

Physics 410/510 Solid State Physics
Spring 2015
Homework #3

Kittel 4.4, 4.5, 4.6, 5.1, 5.2, 5.3, 6.1

For 510 students or extra credit for 410 students:

Kittel 6.2

- A. Work through and reproduce the derivation for the quantization of elastic waves in Appendix C.
- B. Show that lattices with 1, 2, 3, 4, and 6-fold rotational symmetry (with corresponding rotations by 2π , $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations) are allowed, but lattices with 5 and 7-fold rotational symmetry cannot exist.

(b) By substitution of u_s in this expression, show that the time-average total energy per atom is

$$\frac{1}{4} M \omega^2 u^2 + \frac{1}{2} C (1 - \cos Ka) u^2 = \frac{1}{2} M \omega^2 u^2 ,$$

where in the last step we have used the dispersion relation (9) for this problem.

2. **Continuum wave equation.** Show that for long wavelengths the equation of motion (2) reduces to the continuum elastic wave equation

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2} ,$$

where v is the velocity of sound.

3. **Basis of two unlike atoms.** For the problem treated by (18) to (26), find the amplitude ratios u/v for the two branches at $K_{\max} = \pi/a$. Show that at this value of K the two lattices act as if decoupled: one lattice remains at rest while the other lattice moves.
4. **Kohn anomaly.** We suppose that the interplanar force constant C_p between planes s and $s + p$ is of the form

$$C_p = A \frac{\sin pk_0 a}{pa} ,$$

where A and k_0 are constants and p runs over all integers. Such a form is expected in metals. Use this and Eq. (16a) to find an expression for ω^2 and also for $\partial\omega^2/\partial K$. Prove that $\partial\omega^2/\partial K$ is infinite when $K = k_0$. Thus a plot of ω^2 versus K or of ω versus K has a vertical tangent at k_0 ; there is a kink at k_0 in the phonon dispersion relation $\omega(K)$.

5. **Diatomic chain.** Consider the normal modes of a linear chain in which the force constants between nearest-neighbor atoms are alternately C and $10C$. Let the masses be equal, and let the nearest-neighbor separation be $a/2$. Find $\omega(K)$ at $K = 0$ and $K = \pi/a$. Sketch in the dispersion relation by eye. This problem simulates a crystal of diatomic molecules such as H_2 .
6. **Atomic vibrations in a metal.** Consider point ions of mass M and charge e immersed in a uniform sea of conduction electrons. The ions are imagined to be in stable equilibrium when at regular lattice points. If one ion is displaced a small distance r from its equilibrium position, the restoring force is largely due to the electric charge within the sphere of radius r centered at the equilibrium position. Take the number density of ions (or of conduction electrons) as $3/4\pi R^3$, which defines R . (a) Show that the frequency of a single ion set into oscillation is $\omega = (e^2/MR^3)^{1/2}$. (b) Estimate the value of this frequency for sodium, roughly. (c) From (a), (b), and some common sense, estimate the order of magnitude of the velocity of sound in the metal.
- *7. **Soft phonon modes.** Consider a line of ions of equal mass but alternating in charge, with $e_p = e(-1)^p$ as the charge on the p th ion. The interatomic potential is

*This problem is rather difficult.

$200 \text{ W cm}^{-1} \text{ K}^{-1}$ at 30 K. The maximum of the thermal conductivity in sapphire is greater than the maximum of $100 \text{ W cm}^{-1} \text{ K}^{-1}$ in copper. Metallic gallium, however, has a conductivity of $845 \text{ W cm}^{-1} \text{ K}^{-1}$ at 1.8 K. The electronic contribution to the thermal conductivity of metals is treated in Chapter 6.

In an otherwise perfect crystal, the distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering. The random distribution of isotopic mass disturbs the periodicity of the density as seen by an elastic wave. In some substances scattering of phonons by isotopes is comparable in importance to scattering by other phonons. Results for germanium are shown in Fig. 19. Enhanced thermal conductivity has been observed also in isotopically pure silicon and diamond; the latter has device importance as a heat sink for laser sources.

Problems

1. **Singularity in density of states.** (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of N atoms with nearest-neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}}.$$

where ω_m is the maximum frequency. (b) Suppose that an optical phonon branch has the form $\omega(K) = \omega_0 - AK^2$, near $K = 0$ in three dimensions. Show that $D(\omega) = (L/2\pi)^3 (2\pi/A^{3/2})(\omega_0 - \omega)^{1/2}$ for $\omega < \omega_0$ and $D(\omega) = 0$ for $\omega > \omega_0$. Here the density of modes is discontinuous.

2. **Rms thermal dilation of crystal cell.** (a) Estimate for 300 K the root mean square thermal dilation $\Delta V/V$ for a primitive cell of sodium. Take the bulk modulus as $7 \times 10^{10} \text{ erg cm}^{-3}$. Note that the Debye temperature 158 K is less than 300 K, so that the thermal energy is of the order of $k_B T$. (b) Use this result to estimate the root mean square thermal fluctuation $\Delta a/a$ of the lattice parameter.
3. **Zero point lattice displacement and strain.** (a) In the Debye approximation, show that the mean square displacement of an atom at absolute zero is $\langle R^2 \rangle = 3\hbar\omega_D^2/8\pi^2\rho v^3$, where v is the velocity of sound. Start from the result (4.29) summed over the independent lattice modes: $\langle R^2 \rangle = (\hbar/2\rho V)\Sigma\omega^{-1}$. We have included a factor of $\frac{1}{2}$ to go from mean square amplitude to mean square displacement. (b) Show that $\Sigma\omega^{-1}$ and $\langle R^2 \rangle$ diverge for a one-dimensional lattice, but that the mean square strain is finite. Consider $\langle (\partial R/\partial x)^2 \rangle = \frac{1}{2}\Sigma K^2 u_0^2$ as the mean square strain, and show that it is equal to $\hbar\omega_D^2 L/4MNv^3$ for a line of N atoms each of mass M , counting longitudinal modes only. The divergence of R^2 is not significant for any physical measurement.
4. **Heat capacity of layer lattice.** (a) Consider a dielectric crystal made up of layers of atoms, with rigid coupling between layers so that the motion of the atoms is restricted to the plane of the layer. Show that the phonon heat capacity in the Debye approximation in the low temperature limit is proportional to T^2 .

$200 \text{ W cm}^{-1} \text{ K}^{-1}$ at 30 K. The maximum of the thermal conductivity in sapphire is greater than the maximum of $100 \text{ W cm}^{-1} \text{ K}^{-1}$ in copper. Metallic gallium, however, has a conductivity of $845 \text{ W cm}^{-1} \text{ K}^{-1}$ at 1.8 K. The electronic contribution to the thermal conductivity of metals is treated in Chapter 6.

In an otherwise perfect crystal, the distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering. The random distribution of isotopic mass disturbs the periodicity of the density as seen by an elastic wave. In some substances scattering of phonons by isotopes is comparable in importance to scattering by other phonons. Results for germanium are shown in Fig. 19. Enhanced thermal conductivity has been observed also in isotopically pure silicon and diamond; the latter has device importance as a heat sink for laser sources.

Problems

1. **Singularity in density of states.** (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of N atoms with nearest-neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}}.$$

where ω_m is the maximum frequency. (b) Suppose that an optical phonon branch has the form $\omega(K) = \omega_0 - AK^2$, near $K = 0$ in three dimensions. Show that $D(\omega) = (L/2\pi)^3 (2\pi/A^{3/2})(\omega_0 - \omega)^{1/2}$ for $\omega < \omega_0$ and $D(\omega) = 0$ for $\omega > \omega_0$. Here the density of modes is discontinuous.

2. **Rms thermal dilation of crystal cell.** (a) Estimate for 300 K the root mean square thermal dilation $\Delta V/V$ for a primitive cell of sodium. Take the bulk modulus as $7 \times 10^{10} \text{ erg cm}^{-3}$. Note that the Debye temperature 158 K is less than 300 K, so that the thermal energy is of the order of $k_B T$. (b) Use this result to estimate the root mean square thermal fluctuation $\Delta a/a$ of the lattice parameter.
3. **Zero point lattice displacement and strain.** (a) In the Debye approximation, show that the mean square displacement of an atom at absolute zero is $\langle R^2 \rangle = 3\hbar\omega_D^2/8\pi^2\rho v^3$, where v is the velocity of sound. Start from the result (4.29) summed over the independent lattice modes: $\langle R^2 \rangle = (\hbar/2\rho V)\Sigma\omega^{-1}$. We have included a factor of $\frac{1}{2}$ to go from mean square amplitude to mean square displacement. (b) Show that $\Sigma\omega^{-1}$ and $\langle R^2 \rangle$ diverge for a one-dimensional lattice, but that the mean square strain is finite. Consider $\langle (\partial R/\partial x)^2 \rangle = \frac{1}{2}\Sigma K^2 u_0^2$ as the mean square strain, and show that it is equal to $\hbar\omega_D^2 L/4MNv^3$ for a line of N atoms each of mass M , counting longitudinal modes only. The divergence of R^2 is not significant for any physical measurement.
4. **Heat capacity of layer lattice.** (a) Consider a dielectric crystal made up of layers of atoms, with rigid coupling between layers so that the motion of the atoms is restricted to the plane of the layer. Show that the phonon heat capacity in the Debye approximation in the low temperature limit is proportional to T^2 .

Table 5 Experimental Lorenz numbers

Metal	$L \times 10^8$ watt-ohm/deg ²		Metal	$L \times 10^8$ watt-ohm/deg ²	
	0°C	100°C		0°C	100°C
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Su	2.52	2.49
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

The Lorenz number L is defined as

$$L = K/\sigma T, \quad (58)$$

and according to (57) should have the value

$$\begin{aligned} L &= \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.72 \times 10^{-13} \text{ (erg/esu-deg)}^2 \\ &= 2.45 \times 10^{-8} \text{ watt-ohm/deg}^2. \end{aligned} \quad (59)$$

This remarkable result involves neither n nor m . Experimental values of L at 0°C and at 100°C as given in Table 5 are in good agreement with (59).

Problems

- Kinetic energy of electron gas.** Show that the kinetic energy of a three-dimensional gas of N free electrons at 0 K is

$$U_0 = \frac{3}{5} N \epsilon_F. \quad (60)$$

- Pressure and bulk modulus of an electron gas.** (a) Derive a relation connecting the pressure and volume of an electron gas at 0 K. Hint: Use the result of Problem 1 and the relation between ϵ_F and electron concentration. The result may be written as $p = \frac{2}{3}(U_0/V)$. (b) Show that the bulk modulus $B = -V(\partial p/\partial V)$ of an electron gas at 0 K is $B = 5p/3 = 10U_0/9V$. (c) Estimate for potassium, using Table 1, the value of the electron gas contribution to B .
- Chemical potential in two dimensions.** Show that the chemical potential of a Fermi gas in two dimensions is given by:

$$\mu(T) = k_B T \ln [\exp(\pi n \hbar^2 / m k_B T) - 1], \quad (61)$$

for n electrons per unit area. Note: The density of orbitals of a free electron gas in two dimensions is independent of energy: $D(\epsilon) = m/\pi \hbar^2$, per unit area of specimen.

Phonon Coordinates

The transformation from the particle coordinates q_s to the phonon coordinates Q_k is used in all periodic lattice problems. We let

$$q_s = N^{-1/2} \sum_k Q_k \exp(iksa) , \quad (4)$$

consistent with the inverse transformation

$$Q_k = N^{-1/2} \sum_s q_s \exp(-iksa) . \quad (5)$$

Here the N values of the wavevector k allowed by the periodic boundary condition $q_s = q_{s+N}$ are given by:

$$k = 2\pi n/Na ; n = 0, \pm 1, \pm 2, \dots, \pm\left(\frac{1}{2}N - 1\right), \frac{1}{2}N . \quad (6)$$

We need the transformation from the particle momentum p_s to the momentum P_k that is canonically conjugate to the coordinate Q_k . The transformation is

$$p_s = N^{-1/2} \sum_k P_k \exp(-iksa); P_k = N^{-1/2} \sum_s p_s \exp(iksa) . \quad (7)$$

This is not quite what one would obtain by the naive substitution of p for q and P for Q in (4) and (5), because k and $-k$ have been interchanged between (4) and (7).

We verify that our choice of P_k and Q_k satisfies the quantum commutation relation for canonical variables. We form the commutator

$$\begin{aligned} [Q_k, P_{k'}] &= N^{-1} \left[\sum_r q_r \exp(-ikra), \sum_s p_s \exp(ik'sa) \right] \\ &= N^{-1} \sum_r \sum_s [q_r, p_s] \exp[-i(kr - k's)a] . \end{aligned} \quad (8)$$

Because the operators q, p are conjugate, they satisfy the commutation relation

$$[q_r, p_s] = i\hbar\delta(r, s) , \quad (9)$$

where $\delta(r, s)$ is the Kronecker delta symbol.

Thus (8) becomes

$$[Q_k, P_{k'}] = N^{-1} i\hbar \sum_r \exp[-i(k - k')ra] = i\hbar\delta(k, k') , \quad (10)$$

so that Q_k, P_k also are conjugate variables. Here we have evaluated the summation as

$$\begin{aligned} \sum_r \exp[-i(k - k')ra] &= \sum_r \exp[-i2\pi(n - n')r/N] \\ &= N\delta(n, n') = N\delta(k, k') , \end{aligned} \quad (11)$$

where we have used (6) and a standard result for the finite series in (11).

We carry out the transformations (7) and (4) on the hamiltonian (1), and make use of the summation (11):

$$\begin{aligned}\sum_s p_s^2 &= N^{-1} \sum_s \sum_k \sum_{k'} P_k P_{k'} \exp[-i(k+k')sa] \\ &= \sum_k \sum_{k'} P_k P_{k'} \delta(-k, k') = \sum_k P_k P_{-k} ;\end{aligned}\quad (12)$$

$$\begin{aligned}\sum_s (q_{s+1} - q_s)^2 &= N^{-1} \sum_s \sum_k \sum_{k'} Q_k Q_{k'} \exp(iks a) [\exp(ika) - 1] \\ &\quad \times \exp(ik's a) [\exp(ik'a) - 1] = 2 \sum_k Q_k Q_{-k} (1 - \cos ka) .\end{aligned}\quad (13)$$

Thus the hamiltonian (1) becomes, in phonon coordinates,

$$H = \sum_k \left\{ \frac{1}{2M} P_k P_{-k} + C Q_k Q_{-k} (1 - \cos ka) \right\} .\quad (14)$$

If we introduce the symbol ω_k defined by

$$\omega_k \equiv (2C/M)^{1/2} (1 - \cos ka)^{1/2} ,\quad (15)$$

we have the phonon hamiltonian in the form

$$H = \sum_k \left\{ \frac{1}{2M} P_k P_{-k} + \frac{1}{2} M \omega_k^2 Q_k Q_{-k} \right\} .\quad (16)$$

The equation of motion of the phonon coordinate operator Q_k is found by the standard prescription of quantum mechanics:

$$i\hbar \dot{Q}_k = [Q_k, H] = i\hbar P_{-k}/M ,\quad (17)$$

with H given by (14). Further, using the commutator (17),

$$i\hbar \ddot{Q}_k = [\dot{Q}_k, H] = M^{-1} [P_{-k}, H] = i\hbar \omega_k^2 Q_k ,\quad (18)$$

so that

$$\ddot{Q}_k + \omega_k^2 Q_k = 0 .\quad (19)$$

This is the equation of motion of a harmonic oscillator with the frequency ω_k .

The energy eigenvalues of a quantum harmonic oscillator are

$$\epsilon_k = \left(n_k + \frac{1}{2} \right) \hbar \omega_k ,\quad (20)$$

where the quantum number $n_k = 0, 1, 2, \dots$. The energy of the entire system of all phonons is

$$U = \sum_k \left(n_k + \frac{1}{2} \right) \hbar \omega_k .\quad (21)$$

This result demonstrates the quantization of the energy of elastic waves on a line.

Creation and Annihilation Operators

It is helpful in advanced work to transform the phonon hamiltonian (16) into the form of a set of harmonic oscillators:

$$H = \sum_k \hbar \omega_k \left(a_k^+ a_k + \frac{1}{2} \right) . \quad (22)$$

Here a_k^+ , a_k are harmonic oscillator operators, also called creation and destruction operators or boson operators. The transformation is derived below.

The boson creation operator a^+ which “creates a phonon” is defined by the property

$$a^+ |n\rangle = (n+1)^{1/2} |n+1\rangle , \quad (23)$$

when acting on a harmonic oscillator state of quantum number n , and the boson annihilation operator a which “destroys a phonon” is defined by the property

$$a |n\rangle = n^{1/2} |n-1\rangle . \quad (24)$$

It follows that

$$a^+ a |n\rangle = a^+ n^{1/2} |n-1\rangle = n |n\rangle , \quad (25)$$

so that $|n\rangle$ is an eigenstate of the operator $a^+ a$ with the integral eigenvalue n , called the quantum number or occupancy of the oscillator. When the phonon mode k is in the eigenstate labeled by n_k , we may say that there are n_k phonons in the mode. The eigenvalues of (22) are $U = \sum (n_k + \frac{1}{2}) \hbar \omega_k$, in agreement with (21).

Because

$$a a^+ |n\rangle = a (n+1)^{1/2} |n+1\rangle = (n+1) |n\rangle , \quad (26)$$

the commutator of the boson wave operators a_k^+ and a_k satisfies the relation

$$[a, a^+] \equiv a a^+ - a^+ a = 1 . \quad (27)$$

We still have to prove that the hamiltonian (16) can be expressed as (19) in terms of the phonon operators a_k^+ , a_k . This can be done by the transformation

$$a_k^+ = (2\hbar)^{-1/2} [(M\omega_k)^{1/2} Q_{-k} - i(M\omega_k)^{-1/2} P_k] ; \quad (28)$$

$$a_k = (2\hbar)^{-1/2} [(M\omega_k)^{1/2} Q_k + i(M\omega_k)^{-1/2} P_{-k}] . \quad (29)$$

The inverse relations are

$$Q_k = (\hbar/2M\omega_k)^{1/2} (a_k + a_{-k}^+) ; \quad (30)$$

$$P_k = i(\hbar M\omega_k/2)^{1/2} (a_k^+ - a_{-k}) . \quad (31)$$

By (4), (5), and (29) the particle position operator becomes

$$q_s = \sum_k (\hbar/2NM\omega_k)^{1/2} [a_k \exp(iks) + a_k^+ \exp(-iks)] . \quad (32)$$

This equation relates the particle displacement operator to the phonon creation and annihilation operators.

To obtain (29) from (28), we use the properties

$$Q_{-k}^+ = Q_k ; \quad P_k^+ = P_{-k} \quad (33)$$

which follow from (5) and (7) by use of the quantum mechanical requirement that q_s and p_s be hermitian operators:

$$q_s = q_s^+ ; \quad p_s = p_s^+ . \quad (34)$$

Then (28) follows from the transformations (4), (5), and (7). We verify that the commutation relation (33) is satisfied by the operators defined by (28) and (29):

$$\begin{aligned} [a_k, a_k^+] &= (2\hbar)^{-1}(M\omega_k[Q_k, Q_{-k}] - i[Q_k, P_k] + i[P_{-k}, Q_{-k}] \\ &\quad + [P_{-k}, P_k]/M\omega_k) . \end{aligned} \quad (35)$$

By use of $[Q_k, P_{k'}] = i\hbar\delta(k, k')$ from (10) we have

$$[a_k, a_k^+] = \delta(k, k') . \quad (36)$$

It remains to show that the versions of (16) and (22) of the phonon hamiltonian are identical. We note that $\omega_k = \omega_{-k}$ from (15), and we form

$$\hbar\omega_k(a_k^+ a_k + a_{-k}^+ a_{-k}) = \frac{1}{2M}(P_k P_{-k} + P_{-k} P_k) + \frac{1}{2}M\omega_k^2(Q_k Q_{-k} + Q_{-k} Q_k) .$$

This exhibits the equivalence of the two expressions (14) and (22) for H . We identify $\omega_k = (2C/M)^{1/2}(1 - \cos ka)^{1/2}$ in (15) with the classical frequency of the oscillator mode of wavevector k .

APPENDIX D: FERMI-DIRAC DISTRIBUTION FUNCTION¹

The Fermi-Dirac distribution function¹ may be derived in several steps by use of a modern approach to statistical mechanics. We outline the argument here. The notation is such that conventional entropy S is related to the fundamental entropy σ by $S = k_B\sigma$, and the Kelvin temperature T is related to the fundamental temperature τ by $\tau = k_B T$, where k_B is the Boltzmann constant with the value 1.38066×10^{-23} J K.

The leading quantities are the entropy, the temperature, the Boltzmann factor, the chemical potential, the Gibbs factor, and the distribution functions. The

¹This appendix follows closely the introduction to C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed., Freeman, 1980.