continuous and we can choose $\delta = 0$), we assume for the Gibbs free energy G' [9.6 Chap. 3, generally assumed for displacive transitions],

$$G = G_0 + \frac{1}{2}\beta(T - T_0)P^2 + \frac{1}{4}\gamma P^4 + \frac{1}{6}\delta P^6; \quad \beta, \delta > 0. \tag{9.39}$$

(By symmetry, only even powers are possible. Also, in a second-order transition, P is continuous at the transition temperature T_c, whereas in a first-order one it is not.) From this we can calculate

$$E = \frac{\partial G}{\partial P} = \beta(T - T_0)P + \gamma P^3 + \delta P^5, \tag{9.40}$$

$$\frac{1}{\chi} = \frac{\partial E}{\partial P} = \beta(T - T_0) + 3\gamma P^2 + 5\delta P^4. \tag{9.41}$$

Notice in the paraelectric phase, $P = 0$ so $E = 0$ and $\chi = 1/\beta(T - T_0)$, and therefore Curie–Weiss behavior is included in (9.39). For $T < T_c$ and $E = 0$ for second order where $\delta = 0$, $\beta(T - T_0)P + \gamma P^3 = 0$, so

$$P^2 = -\frac{\beta}{\gamma}(T - T_0), \tag{9.42}$$

or

$$P = \pm\sqrt{\frac{\beta}{\gamma}(T_0 - T)}, \tag{9.43}$$

which again is Curie–Weiss behavior (we assume $\gamma > 0$). For $T = T_c = T_0$, we can show the stable solution is the polarized one.

For first order set $E = 0$, solve for P and exclude the solution for which the free energy is a maximum. We find (where we assume $\gamma < 0$)

$$P_S = \pm\left[-\frac{\gamma}{2\delta}\left(1 + \sqrt{1 - \frac{4\delta\beta}{\gamma^2}(T - T_0)}\right)\right]^{1/2}.$$

Now, $G(P_{SC}) = G_{\text{polar}} = G_{\text{nonpolar}} = G_0$ at the transition temperature. Using the expression for G (9.39) and the expression that results from setting $E = 0$ (9.40), we find

$$T_c = T_0 - \frac{\gamma}{4\beta} P_{\text{SC}}^2. \tag{9.44}$$

By $E = 0$, we find [using (9.44)]

$$\frac{3\gamma}{4} P_{\text{SC}}^3 + \delta P_{\text{SC}}^5 = 0, \tag{9.45}$$

so

$$P_{\text{SC}}^2 = -\frac{3\gamma}{4\delta}. \tag{9.46}$$

Putting (9.46) into (9.44) gives

$$T_c = T_0 + \frac{3\gamma^2}{16\beta\delta}. \tag{9.47}$$

Figures 9.5, 9.6, and 9.7 give further insight into first- and second-order transitions.

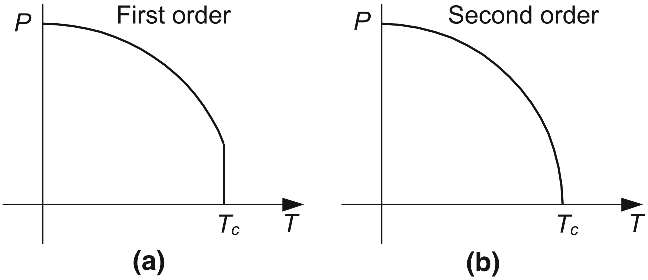

Fig. 9.5 Sketch of (**a**) first-order and (**b**) second-order ferroelectric transitions

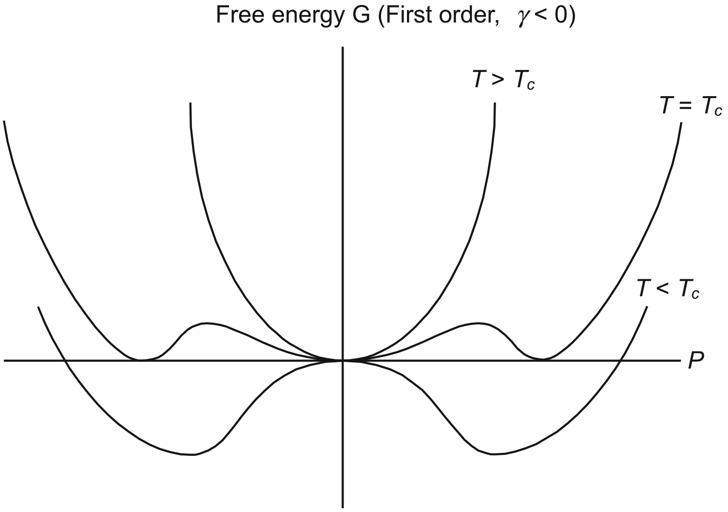

Fig. 9.6 Sketch of variation of Gibbs free energy $G(T, p)$ for first-order transitions

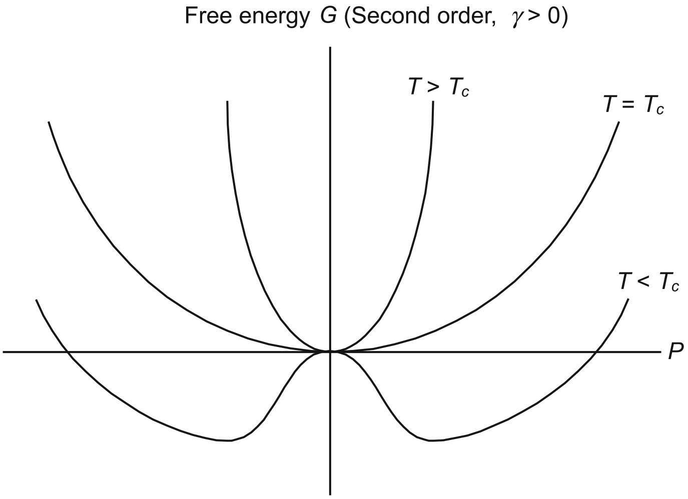

Fig. 9.7 Sketch of variations of Gibbs free energy $G(T, p)$ for second-order transitions

Josiah Willard Gibbs

b. New Haven, Connecticut, USA (1839–1903).

Ensembles; Phase rule; Vector Calculus; Applications of Maxwell's equations to Optics.

Gibbs was another giant of statistical mechanics and introduced the idea of vectors (this work was similar to and independent of the work of Oliver Heaviside). Gibbs approached statistical mechanics through ensembles. For a canonical ensemble, the Partition Function $Z = \mathrm{Tr}(e^{-\beta H})$, Tr is trace, β is $1/kT$, H is the Hamiltonian operator. The derivation of Thermodynamics from state functions can be done from the partition function. Gibbs never married and had a most reserved personality. He graduated from Yale and after travels, including extensive studying in Europe, he returned to Yale and worked in isolation. As suggested above he was noted7 for several contributions besides statistical mechanics.

9.3.2 Further Comment on the Ferroelectric Transition (B, ME)

Suppose we have N permanent, noninteracting dipoles P per unit volume, at temperature T, in an electric field E. At high temperature, simple statistical mechanics shows that the polarizability per molecule is

$$\alpha = \frac{P^2}{3kT}. \tag{9.48}$$

Combining this with the Clausius–Mossotti equation (9.29) gives

$$\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{Np^2}{3k\varepsilon_0(T - T_c)}. \tag{9.49}$$

As $T \to T_c$, we obtain the "polarization catastrophe". For a real crystal, even if this were a reasonable approach, the equation would break down well before $T = T_c$, and at $T = T_c$, we would assume that permanent polarization had set in. Near $T = T_c$, the 1 is negligible, and we have essentially a Curie–Weiss type of behavior. However, this derivation should not be taken too seriously, even though the result is reasonable.

Another way of viewing the ferroelectric transition is by the Lyddane–Sachs–Teller (LST) relation. This is developed in the next chapter, see (10.204). Here an infinite dielectric constant implies a zero-frequency optical mode. This leads to Cochran's theory of ferroelectricity arising from "soft" optic modes. The LST relation can be written

$$\frac{\omega_T^2}{\omega_L^2} = \frac{\varepsilon(\infty)}{\varepsilon(0)}, \tag{9.50}$$

where ω_T is the transverse optical frequency, ω_L is the longitudinal optical frequency (both at low wave vector), $\varepsilon(\infty)$ is the high-frequency limit of the dielectric constant and $\varepsilon(0)$ is the low-frequency (static) limit. Thus a Curie–Weiss behavior for $\varepsilon(0)$ as

$$\frac{1}{\varepsilon(0)} \propto (T - T_c) \tag{9.51}$$

is consistent with

$$\omega_T^2 \propto (T - T_c). \tag{9.52}$$

Cochran has pioneered the approach to a microscopic theory of the onset of spontaneous polarization by the soft mode or "freezing out" (frequency going to zero) of an optic mode of zero wave vector. The vanishing frequency appears to result from a canceling of short-range and long-range (Coulomb) forces between ions. Not all ferroelectric transitions are easily associated with phonon modes. For example, the order–disorder transition is associated with the ordering of protons in potential wells with double minima above the transition. Transition temperatures for some typical ferroelectrics are given in Table 9.1.

Table 9.1 Selected ferroelectric crystals

Type	Crystal	T_c (K)
KDP	KH_2PO_4	123
TGS	Triglycine sulfate	322
Perovskites	$BaTiO_3$	406
	$PbTiO_3$	765
	$LiNbO_3$	1483

From Anderson HL (ed), *A Physicists Desk Reference* 2nd edn, American Institute of Physics, Article 20: Frederikse HPR, p.314, Table 20.02.C.1., 1989, with permission of Springer-Verlag. Original data from Kittel C, *Introduction to Solid State Physics,* 4th edn, p.476, Wiley, NY, 1971

9.3.3 One-Dimensional Model of the Soft Model of Ferroelectric Transitions (A)

In order to get a better picture of what the soft mode theory involves, we present a one-dimensional model below that is designed to show ferroelectric behavior. Anderson and Cochran have suggested that the phase transition in certain ferroelectrics results from an instability of one of the normal vibrational modes of the lattice. Suppose that at some temperature T_c

(a) An infinite-wavelength optical mode is accompanied by the condition that the vibrational frequency ω for that mode is zero.
(b) The effective restoring force for this mode for the ion displacements equals zero. This condition has prompted the terminology, “soft” mode ferroelectrics.

If these conditions are satisfied, it is seen that the static ion displacements would give rise to a “frozen-in” electric dipole moment–that is, spontaneous polarization. The idea is shown in Fig. 9.8.

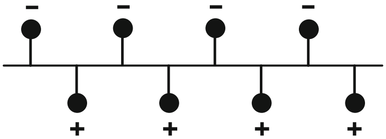

Fig. 9.8 Schematic for ferroelectric mode in one dimension

We now consider a one-dimensional lattice consisting of two atoms per unit cell, see Fig. 9.9. The atoms (ions) have, respectively, mass m_1 and m_2 with charge $e_1 = e$ and $e_2 = -e$. The equilibrium separation distance between atoms is the distance $a/2$.

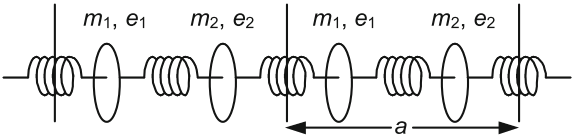

Fig. 9.9 One-dimensional model for ferroelectric transition (masses m_i, charges e_i)

It should be pointed out that in an ionic, one-dimensional model, a unit cell exhibits a nonzero electric polarization—even when the ions are in their equilibrium positions. However, in three dimensions, one can find a unit cell that possesses zero polarization when the atoms are in equilibrium positions. Since our interest is to present a model that reflects important features of the more complicated three-dimensional model, we are interested only in the electric polarization that arises because of displacements away from equilibrium positions. We could propose for the one-dimensional model the existence of fixed charges that will cancel the equilibrium position polarization but that have no other effect. At any rate, we will disregard equilibrium position polarization.

We define x_{kb} as the displacement from its equilibrium position of the bth atom (b = 1, 2) in the kth unit cell. For N atoms, we assume that the displacements of the atoms from equilibrium give rise to a polarization, P, where

$$P = \frac{1}{N}\sum_{k',b'} x_{k'b'}e_b. \tag{9.53}$$

The equation of motion of the bth atom in the kth unit cell can be written

$$m_b\ddot{x}_{kb} + \sum_{k',b'} J_{bb'}(k-k')x_{k'b'} = ce_bP, \tag{9.54}$$

where

$$J_{bb'}(k-k') = \frac{\partial^2 V}{\partial x_{kb}\partial x_{k'b'}}. \tag{9.55}$$

This equation is, of course, Newton's second law, $F = ma$, applied to a particular ion. The second term on the left-hand side represents a "spring-like" interaction obtained from a power series expansion to the second order of the potential energy, V, of the crystal. The right-hand side represents a long-range electrical force represented by a local electric field that is proportional to the local electric field $E_{\text{loc}} = cP$, where c is a constant.

As a further approximation, we assume the spring-like interactions are nearest neighbors, so

$$V = \frac{\gamma}{2}\sum_{k''}\left(x_{k''2} - x_{k''1}\right)^2 + \frac{\gamma}{2}\sum_{k''}\left(x_{k''+1,1} - x_{k''2}\right)^2, \tag{9.56}$$

where γ is the spring constant. By direct calculation, we find for the $J_{bb'}$

$$\begin{aligned} J_{11}(k'-k) &= 2\gamma\delta_k^{k'} = J_{22}(k'-k), \\ J_{12}(k'-k) &= -\gamma\left(\delta_k^{k'} + \delta_k^{k'+1}\right), \\ J_{21}(k'-k) &= -\gamma\left(\delta_k^{k'} + \delta_k^{k'-1}\right). \end{aligned} \tag{9.57}$$

We rewrite our dynamical equation in terms of $h = k' - k$

$$m_b \ddot{x}_{kb} + \sum_{h,b'} J_{bb'}(h) x_{h+k,b'} = \frac{ce_b}{N} \sum_{h,b'} x_{h+k,b'} e_{b'}. \tag{9.58}$$

Since this equation is translationally invariant, it has solutions that satisfy Bloch's theorem. Thus, there exists a wave vector k such that

$$x_{kb} = \exp(\mathrm{i}kqa) x_{ob}, \tag{9.59}$$

where x_{ob} is the displacement of the bth atom in the cell chosen as the origin for the lattice vectors. Substituting, we find

$$m_b \ddot{x}_{kb} + \sum_{h,b'} J_{bb'}(k) \exp(\mathrm{i}hqa) x_{ob'} = \frac{ce_b}{N} \sum_{h,b'} \exp(\mathrm{i}hqa) x_{ob'} e_{b'}. \tag{9.60}$$

We simplify by defining

$$G_{bb'}(q) = \sum_h J_{bb'}(h) \exp(\mathrm{i}hqa). \tag{9.61}$$

Using the results for $J_{bb'}$, we find

$$\begin{aligned} G_{11} &= 2\gamma = G_{22}, \\ G_{12} &= -\gamma[1 + \exp(\mathrm{i}qa)], \\ G_{21} &= -\gamma[1 - \exp(-\mathrm{i}qa)]. \end{aligned} \tag{9.62}$$

In addition, since

$$\sum_h \exp(\mathrm{i}hqa) = N\delta_q^0, \tag{9.63}$$

we finally obtain,

$$m_b \ddot{x}_{ob} + \sum_{b'} G_{bb'}(q) x_{ob'} = ce_b \sum_{b'} \delta_q^0 x_{ob'} e_{b'}. \tag{9.64}$$

As in the ordinary theory of vibrations, we assume x_{ob} contains a time factor $\exp(\mathrm{i}\omega t)$, so

$$\ddot{x}_{ob} = -\omega^2 x_{ob}. \tag{9.65}$$

The polarization term only affects the $q \to 0$ solution, which we look at now. Letting $q = 0$, and $e_1 = -e_2 = e$, we obtain the following two equations:

$$-m_1\omega^2 x_{o1} + 2\gamma x_{o1} - 2\gamma x_{o2} = ce(x_{o1}e - x_{o2}e), \tag{9.66}$$

and

$$-m_2\omega^2 x_{o2} - 2\gamma x_{o1} + 2\gamma x_{o2} = -ce(x_{o1}e - x_{o2}e). \tag{9.67}$$

These two equations can be written in matrix form:

$$\begin{bmatrix} -m_1\omega^2 + d & -d \\ -d & -m_1\omega^2 + d \end{bmatrix} \begin{bmatrix} x_{o1} \\ x_{o2} \end{bmatrix} = 0, \tag{9.68}$$

where $d = 2\gamma - ce^2$. From the secular equation, we obtain the following:

$$\omega^2 \left[m_1 m_2 \omega^2 - (m_1 + m_2)d \right] = 0. \tag{9.69}$$

The solution $\omega = 0$ is the long-wavelength acoustic mode frequency. The other solution, $\omega^2 = d/\mu$ with $1/\mu = 1/m_1 + 1/m_2$, is the optic mode long-wavelength frequency. For this frequency

$$-m_1 x_{o1} = m_2 x_{o2}. \tag{9.70}$$

So,

$$P = x_{o1}e\left(1 + \frac{m_1}{m_2}\right), \tag{9.71}$$

and $P \neq 0$ if $x_{o1} \neq 0$. Suppose

$$\lim_{T \to T_c} \left[2\gamma(T) - ce^2 \right] = 0, \tag{9.72}$$

then

$$\omega^2 = \frac{d}{\mu} \to 0 \quad \text{at} \quad T = T_c, \tag{9.73}$$

and

$$F_1 = m_1 \ddot{x}_{o1} = d(x_{o1} + x_{o2}) \to 0 \,\text{as}\, T \to T_c. \tag{9.74}$$

So, a solution is x_{o1} = constant $\neq 0$. That is, the model shows a ferroelectric solution for $T \to T_c$.

9.3.4 Multiferroics (A)

We consider the simultaneous situation of magnetic and dielectric order. That is, we consider situations in which magnetic fields may control electric effects and conversely electric fields may affect magnetic effects. A simple definition of the kind of multiferroic that is of most interest nowadays is a material that shows both ferroelectric and ferromagnetic behavior. Although this behavior was considered by Pierre Curie in the late 19th century, it was only found in the mid 20th century, and then in only a material with very weak coupling. More recently, materials have been found which show much stronger coupling and the interest in them has consequently grown. Generally, multiferroic materials need some asymmetry in the crystal structure. However, recently they have been found surprisingly in cubic perovskite $LaMn_3Cr_4O_{12}$ (X. Wang et al., *Phys. Rev. Lett.* **115**, 087601, 2015). For a review of somewhat older work see S. W. Cheong and M. Mostovoy, *Nature Mater.* **6**, 13–20 (2007). Multiferroics seem to have possible applications to spintronics as well as memory devices in multiferroics. Multiferroics also have connections with topological insulators (see Sect. 12.7.4), and are a very hot topic.

9.4 Dielectric Screening and Plasma Oscillations (B)

We begin now to discuss more complex issues. We want to discuss the nature of a gas of interacting electrons. This topic is closely related to the occurrence of oscillations in gas-discharge plasmas and is linked to earlier work of Langmuir and Tonks.[4] We begin by considering the subject of plasma oscillations. The general idea can be presented from a classical viewpoint, so we start by assuming the simultaneous validity of Newton's laws and Maxwell's equations.

Let n_0 be the number density of electrons in equilibrium. We assume an equal distribution of positive charge that remains uniform and, thus, supplies a constant background. We will consider one dimension only and, thus, consider only longitudinal plasma oscillations.

Let $u(x, t)$ represent the displacement of electrons whose equilibrium position is x and refer to Fig. 9.10 to compute the change in density Let e represent the

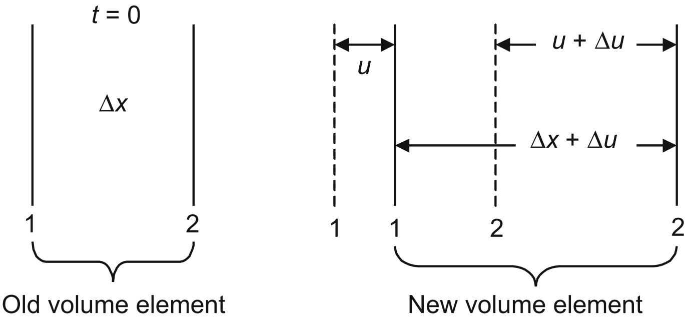

Fig. 9.10 Schematic used to discuss plasma vibration

---

[4] See Tonks and Langmuir [9.19].

magnitude of the electronic charge. Since the positive charge remains at rest, the total charge density is given by $\rho = -(n - n_0)e$. Since the same number of electrons is contained in the new volume as the old volume.

$$n = \frac{n_0 \Delta x}{(\Delta x + \Delta u)} \cong n_0 \left(1 - \frac{\mathrm{d}u}{\mathrm{d}x}\right). \tag{9.75}$$

Thus,

$$\rho = n_0 e \frac{\mathrm{d}u}{\mathrm{d}x}. \tag{9.76}$$

In one-dimension, Gauss' law is

$$\frac{\mathrm{d}E_x}{\mathrm{d}x} = \frac{\rho}{\varepsilon_0} = \frac{n_0 e}{\varepsilon_0}\frac{\mathrm{d}u}{\mathrm{d}x}. \tag{9.77}$$

Integrating and using the boundary condition that $(E_x)_{n=0} = 0$, we have

$$E_x = \frac{n_0 e}{\varepsilon_0} u. \tag{9.78}$$

A simpler derivation is discussed in the optics chapter (see Sect. 10.9). Using Newton's second law with force $-eE_x$, we have

$$m \frac{\mathrm{d}^2 u}{\mathrm{d}t^2} = -\frac{n_0 e^2}{\varepsilon_0} u, \tag{9.79}$$

with solution

$$u = u_0 \cos(\omega_p t + \text{const.}), \tag{9.80}$$

where

$$\omega_p = \sqrt{n_0 e^2 / m\varepsilon_0} \tag{9.81}$$

is the plasma frequency of electron oscillation. The quanta associated with this type of excitation are called plasmons. For a typical gas in a discharge tube, $\omega_P \cong 10^{10}\ \mathrm{s}^{-1}$, while for a typical metal, $\omega_P \cong 10^{16}\ \mathrm{s}^{-1}$.

More detailed discussions of plasma effects and electrons can be made by using frequency- and wave-vector-dependent dielectric constants. See Sect. 9.5.3 for further details where we will discuss screening in some detail. We define $\varepsilon(q, \omega)$ as the proportionality constant between the space and time Fourier transform components of the electric field and electric displacement vectors. We generally assume $\varepsilon(\omega) = \varepsilon(q = 0, \omega)$ provides an adequate description of dielectric properties when $q^{-1} \gg a$, where a is the lattice spacing. It is necessary to use $\varepsilon(q, \omega)$ when spatial variations not too much larger than the lattice constant are important.

The basic idea is contained in (9.82) and (9.83). For electrical interactions, if the actual perturbation of the potential is of the form

$$V' = \int\int v'(q,\omega)\,\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\,\exp(\mathrm{i}\omega t)\mathrm{d}q\cdot\mathrm{d}\omega. \tag{9.82}$$

Then, the perturbation of the energy is given by

$$\varepsilon' = \int\int \frac{v'(q,\omega)}{\varepsilon(q,\omega)}\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\,\exp(\mathrm{i}\omega t)\mathrm{d}q\cdot\mathrm{d}\omega. \tag{9.83}$$

$\varepsilon(q,\omega)$ is used to discuss (a) plasmons, (b) the ground-state energy of a many-electron system, (c) screening and Friedel oscillation in charge around a charged impurity in a sea of electrons, (d) the Kohn effect (a singularity in the dielectric constant that implies a change in phonon frequency), and (e) even other elementary energy excitations, provided enough physics is included in $\varepsilon(q,\omega)$. Some of this is elaborated in Sect. 9.5.

We now discuss two kinds of waves that can occur in plasmas. The first kind concerns waves that propagate in a region with only one type of charge carrier, and in the second we consider both signs of charge carrier. In both cases we assume overall charge neutrality. Both cases deal with electromagnetic waves propagating in a charged media in the direction of a constant magnetic field. Both cases only relate somewhat indirectly to dielectric properties through the Coulomb interaction. They seem to be worth discussing as an aside.

9.4.1 Helicons (EE)

Here we consider electrons as the charge carriers. The helicons are low-frequency (much lower than the cyclotron frequency) waves of circularly polarized electromagnetic radiation that propagate, with little attenuation, along the direction of the external magnetic field. They have been observed in sodium at high field ($\sim$2.5 *T*) and low temperatures ($\sim$4 K). The existence of these waves was predicted by P. Aigrain in 1960. Since their frequency depends on the Hall coefficient, they have been used to measure it in solids. Their dispersion relation shows that lower frequencies have lower velocities. When high-frequency helicons are observed in the ionosphere, they are called whistlers (because of the way their signal sounds when converted to audio).

For electrons (charge $-e$) in $\boldsymbol{E}$ and $\boldsymbol{B}$ fields with drift velocity $\boldsymbol{v}$, relaxation time τ, and effective mass m, we have

$$m\left(\frac{\mathrm{d}}{\mathrm{d}t}+\frac{1}{\tau}\right)\boldsymbol{v} = -e(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B}). \tag{9.84}$$

Assuming $\boldsymbol{B} = B\hat{\boldsymbol{k}}$ and low frequencies so $\omega\tau \ll 1$, we can neglect the time derivatives and so

$$\begin{aligned} v_x &= -\frac{e\tau E_x}{m} - \omega_c \tau v_y, \\ v_y &= -\frac{e\tau E_y}{m} + \omega_c \tau v_x, \\ v_z &= -\frac{e\tau E_z}{m}, \end{aligned} \tag{9.85}$$

where $\omega_c = eB/m$ is the cyclotron frequency. Letting, $\sigma_0 = m/ne^2\tau,$ where n is the number of charges per unit volume, and the Hall coefficient $R_H = -1/ne,$ we can write (noting $\boldsymbol{j} = -ne\boldsymbol{v}, \boldsymbol{j} = \boldsymbol{v}/R_H$):

$$v_x = \sigma_0 R_H \left(E_x + B v_y\right), \tag{9.86}$$

$$v_y = \sigma_0 R_H \left(E_y - B v_x\right). \tag{9.87}$$

Neglecting the displacement current, from Maxwell's equations we have:

$$\begin{aligned} \nabla \times \boldsymbol{B} &= \mu_0 \boldsymbol{j}, \\ \nabla \times \boldsymbol{E} &= -\frac{\partial \boldsymbol{B}}{\partial t}. \end{aligned}$$

Assuming $\nabla \cdot \mathrm{E} = 0$ (overall neutrality), these give

$$\nabla^2 \boldsymbol{E} = \mu_0 \frac{\partial \boldsymbol{j}}{\partial t}. \tag{9.88}$$

If solutions of the form $\boldsymbol{E} = \boldsymbol{E}_0 \exp[\mathrm{i}(kx - \omega t)]$ and $v = v_0 \exp[\mathrm{i}(kx - \omega t)]$ are sought, we require:

$$\begin{aligned} -k^2 \boldsymbol{E} &= -\mathrm{i}\omega\mu_0 \frac{\boldsymbol{v}}{R_H}, \\ E_x &= \mathrm{i}\frac{\omega\mu_0}{k^2}\frac{v_x}{R_H}, \\ E_y &= \mathrm{i}\frac{\omega\mu_0}{k^2}\frac{v_y}{R_H}. \end{aligned}$$

Thus

$$\begin{aligned} \left(1 - \mathrm{i}\sigma_0 \frac{\omega\mu_0}{k^2}\right) v_x - \sigma_0 R_H B v_y &= 0, \\ \sigma_0 R_H B v_x + \left(1 - \mathrm{i}\sigma_0 \frac{\omega\mu_0}{k^2}\right) v_y &= 0. \end{aligned} \tag{9.89}$$

Assuming large conductivity, $\sigma_0\omega\mu_0/k^2 \gg 1$, and large B, we find:

$$\omega = \frac{k^2}{\mu_0}|R_H|B = \frac{k^2}{\mu_0 ne}B, \tag{9.90}$$

or the phase velocity is

$$v_p = \frac{\omega}{k} = \sqrt{\frac{\omega B}{\mu_0 ne}}, \tag{9.91}$$

independent of m. Note the group velocity is just twice the phase velocity. Since the plasma frequency ω_p is $(ne^2/m\varepsilon_0)^{1/2}$, we can write also

$$v_p = c\sqrt{\frac{\omega\omega_c}{\omega_p^2}}. \tag{9.92}$$

Typically v_p is of the order of sound velocities.

9.4.2 Alfvén Waves (EE)

Alfvén waves occur in a material with two kinds of charge carriers (say electrons and holes). As for helicon waves, we assume a large magnetic field with electro-magnetic radiation propagating along the field. Alfvén waves have been observed in Bi, a semimetal at 4 K. The basic assumptions and equations are:

1. $\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}$, neglecting displacement current.
2. $\nabla \times E = -\partial \boldsymbol{B}/\partial t$, Faraday's law.
3. $\rho\dot{v} = \boldsymbol{j} \times \boldsymbol{B}$, where $\boldsymbol{v}$ is the fluid velocity, and the force per unit volume is dominated by magnetic forces.
4. $\boldsymbol{E} = -(\boldsymbol{v} \times \boldsymbol{B})$, from the generalized Ohm's law $j/\sigma = \boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}$ with infinite conductivity.
5. $\boldsymbol{B} = B_x\hat{\boldsymbol{i}} + B_y\hat{\boldsymbol{j}}$, where $B_x = B_0$ and is constant while $B_y = B_1\ (t)$.
6. Only the j_x, E_x, and v_y components need be considered (v_y is the velocity of the plasma in the y direction and oscillates with time).
7. $\dot{v} = \partial \boldsymbol{v}/\partial t$, as we neglect $(\boldsymbol{v} \cdot \nabla)\boldsymbol{v}$ by assuming small hydrodynamic motion. Also we assume the density ρ is constant in time.

Combining (1), (3), and (7) we have

$$\mu_0\rho\frac{\partial v_y}{\partial t} = [(\nabla \times \boldsymbol{B}) \times \boldsymbol{B}]_y \cong \frac{\partial B_1}{\partial x}B_0. \tag{9.93}$$

By (4)

$$E_z = -B_0 v_y,$$

so

$$-\frac{\mu_0 \rho}{B_0}\frac{\partial E_z}{\partial t} = B_0 \frac{\partial B_1}{\partial x}. \tag{9.94}$$

By (2)

$$\frac{\partial E_z}{\partial x} = -\frac{\partial B_1}{\partial t},$$

so

$$\frac{\partial^2 E_z}{\partial t^2} = -\frac{B_0^2}{\mu_0 \rho}\frac{\partial^2 B_1}{\partial x \partial t} = +\frac{B_0^2}{\mu_0 \rho}\frac{\partial^2 E_z}{\partial x^2}. \tag{9.95}$$

This is the equation of a wave with velocity

$$v_A = \frac{B}{\sqrt{\mu_0 \rho}}, \tag{9.96}$$

the Alfvén velocity. For electrons and holes of equal number density n and effective masses m_e and m_h,

$$v_A = \frac{B}{\sqrt{\mu_0 n (m_e + m_h)}}, \tag{9.97}$$

Notice that $v_A = (B^2/\mu_0 \rho)^{1/2}$ is the velocity in a string of tension B^2/μ_0 and density ρ. In some sense, the media behaves as if the charges and magnetic flux lines move together.

A unified treatment of helicon and Alfvén waves can be found in Elliot and Gibson [9.5] and Platzman and Wolff [9.15]. Alfvén waves are also discussed in space physics, e.g. in connection with the solar wind.

9.4.3 Plasmonics (EE)

Light waves incident on a metal dielectric interface can, under appropriate circumstances, induce surface plasmon waves of the same frequency as the light. The surface plasmons have wavelengths much less than the wavelengths of the light. In effect, this allows the optical signal to be squeezed into nanowires that carry much more information than an electronic wire. Thus, plasmonics may combine the virtues of fiber optics (high frequencies and high bandwidths) and electronics (very small wire interconnects). Plasmonics does have a limitation in that the amplitude of the plasmons tends to die out in a short distance (of order perhaps millimeters, more or less, depending on the device). Kittel [23, p. 302] has a couple of problems that illustrate surface and interface plasmons (for a single metallic surface, not a thin film, the surface plasmon frequency is $(1/\sqrt{2})$ times the volume plasmon frequency). For further details on how thin film metals can be used to change the plasmon frequency, as well as a discussion of other ideas and applications see, H. A. Atwater, "The Promise of Plasmonics," *Sci. Am.*, April 2007, pp. 56–63, and references cited therein.

9.5 Free-Electron Screening

9.5.1 Introduction (B)

If you place one charge in the midst of other charges, they will redistribute themselves in such a way as to "damp out" the long-range effects of the original charge. This long-range damping is an aspect of screening. Its origin resides in the Coulomb interactions of charges. This phenomenon was originally treated classically by the Debye–Huckel theory. A semiclassical form is called the Thomas–Fermi Approximation, which also assumes a free-electron gas. Neither the Debye–Huckel Theory nor the Thomas–Fermi model treats screening accurately at small distances. To do this, it is necessary to use the Lindhard theory.

We begin with the linearized Thomas–Fermi and Debye–Huckel methods and show how to use them to calculate the screening due to a single charged impurity. Perhaps the best way to derive this material is through the dielectric function and derive the Lindhard expression for it for a free-electron gas. The Lindhard expression for $\varepsilon(\omega \to 0, q)$ for small q then gives us the Thomas–Fermi expression. Generalization of the dielectric function to band electrons can also be made. The Lindhard approach follows in Sect. 9.5.3.

9.5.2 The Thomas–Fermi and Debye–Huckel Methods (A, EE)

We assume an electron gas with a uniform background charge (jellium). We assume a point charge of charge Ze ($e > 0$) is placed in the jellium. This will produce a potential $\varphi(r)$, which we assume to be weak and to vary slowly over a distance of order $1/k_F$ where k_F is the wave vector of the electrons whose energy equals the Fermi energy. For distances close to the impurity, where the potential is neither weak nor slowly varying our results will not be a very good approximation.

Consistent with the slowly varying potential approximation, we assume it is valid to think of the electron energy as a function of position.

$$E_k = \frac{\hbar^2 k^2}{2m} - e\varphi(\boldsymbol{r}), \tag{9.98}$$

where $\hbar$ is Planck's constant (divided by 2π), $\boldsymbol{k}$ is the wave vector, and m is the electronic effective mass.

In order to exhibit the effects of screening, we need to solve for the potential φ. We assume the static dielectric constant is ε and ρ is the charge density. Poisson's equation is

$$\nabla^2 \varphi = \frac{-\rho}{\varepsilon}, \tag{9.99}$$

where the charge density is

$$\rho = eZ\delta(\mathbf{r}) + n_0 e - ne, \tag{9.100}$$

where $eZ\delta(\boldsymbol{r})$ is the charge density of the added charge. For the spin $^1/_2$ electrons obeying Fermi–Dirac statistics, the number density (assuming local spatial equilibrium) is

$$n = \int \frac{1}{\exp[\beta(E_k - \mu)] + 1} \frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}, \tag{9.101}$$

where $\beta = 1/k_B T$ and k_B is the Boltzmann constant. When $\varphi = 0$, then $n = n_0$, so

$$n_0 = n_0(\mu) = \int \frac{1}{\exp\left[\beta\left(\left(\hbar^2 k^2/2m\right) - \mu\right)\right] + 1} \frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}. \tag{9.102}$$

Note by (9.98) and (9.102), we also have

$$n = n_0[\mu + e\varphi(\boldsymbol{r})]. \tag{9.103}$$

This means the charge density can be written

$$\rho = eZ\delta(\boldsymbol{r}) + \rho^{\mathrm{ind}}(\boldsymbol{r}), \tag{9.104}$$

where

$$\rho^{\mathrm{ind}}(\boldsymbol{r}) = -e[n_0(\mu + e\varphi(\boldsymbol{r})) - n_0(\mu)]. \tag{9.105}$$

We limit ourselves to weak potentials. We can then expand n_0 in powers of φ and obtain:

$$\rho^{\mathrm{ind}}(\boldsymbol{r}) = -e^2 \frac{\partial n_0}{\partial \mu} \varphi(\boldsymbol{r}). \tag{9.106}$$

The Poisson equation then becomes

$$\nabla^2 \varphi = -\frac{1}{\varepsilon}\left[Ze\delta(r) - e^2 \frac{\partial n_0}{\partial \mu} \varphi(\boldsymbol{r})\right]. \tag{9.107}$$

A convenient way to solve this equation is by the use of Fourier transforms. The Fourier transform of the potential can be written

$$\varphi(\boldsymbol{q}) = \int \varphi(\boldsymbol{r}) \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}) \mathrm{d}\boldsymbol{r}, \tag{9.108}$$

with inverse

$$\varphi(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int \varphi(\boldsymbol{q}) \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}) \mathrm{d}\boldsymbol{q}, \tag{9.109}$$

and the Dirac delta function can be represented by

$$\delta(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}) \mathrm{d}\boldsymbol{q}. \tag{9.110}$$

Taking the Fourier transform of (9.107), we have

$$q^2 \varphi(\boldsymbol{q}) = \frac{1}{\varepsilon}\left[Ze - e^2 \frac{\partial n_0}{\partial \mu} \varphi(\boldsymbol{q})\right]. \tag{9.111}$$

Defining the screening parameter as

$$k_S^2 = \frac{e^2}{\varepsilon} \frac{\partial n_0}{\partial \mu}, \tag{9.112}$$

we find from (9.111) that

$$\varphi(\boldsymbol{q}) = \frac{Ze}{\varepsilon} \frac{1}{q^2 + k_S^2}. \tag{9.113}$$

Then, using (9.109), we find from (9.113) that

$$\varphi(\boldsymbol{r}) = \frac{Ze}{4\pi\varepsilon r} \exp(-k_S r). \tag{9.114}$$

Equations (9.112) and (9.114) are the basic equations for screening.

For the classical nondegenerate case, we have from (9.102)

$$n_0(\mu) = \exp(\beta\mu)\int \exp\left(-\beta\hbar^2 k^2/2m\right)\frac{\mathrm{d}\boldsymbol{k}}{4\pi^3}, \tag{9.115}$$

so that by (9.112)

$$k_S^2 = \frac{e^2}{\varepsilon}\frac{n_0}{k_B T}, \tag{9.116}$$

we get the classical Debye–Huckel result. For the degenerate case, it is convenient to rewrite (9.102) as

$$n_0(\mu) = \int D(E)f(E)\mathrm{d}E, \tag{9.117}$$

so

$$\frac{\partial n_0}{\partial \mu} = \int D(E)\frac{\partial f}{\partial \mu}\mathrm{d}E, \tag{9.118}$$

where $D(E)$ is the density of states per unit volume and $f(E)$ is the Fermi function

$$f(E) = \frac{1}{\exp[\beta(E-\mu)]+1}. \tag{9.119}$$

since

$$\frac{\partial f(E)}{\partial \mu} \cong \delta(E-\mu), \tag{9.120}$$

at low temperatures when compared with the Fermi temperature; so we have

$$\frac{\partial n_0}{\partial \mu} \cong D(\mu). \tag{9.121}$$

Since the free-electron density of states per unit volume is

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}, \tag{9.122}$$

and the Fermi energy at absolute zero is

$$\mu = \frac{\hbar^2}{2m}\left(3\pi^2 n_0\right)^{2/3}, \tag{9.123}$$

where $n_0 = N/V$, we find

$$D(\mu) = \frac{3n_0}{2\mu}, \tag{9.124}$$

which by (9.121) and (9.112) gives the linearized Thomas–Fermi approximation. If we further use

$$\mu = \frac{3}{2}k_B T_F, \tag{9.125}$$

we find

$$k_S^2 = \frac{e^2}{\varepsilon}\frac{n_0}{k_B T_F}, \tag{9.126}$$

which looks just like the Debye–Huckel result except T is replaced by the Fermi temperature T_F. In general, by (9.112), (9.118), (9.119), and (9.122), we have for free-electrons,

$$k_S^2 = \frac{e^2 n_0}{\varepsilon k_B T_F}\frac{F'_{1/2}(\eta)}{F_{1/2}(\eta)}, \tag{9.127}$$

where $\eta = \mu/k_B T$ and

$$F_{1/2}(\eta) = \int\limits_0^\infty \frac{\sqrt{x}dx}{\exp(x-\eta)+1} \tag{9.128}$$

is the Fermi integral. Typical screening lengths $1/k_S$ for good metals are of order 1 Å, whereas for typical semiconductors 60 Å is more appropriate. For $\eta \ll -1$, $F'_{1/2}(\eta)/F_{1/2}(\eta) \approx 1$, which corresponds to the classical Debye–Huckel theory, and for $\eta \gg 1$, $F'_{1/2}(\eta)/F_{1/2}(\eta)) = 3/(2\eta)$ is the Thomas–Fermi result.

9.5.3 *The Lindhard Theory of Screening (A)*

Here we do a more general discussion that is self-consistent.[5] We start with the idea of an external potential that determines a set of electronic states. Electronic states in turn give rise to a charge density from which a potential can be determined. We wish to

---

[5] This topic is also treated in Ziman JM [25, Chap. 5], and Grosso and Paravicini [55 p 245ff].

show how we can determine a charge density and a potential in a self-consistent way by using the concept of a frequency- and wave-vector-dependent dielectric constant.

The specific problem we wish to solve is that of the self-consistent response to an applied field. We will assume small applied fields and linear responses. The electronic response to the applied field is called screening, and it arises from the interaction of the electrons with each other and with the external field. Only screening by a free-electron gas will be considered.

Let a charge ρ^{ext} be placed in jellium, and let it produce a potential φ^{ext} (by itself). Let φ be the potential caused by the extra charge, the free-electrons, and the uniform background charge (i.e. extra charge plus jellium). We also let be the corresponding charge density. Then

$$\nabla^2 \varphi^{\text{ext}} = -\frac{\rho^{\text{ext}}}{\varepsilon}, \tag{9.129}$$

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon}. \tag{9.130}$$

The induced charge density ρ^{ind} is then defined by

$$\rho^{\text{ind}} = \rho - \rho^{\text{ext}}. \tag{9.131}$$

We Fourier analyze the equations in both the space and time domains:

$$q^2 \varphi^{\text{ext}}(\boldsymbol{q}, \omega) = \frac{\rho^{\text{ext}}(\boldsymbol{q}, \omega)}{\varepsilon}, \tag{9.132a}$$

$$q^2 \varphi(\boldsymbol{q}, \omega) = \frac{\rho(\boldsymbol{q}, \omega)}{\varepsilon}, \tag{9.132b}$$

$$\rho(\boldsymbol{q}, \omega) = \rho^{\text{ext}}(\boldsymbol{q}, \omega) + \rho^{\text{ind}}(\boldsymbol{q}, \omega). \tag{9.132c}$$

Subtracting (9.132a) from (9.132b) and using (9.132c) yields:

$$\varepsilon q^2 [\varphi(\boldsymbol{q}, \omega) - \varphi^{\text{ext}}(\boldsymbol{q}, \omega)] = \rho^{\text{ind}}(\boldsymbol{q}, \omega). \tag{9.133}$$

We have assumed weak field and linear responses, so we write

$$\rho^{\text{ind}}(\boldsymbol{q}, \omega) = g(\boldsymbol{q}, \omega)\varphi(\boldsymbol{q}, \omega), \tag{9.134}$$

which defines $g(\boldsymbol{q}, \omega)$. Thus, (9.133) and (9.134) give this as

$$\varepsilon q^2 [\varphi(\boldsymbol{q}, \omega) - \varphi^{\text{ext}}(\boldsymbol{q}, \omega)] = g(\boldsymbol{q}, \omega)\varphi(\boldsymbol{q}, \omega). \tag{9.135}$$

Thus,

$$\varphi(\boldsymbol{q},\omega) = \frac{\varphi^{\text{ext}}(\boldsymbol{q},\omega)}{\varepsilon(\boldsymbol{q},\omega)}, \tag{9.136}$$

where

$$\varepsilon(\boldsymbol{q},\omega) = 1 - \frac{g(\boldsymbol{q},\omega)}{\varepsilon q^2}. \tag{9.137}$$

To proceed further, we need to calculate $\varepsilon(\boldsymbol{q}, \omega)$ directly. In the process of doing this, we will verify the correctness of the linear response assumption. We write the Schrödinger equation as

$$\mathcal{H}_0|\boldsymbol{k}\rangle = E_{\boldsymbol{k}}|\boldsymbol{k}\rangle. \tag{9.138}$$

We assume an external perturbation of the form

$$\delta V(\boldsymbol{r},t) = [V \exp(\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}+\omega t)) + V \exp(-\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}+\omega t))] \exp(\alpha t). \tag{9.139}$$

The factor $\exp(\alpha t)$ has been introduced so that the perturbation vanishes as $t = -\infty$, or in other words, as the perturbation is slowly turned on. V is assumed real. Let

$$\mathcal{H} = \mathcal{H}_0 + \delta V. \tag{9.140}$$

We then seek an approximate solution of the time-dependent Schrödinger wave equation

$$\mathcal{H}\psi = \mathrm{i}\hbar\frac{\partial\psi}{\partial t}. \tag{9.141}$$

We seek solutions of the form

$$|\psi\rangle = \sum\nolimits_{\mathbf{k}'} C_{\mathbf{k}'}(t)\exp(-\mathrm{i}E_{\mathbf{k}'}t/\hbar)|\mathbf{k}'\rangle. \tag{9.142}$$

Substituting,

$$\begin{aligned}\sum_{\mathbf{k}'}(\mathcal{H}_0+\delta V)C_{\boldsymbol{k}'}(t)\exp(-iE_{\boldsymbol{k}'}t/\hbar)|\boldsymbol{k}'\rangle \\ = \mathrm{i}\hbar\frac{\partial}{\partial t}\sum_{\boldsymbol{k}'}C_{\boldsymbol{k}'}(t)\exp(-\mathrm{i}E_{\boldsymbol{k}'}t/\hbar)|\boldsymbol{k}'\rangle.\end{aligned} \tag{9.143}$$

Using (9.138) to cancel two terms in (9.143), we have

$$\sum_{\boldsymbol{k}'}\delta V C_{\boldsymbol{k}'}(t)\exp(-\mathrm{i}E_{\boldsymbol{k}'}t/\hbar)|\boldsymbol{k}'\rangle = \mathrm{i}\hbar\sum_{\boldsymbol{k}'}\dot{C}_{\boldsymbol{k}'}(t)\exp(-\mathrm{i}E_{\boldsymbol{k}'}t/\hbar)|\boldsymbol{k}'\rangle. \tag{9.144}$$

Using

$$\langle \boldsymbol{k}''|\boldsymbol{k}'\rangle = \delta_{\boldsymbol{k}'}^{\boldsymbol{k}''}, \tag{9.145}$$

$$\langle \boldsymbol{k}''|\delta V|\boldsymbol{k}'\rangle = \langle \boldsymbol{k}''|\delta V|\boldsymbol{k}'\underline{\pm}\boldsymbol{q}\rangle \delta_{\boldsymbol{k}'}^{\boldsymbol{k}''\pm\boldsymbol{q}}, \tag{9.146}$$

$$\begin{aligned} \dot{C}_{\boldsymbol{k}''}(t) &= \frac{1}{\mathrm{i}\hbar} C_{\boldsymbol{k}''+\boldsymbol{q}} \exp\left(-\mathrm{i}E_{\boldsymbol{k}''+\boldsymbol{q}}t/\hbar\right)\langle \boldsymbol{k}''|\delta V|\boldsymbol{k}''+\boldsymbol{q}\rangle \exp(\mathrm{i}E_{\boldsymbol{k}''}t/\hbar) \\ &+ \frac{1}{\mathrm{i}\hbar} C_{\boldsymbol{k}''-\boldsymbol{q}} \exp\left(-\mathrm{i}E_{\boldsymbol{k}''-\boldsymbol{q}}t/\hbar\right)\langle \boldsymbol{k}''|\delta V|\boldsymbol{k}''-\boldsymbol{q}\rangle \exp(\mathrm{i}E_{\boldsymbol{k}''}t/\hbar). \end{aligned} \tag{9.147}$$

Using (9.139), we have

$$\begin{aligned} \dot{C}_{\boldsymbol{k}''}(t) &= \frac{1}{\mathrm{i}\hbar} C_{\boldsymbol{k}''+\boldsymbol{q}} \exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}''+\boldsymbol{q}} - E_{\boldsymbol{k}''}\right)t/\hbar\right) V \exp(-\mathrm{i}\omega t) \exp(\alpha t) \\ &+ \frac{1}{\mathrm{i}\hbar} C_{\boldsymbol{k}''-\boldsymbol{q}} \exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}''-\boldsymbol{q}} - E_{\boldsymbol{k}''}\right)t/\hbar\right) V \exp(\mathrm{i}\omega t) \exp(\alpha t). \end{aligned} \tag{9.148}$$

We assume a weak perturbation, and we begin in the state $\boldsymbol{k}$ with probability $f_0(\boldsymbol{k})$, so we have

$$C_{\boldsymbol{k}''}(t) = \sqrt{f_0(\boldsymbol{k})}\delta_{\boldsymbol{k}'',\boldsymbol{k}} + \lambda C_{\boldsymbol{k}''}^{(1)}(t). \tag{9.149}$$

We write out (9.147) to first order for two interesting cases:

$$\begin{aligned} \dot{C}_{\boldsymbol{k}+\boldsymbol{q}}(t) &= \lambda \dot{C}_{\boldsymbol{k}+\boldsymbol{q}}^{(1)}(t) \\ &= \left(\frac{1}{\mathrm{i}\hbar}\right)\sqrt{f_0(\boldsymbol{k})} \exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}}\right)t/\hbar\right) V \exp(\mathrm{i}\omega \mathrm{t}) \exp(\alpha t), \end{aligned} \tag{9.150}$$

$$\begin{aligned} \dot{C}_{\boldsymbol{k}-\boldsymbol{q}}(t) &= \lambda \dot{C}_{\boldsymbol{k}-\boldsymbol{q}}^{(1)}(t) \\ &= \left(\frac{1}{\mathrm{i}\hbar}\right)\sqrt{f_0(\boldsymbol{k})} \exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}}\right)t/\hbar\right) V \exp(-\mathrm{i}\omega \mathrm{t}) \exp(\alpha t). \end{aligned} \tag{9.151}$$

Integrating, we find, since $C_{\boldsymbol{k}\pm\boldsymbol{q}}(\infty) = 0$

$$C_{\boldsymbol{k}+\boldsymbol{q}}(t) = \sqrt{f_0(\boldsymbol{k})} \frac{\exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}}\right)t/\hbar\right) V \exp(\mathrm{i}\omega t) \exp(\alpha t)}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} - \hbar\omega + \mathrm{i}\hbar\alpha}, \tag{9.152}$$

$$C_{\boldsymbol{k}-\boldsymbol{q}}(t) = \sqrt{f_0(\boldsymbol{k})} \frac{\exp\left(-\mathrm{i}\left(E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}}\right)t/\hbar\right) V \exp(-\mathrm{i}\omega t) \exp(\alpha t)}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}} + \hbar\omega + \mathrm{i}\hbar\alpha}. \tag{9.153}$$

We write (9.142) as

$$\psi^{(\boldsymbol{k})} = \sum_{\boldsymbol{k}'} C_{\boldsymbol{k}'}(t)\ \exp(-\mathrm{i}E_{\boldsymbol{k}'}t/\hbar)\psi_{\boldsymbol{k}'}, \tag{9.154}$$

where

$$\psi_{\boldsymbol{k}'}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}, \tag{9.155}$$

and Ω is the volume. We put a superscript on ψ because we assume we start in the state $\boldsymbol{k}$. More specifically, (9.153) can be written as

$$\begin{aligned}\psi^{(\boldsymbol{k})} &= \exp(-\mathrm{i}E_{\boldsymbol{k}}t/\hbar)\sqrt{f_0(\boldsymbol{k})}\psi_{\boldsymbol{k}} \\ &\quad + C_{\boldsymbol{k}+\boldsymbol{q}}(t)\ \exp\left(-\mathrm{i}E_{\boldsymbol{k}+\boldsymbol{q}}t/\hbar\right)\psi_{\boldsymbol{k}+\boldsymbol{q}} + C_{\boldsymbol{k}-\boldsymbol{q}}(t)\ \exp\left(-\mathrm{i}E_{\boldsymbol{k}-\boldsymbol{q}}t/\hbar\right)\psi_{\boldsymbol{k}-\boldsymbol{q}}.\end{aligned} \tag{9.156}$$

Any charge density in jellium is an induced charge density (in equilibrium, jellium is uniform and has a net density of zero). Thus,

$$\rho^{\mathrm{ind}} = \frac{eN}{\Omega} - e\sum_{\boldsymbol{k}}\left|\psi^{(\boldsymbol{k})}\right|^2. \tag{9.157}$$

Now, note

$$\left|\psi^{(\boldsymbol{k})}\right|^2 = \frac{1}{\Omega} \quad \text{and} \quad \sum_{\text{all}\,\boldsymbol{k}} f_0(\boldsymbol{k}) = N, \tag{9.158}$$

so putting (9.155) into (9.156) and retaining no terms beyond first order,

$$\begin{aligned}\rho^{\mathrm{ind}} = \frac{eN}{\Omega} - \frac{e}{\Omega}\sum_{k} f_0(\mathrm{k})\Bigg\{1 &+ \frac{V\ \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\ \exp(\mathrm{i}\omega t)\ \exp(\alpha t)}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} - \hbar\omega + \mathrm{i}\hbar\alpha} \\ &+ \frac{V\ \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\ \exp(-\mathrm{i}\omega t)\ \exp(\alpha t)}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} + \hbar\omega + \mathrm{i}\hbar\alpha} + \text{c.c.}\Bigg\},\end{aligned} \tag{9.159}$$

or

$$\rho^{\mathrm{ind}} = -\frac{e}{\Omega}\sum_{\boldsymbol{k}}\left\{\frac{[f_0(\boldsymbol{k}) - f_0(\boldsymbol{k}+\boldsymbol{q})]V\ \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\ \exp(\mathrm{i}\omega t)\ \exp(\alpha t)}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}+\boldsymbol{q}} - \hbar\omega + \mathrm{i}\hbar\alpha} + c.c.\right\}. \tag{9.160}$$

Using

$$V(\boldsymbol{q},\omega) = -e\varphi(\boldsymbol{q},\omega), \tag{9.161}$$

and identifying $\rho^{\text{ind}}(\boldsymbol{q}, \omega)$ as the coefficient of $\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\exp(\mathrm{i}\,\omega t)$, we have

$$\rho^{\text{ind}}(\boldsymbol{q},\omega) = -\frac{e^2}{\Omega}\sum_{\boldsymbol{k}}\left\{\frac{f_0(\boldsymbol{k}) - f_0(\boldsymbol{k}-\boldsymbol{q})}{E_{\boldsymbol{k}-\boldsymbol{q}} - E_{\boldsymbol{k}} - \hbar\omega + \mathrm{i}\hbar\alpha}\right\}\varphi(\boldsymbol{q},\omega). \tag{9.162}$$

By (9.134) we find $g(\boldsymbol{q}, \omega)$ and by (9.137), we thus find

$$\varepsilon(\boldsymbol{q},\omega) = 1 + \frac{e^2}{\varepsilon\Omega q^2}\sum_{\boldsymbol{k}}\frac{f_0(\boldsymbol{k}) - f_0(\boldsymbol{k}-\boldsymbol{q})}{E_{\boldsymbol{k}-\boldsymbol{q}} - E_{\boldsymbol{k}} - \hbar\omega + \mathrm{i}\hbar\alpha}. \tag{9.163}$$

Finally, a few notes are provided on notation. We can redefine the Fourier components so as to change the sign of $\boldsymbol{q}$. For example, we can say

$$\varphi(\boldsymbol{r}) = \frac{1}{(2\pi)^2}\int\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\varphi(\boldsymbol{q})\mathrm{d}\boldsymbol{q}. \tag{9.164}$$

Then defining

$$v_q = \frac{e^2}{\varepsilon\Omega q^2}, \tag{9.165}$$

gives $\varepsilon(\boldsymbol{q}, \omega)$ in the form given in many textbooks:

$$\varepsilon(\boldsymbol{q},\omega) = 1 - v_q\sum_{\boldsymbol{k}}\frac{f_0(\boldsymbol{k}+\boldsymbol{q}) - f_0(\boldsymbol{k})}{E_{\boldsymbol{k}+\boldsymbol{q}} - E_{\boldsymbol{k}} - \hbar\omega + \mathrm{i}\hbar\alpha}. \tag{9.166}$$

The limit as $\alpha \to 0$ is tacitly implied in (9.166). In the limit as q becomes small, (9.165) gives, as we will show below, the Thomas–Fermi approximation (when $\omega = 0$). Two notable effects follow from (9.165), but they are not included in the small q limit. An expression for $\varepsilon(q, 0)$ at large q is readily obtained for our free-electron case. The result for $\omega = 0$ is

$$\varepsilon(\boldsymbol{q},\omega) = 1 + (\text{constant})D(E_F)\left[\frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right], \tag{9.167}$$

where $D(E_F)$ is the density of states at the Fermi energy and $x = q/2k_F$ with k_F being the wave vector at the Fermi energy. This expression has a singularity at $q = 2k_F$, which causes the screening of a charged impurity to have a weakly decaying oscillating term (beyond the Fermi–Thomas potential). This is the origin of *Friedel oscillations*. The Friedel oscillations damp out with distance due to electron scattering. At finite temperature, the singularity disappears causing the Friedel oscillation to damp out.

Further, since ion–ion interactions are screening by $\varepsilon(q)$, the singularity at $q = 2k_F$ is reflected in the phonon spectrum. Kinks in the phonon spectrum due to the singularity in $\varepsilon(q)$ are called *Kohn anomalies.*

Finally, we look at (9.165) for small q, $\omega = 0$ and $\alpha = 0$. We find

$$\begin{aligned}\varepsilon(\boldsymbol{q},\omega) &= 1 - \frac{e^2}{\varepsilon\Omega q^2}\sum_{\boldsymbol{k}}\frac{\partial f_0/\partial \boldsymbol{k}}{\partial E_{\boldsymbol{k}}/\partial \boldsymbol{k}} \\ &= 1 - \frac{e^2}{\varepsilon q^2}\sum_{\mathrm{k}} D(E)\frac{\partial f}{\partial E}dE = 1 + \frac{k_S^2}{q^2}.\end{aligned} \tag{9.168}$$

and hence comparing to previous work, we get exactly the Thomas–Fermi approximation.

Jacques Friedel

b. Paris, France (1921–2014)

Dislocations; Friedel Oscillations and Friedel Sum Rule; Many insights into metals and alloys and physical metallurgy

Friedel, while best known for the oscillation of charge around a charged impurity, worked in many areas, including the effect of dislocations on materials. He was a co-founder of the Laboratory of Solid State Physics at Orsay, France and one of founders of the discipline of Materials Science. He was noted for simple models used to explain complex phenomena.

Problems

9.1 Show that $E_0' = E_0 + P/\varepsilon_0$, where E_0 is the electric field between the plates before the slab is inserted (9.19).

9.2 Show that $E_1 = -P/\varepsilon_0$ (see Fig. 9.2).

9.3 Show that $E_2 = P/3\varepsilon_0$ (9.23).

9.4 Show for cubic crystals that $E_3 = 0$ (chapter notation is used).

9.5 If we have N permanent free dipoles p per unit volume in an electric field E, find an expression for the polarization. At high temperatures show that the polarizability (per molecule) is $\alpha = p^2/3kT$. What magnetic situation is this analogous to?

9.6 Use (9.30) and (9.48) to show (9.49)

$$\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{Np^2}{3k\varepsilon_0(T - T_c)}.$$

Find T_c. How likely is this to apply to any real material?

9.7 Use the trial wave function $\psi = \psi_{100}$ $(1 + pz)$ (where p is the variational parameter) for a hydrogen atom (in an external electric field in the z direction) to show that we obtain for the polarizability $16\pi\varepsilon_0 a_0^3$. (ψ_{100} is the ground-state wave function of the unperturbed hydrogen atom, a_0 is the radius of the first Bohr orbit of the hydrogen atom, and the exact polarizability is $18\pi\varepsilon_0 a_0^3$.)

9.8 (a) Given the Gibbs free energy[6]

$$\begin{aligned} &G = G_0 + \tfrac{1}{2}\beta(T - T_0)P^2 + \tfrac{1}{4}\gamma P^4 + \tfrac{1}{6}\delta P^6; \\ &\beta, \delta > 0,\ \gamma < 0 \quad (\text{first order}), \end{aligned}$$

derive an expression for T_c in terms of P_{sc} where $G(P_{sc}) = G_0$ and $E = 0$.
(b) Put the expression for T_c in terms without P_{sc}. That is, fill in the details of Sect. 9.3.1.

---

[6] See e.g. Fatuzzo and Merz [9.6, Chap. 9] or Kittel and Kroemer [10, Subject References] pp. 298–304, i.e. the section called "Landau Theory of Phase Transitions."