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THERMAL ENERGY AT THE NANOSCALE
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THERMAL ENERGY AT THE NANOSCALE

Lessons from Nanoscience: A Lecture Note Series

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(Purdue University, USA)

“Lessons from Nanoscience” aims to present new viewpoints that help understand, integrate, and apply recent developments in nanoscience while also using them to re-think old and familiar subjects. Some of these viewpoints may not yet be in final form, but we hope this series will provide a forum for them to evolve and develop into the textbooks of tomorrow that train and guide our students and young researchers as they turn nanoscience into nanotechnology. To help communicate across disciplines, the series aims to be accessible to anyone with a bachelor’s degree in science or engineering.

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Lessons from Nanoscience:
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Vol. 3

THERMAL ENERGY AT THE NANOSCALE

Timothy S Fisher

Purdue University, USA

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To my wonderful and amazing wife Amy

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Preface

These notes provide a detailed treatment of the thermal energy storage and transport by conduction in natural and fabricated structures. Thermal energy by two main carriers—phonons and electrons—are explored from basic principles. For solid-state transport, a common Landauer framework is used for heat flow, and issues including the quantum of thermal conductance, ballistic interface resistance, and carrier scattering are elucidated. Bulk material properties, such as thermal conductivity, are derived from transport theories, and the effects of spatial confinement on these properties are established.

The foregoing topics themselves are not unique as elements in a book; many other outstanding texts cover these topics admirably and are cited in context herein. At the same time, the present content emphasizes a basic theoretical framework based on the Landauer formalism that is as self-consistent as possible, not only internally but also with respect to similar efforts in this book series on the subject of electrical transport. The other series titles, written by Profs. Supriyo Datta and Mark Lundstrom, have therefore provided much inspiration to the present work, as have my related conversations with these two amazing colleagues. The end result is (hopefully) an accessible exposition on the foundations of the subject that remains concise by avoiding lengthy digressions into the vast array of related contemporary research topics. At the same time, it is my hope that readers, after studying this work, will be ready to enter the field well-equipped to contribute to this wonderful body of research and community of researchers.

T. S. Fisher

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Nomenclature

α	thermal diffusivity (length ² /time)
β	inverse of thermal energy, $(k_B T)^{-1}$ (1/energy)
χ	carrier energy scaled by $k_B T$ (-)
η_a	unit cells per volume of real space (1/volume)
η_e	volumetric electron density (1/volume)
\hat{G}_Q	quantum of thermal conductance (energy/time/temperature)
κ	thermal conductivity (power \times length/(‘area’ \times temperature))
Λ	particle mean free path (length)
\mathcal{D}	plate bending stiffness (force \times distance = energy)
\mathcal{F}	plate loading (force/area)
\mathcal{L}	boundary scattering length scale (length)
\mathcal{T}	carrier transmission function (-)
μ	mass density of a continuum string (mass/length)
ν	Poisson ratio (-)
Ω	number of possible states of a statistical ensemble (-)
ω	frequency (radians/time)
ω_D	Debye frequency (radians/time)
ω_E	Einstein frequency (radians/time)
ϕ	emitter work function (energy)
ρ	mass density (mass/volume)
σ	scattering cross section (area)
σ_e	electrical conductivity (current/(length \times voltage))
τ	scattering time (time)
τ^{-1}	scattering rate (1/time)
τ_b^{-1}	boundary scattering rate (1/time)
θ_D	Debye temperature (temperature)
θ_E	Einstein temperature (temperature)

θ_F	Fermi temperature (temperature)
\vec{G}'_Q	scaled spectral thermal conductance (-)
ε	boson energy (energy)
\vec{a}_i	real-space lattice translational vectors (length)
\vec{b}_i	reciprocal lattice translation vectors (lattice)
\vec{G}	reciprocal lattice vector (1/length)
\vec{R}	real-space lattice vector (length)
\vec{v}_g	group velocity (length/time)
a	lattice constant (length)
c	phase velocity (length/time)
c_0	speed of light in vacuum, 2.99792458×10^8 m/s
c_v	volumetric specific heat (energy/(volume \times temperature))
$D(\omega)$	density of boson states, frequency basis (time/volume)
$D(\varepsilon)$	density of boson states, energy basis (volume energy) ⁻¹
$D(E)$	density of fermion states, energy basis (volume energy) ⁻¹
$D(K)$	density of boson states, \mathbf{k} -space basis (length/volume)
D_α^β	dynamical matrix (force/(length \times mass))
E	energy (energy)
E_b	bond energy (energy)
E_F	Fermi energy (energy)
E_Y	Young's modulus (force/area)
E_{vac}	vacuum energy level (energy)
F	boundary scattering fitting factor (-)
F	force on an atom due to bond stretching (force)
f_i^o	equilibrium carrier distribution function (-)
$f(t)$	forward-wave string displacement (length)
g	spring constant of an interatomic bond (force/length)
G'_Q	spectral thermal conductance (power/temperature, per unit frequency for phonons, or per unit energy for electrons)
$g(t)$	reflected-wave string displacement (length)
G_Q	thermal conductance (power/temperature)
h	plate thickness (length)
J	electrical current density (current/'area')
J_Q	heat flux (power/'area')
K	phonon wavevector (1/length)
k	electron wavevector (1/length)
K_D	Debye wavevector (1/length)
k_F	Fermi wavevector (1/length)

L_e	Lorenz number, dimensionless constant $\times \left(\frac{k_B}{q}\right)^2$
m	atomic mass (mass)
$M(\omega)$	number of phonon modes (-)
$M(E)$	number of electron modes (-)
m_e	electron mass, $9.10938188 \times 10^{-31}$ kg
$M_{dD}(\omega)$	phonon mode density, $d =$ system dimension (1/‘area’)
$M_{dD}(E)$	electron mode density, $d =$ system dimension (1/‘area’)
N	number of atoms (-)
N'	electron number (-)
N_A	Avogadro’s number, 6.0221415×10^{23} (-)
n_i	defect density of impurity scatterers (1/volume)
N_{dD}	number of allowed phonon states, $d =$ system dimension (-)
N_k	number of allowed electron states (-)
N_K	number of phonons with wave vector K (-)
P	acoustic wave power (energy/time)
P_ν	probability of a statistical state (-)
q	elementary electron charge, 1.602×10^{-19} C
r	distance coordinate (length)
R_b	thermal boundary (interface) resistance (temperature/power)
R_b''	area-normalized thermal boundary (interface) resistance (area \times temperature/power)
S	entropy (power/temperature)
t_{12}	interfacial energy transmittance from medium 1 to medium 2 (-)
U	internal energy (energy)
U	potential energy (energy)
u	atomic displacement away from equilibrium (length)
u	specific internal energy (energy/volume)
$u'(x)$	spectral energy density (energy/volume, per unit x , where x is a spectral quantity such as frequency or wavelength)
v_a	acoustic wave velocity (length/time)
v_F	Fermi velocity (length/time)
$y(x, t)$	total string displacement (length)
Z	acoustic impedance of a string under tension (mass/time)

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Chapter 1

Lattice Structure, Phonons, and Electrons

1.1 Introduction

Guessing the technical background of students in a course or readers of a book is always a hazardous enterprise for an instructor, yet one must start a book or a course *somewhere* on the landscape of knowledge. Here, we begin with some essential concepts from condensed-matter physics and statistical mechanics. The definition of essential, too, is questionable and is presently intended to be information that recurs too frequently in the later parts of the text to leave the requisite information to the many excellent reference sources on these subjects.

Our overarching objective is to develop the tools required to predict thermal transport in structures such as the one shown in Fig. 1.1. Arguably the most important thermal characteristic of an object is its thermal conductivity (κ) defined as:

$$\kappa \equiv \frac{[\text{rate of heat flow (in W)}] \times [\text{object length (in m)}]}{[\text{cross-sectional area (in m}^2\text{)}] \times [\text{temperature drop (in K)}]}. \quad (1.1)$$

For roughly a century, thermal conductivity was considered a basic material property in the engineering sense (e.g., with minor accommodation for variations in temperature), and therefore, the effects of the geometric terms in Eq. (1.1) were assumed to normalize with the others such that the final property was independent of size and shape. However, with the advent of microscale fabrication (and later nanoscale fabrication), the technical community was able to create tiny materials that exhibited deviations from the size-independent property assumption. In such circumstances, knowledge of not only a material's size and shape becomes crucial but also the details of the atomic-scale carriers of thermal energy (Chen, 2005). At this

level, in order to retain the utility of the concept of thermal conductivity (and it does remain useful for many purposes) we need to understand many additional factors, including:

- What type of quantum-mechanical carrier dominates heat flow in the material?
- How is thermal energy distributed among these carriers?
- How fast do the carriers move through the material?
- How much thermal energy does each carrier hold as it moves?
- How do the carriers scatter as they move through the material?
- How do the boundaries and interfaces impede carriers?

The answers to these questions require a much deeper perspective on the mechanisms of thermal energy transport than is provided in traditional engineering expositions on heat conduction. Thus we embark here on the first of two background chapters: the present on lattice structure and the subsequent on statistics of energy carriers.

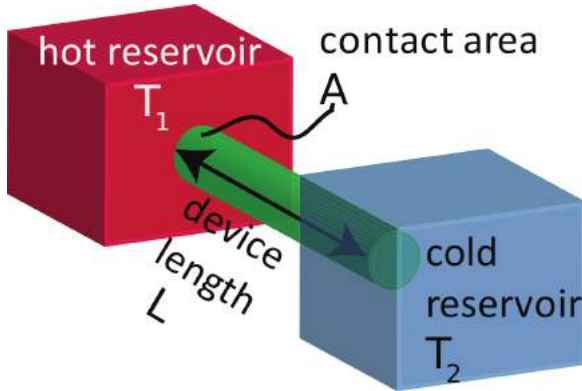


Fig. 1.1 Schematic of a general contact-device-contact arrangement.

The study of thermal energy in any material should rightly begin with a description of the material itself, for thermal energy, unlike other forms of energy such as optical, electronic, and magnetic, is routinely generated, stored, and transported by a diverse set of ‘carriers’. The reason for broader context of thermal energy derives from the second law of thermodynamics, which dictates that all forms of energy tend toward disorder (or ‘thermalization’). In this text, we will make every reasonable attempt to unify the

analysis, i.e., to generalize concepts so that they apply to multiple carriers, but this objective is occasionally elusive. In such cases, the text will make clear the relevant restrictions by carrier and material types. The list of interesting materials and physical structures is almost endless, and therefore given the subject of ‘nanoscale’ physics, the text begins with an admittedly cursory treatment of interatomic bonding but then highlights where possible a compelling structure — the graphene carbon lattice — to illustrate important and unique thermal behavior at the nanoscale.

1.2 Atom-to-Atom Bonding in Solid Lattices

The details of interatomic bonding determine a broad assortment of physical material properties, ranging from mechanical strength to electrical conductivity. The primary interest here relates to the resultant vibrational characteristics of atoms that exist in an ordered arrangement, i.e., in a regular crystal. However, we start with a simpler situation: that of a diatomic molecule.

Figure 1.2 shows a schematic of two atoms separated by an equilibrium distance $r = r_0$ about which the atoms vibrate at various (but restricted) frequencies. A generic potential energy field $U(r)$ between the atoms is shown in the bottom half of the figure, revealing the strong repulsive force ($F = -\partial U/\partial r$) when the atoms are close together ($r < r_0$). The minimum energy (at $r = r_0$) corresponds to the bond energy, as the potential energy asymptotes to zero when the atoms are pulled apart ($r \rightarrow \infty$).

The mathematical form of the potential can be very complicated and is itself the subject of intensive research through both first-principles (*ab initio*) approaches such as density functional theory (Saha *et al.*, 2008) and empirically derived potentials (Tersoff, 1988). For the time being, we consider a simplification of the potential, focusing on the near-minimum region where the potential is typically well approximated by a parabolic relation with respect to the equilibrium displacement $u = r - r_0$ such that $U \sim u^2$. The constant of proportionality plays an important role in the dynamics of molecules and lattices, for it contains the *effective spring constant* g of the bond:

$$U = \frac{1}{2}gu^2. \quad (1.2)$$

This so-called harmonic approximation is depicted in Fig. 1.3. We note that lattice vibrations typically involve small displacements; therefore, the

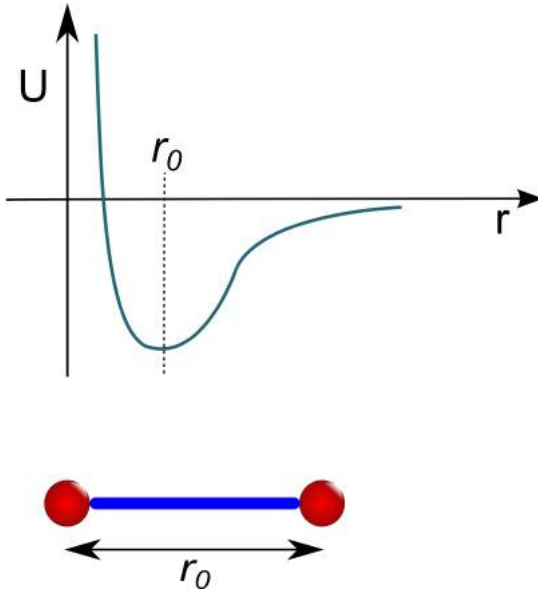


Fig. 1.2 Variation of potential energy field (U) with interatomic distance r . $r = r_0$ corresponds to the equilibrium separation with minimum potential energy.

harmonic approximation tends to predict the overall vibrational states (or what we will call the *vibrational eigenspectrum*) with good accuracy. The deviations, or anharmonicities, however, play an important role in phonon scattering, as discussed in Chapter 5.

One issue that we will cover only briefly is how such bonds form. Referring to Fig. 1.4, when two self-contained atoms [Fig. 1.4(a)] are brought together [Fig. 1.4(b)], their electrons can interact and begin to share orbitals. However, the energies of the orbitals must change because of restrictions imposed by the Pauli exclusion principle on the quantum states of electrons; therefore, upon bonding, the energy levels depicted by horizontal lines in Fig. 1.4, undergo small shifts.

These electronic interactions define the nature and strength of interatomic bonds and can produce many different bond types and energies (E_b), including:

- van der Waals: weak bond due to dipole moments, $E_b \sim 0.01$ eV
- Hydrogen: due to electronegative atoms (e.g., O in H_2O), $E_b \sim 0.1$ eV

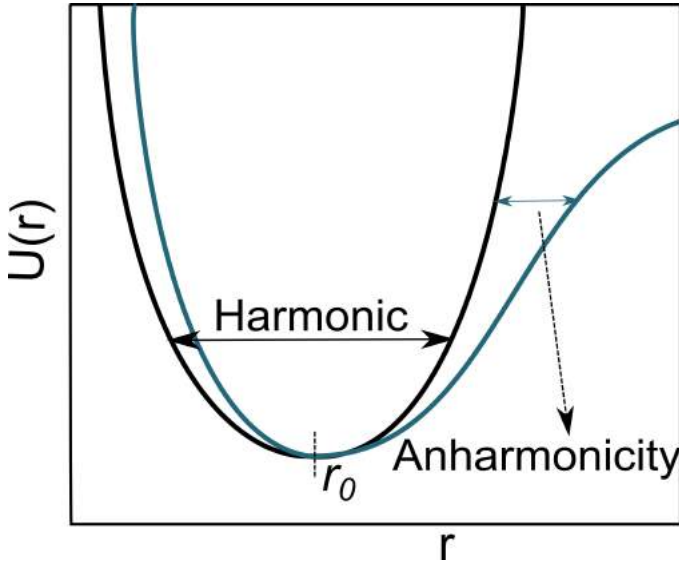


Fig. 1.3 Harmonic approximation to the real interatomic potential with anharmonicity. At small displacements, the harmonic potential is a good approximation.

- Covalent: atoms share valence electrons (e.g., Si and diamond), $E_b = 1 \sim 10$ eV
- Ionic: one atom gives up its electron, forms ions with Coulombic binding forces, $E_b = 1 \sim 10$ eV
- Metallic: like covalent bonds, but with freely moving electrons, $E_b = 1 \sim 10$ eV

We will focus on thermal energy in solid materials, but some of the content such as kinetic theory in Chapter 3 applies equally well to fluid phases. Within the array of solid-state materials, single-crystal structures are the most amenable for initial study, although even these structures become rather complex in three dimensions with various atomic arrangements such as face-centered cubic (fcc), body-centered cubic (bcc), and diamond configurations that are perhaps most familiar to readers. To minimize digression, here we refer the reader to the many excellent textbooks on solid-state physics (Ashcroft and Mermin, 1976; Kittel, 2007) and crystallography (De Graef and McHenry, 2012) for advanced treatment of 3D crystals.

We will focus on one- and two-dimensional lattices for the sake of expediency and because the 2D graphene lattice has high contemporary

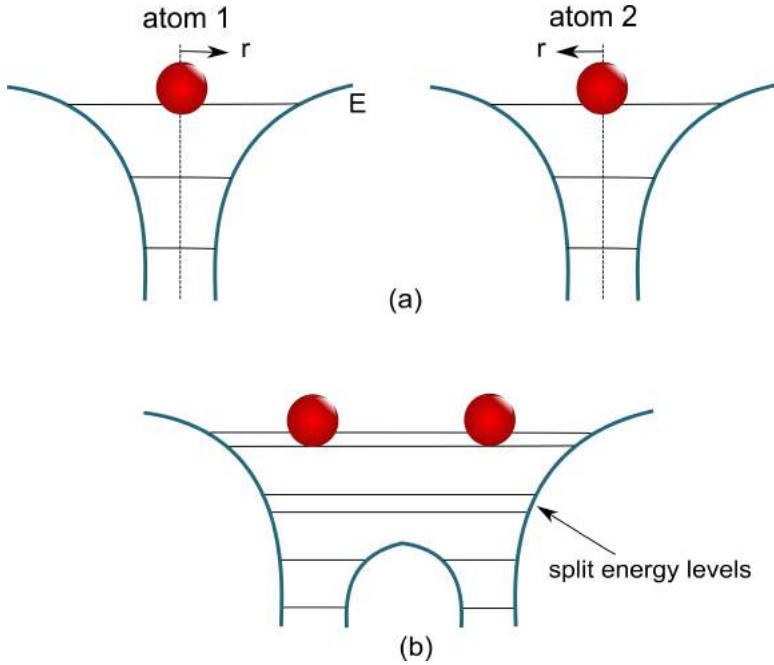


Fig. 1.4 (a) Two isolated, self-contained atoms and associated electron energy states. (b) Quantized energy states upon bond formation between the two isolated atoms. Energy levels are modified as electron orbitals become shared in a bond.

scientific and technological importance. A simple 1D structure is obtained by repeating the diatomic arrangement of Fig. 1.2 indefinitely. Figure 1.5 shows the resulting configuration, with each atom of mass m connected to its neighbor by a bond with spring constant g . The equilibrium separation between atoms is represented by the lattice constant a . Somewhat surprisingly, this simple, idealized structure will enable us to develop almost all the essential tools for analysis of lattice vibrations and their quantum manifestation—called phonons.

Because an ideal crystal extends infinitely in all directions, we must find a way to concentrate the analysis on a smaller region. Fortunately, the regular order, or periodicity, of a crystal lattice makes this task straightforward. A *primitive unit cell* of a lattice is one that, if repeated throughout all space by well-defined translational vectors, would fill the space entirely and with no overlapping regions or void spaces. Figure 1.6 shows an example for a 2D monatomic rectangular lattice. Several possible shapes, positions, and

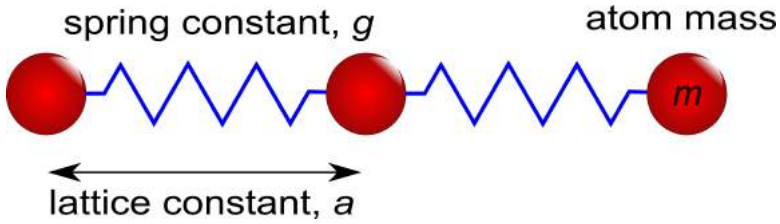


Fig. 1.5 An ideal 1D crystal modeled as periodic atom-spring-atom system.

orientations of the primitive unit cell exist for this lattice, as indicated by the shaded regions. The arrows denote *basis vectors* (\vec{a}_i) that define the periodic translation of the unit cells throughout the domain. The set of all possible translations by integer indexing of basis vectors forms a so-called Bravais lattice, whose discrete points are given by the lattice vector \vec{R} :

$$\vec{R} = \sum_i n_i \vec{a}_i \stackrel{\text{in 2D}}{=} n_1 \vec{a}_1 + n_2 \vec{a}_2. \quad (1.3)$$

For the linear 1D chain, the sole lattice vector is simply the lattice constant a .

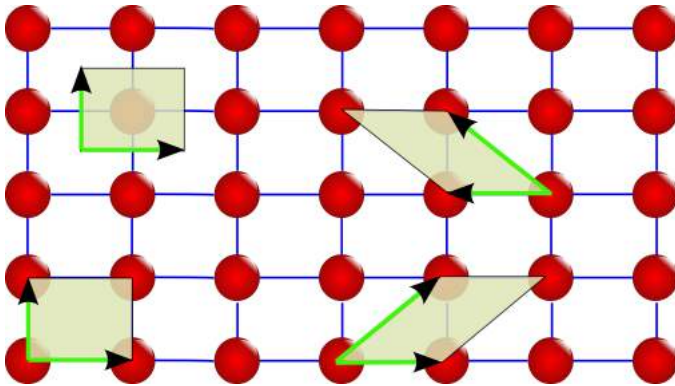


Fig. 1.6 An ideal 2D monatomic rectangular lattice represented by periodic translation of valid primitive cells (shaded green) defined by green basis vectors.

As might be expected given the complexity of our natural world, a Bravais lattice alone cannot describe the atomic positions of all real crystals. For such cases, we resort to defining the positions of multiple atoms

(usually two) at each nodal site in the Bravais lattice. This approach is quite understandable for compounds such as crystalline SiO₂ (quartz), but it is also necessary to describe the lattice geometry of some monatomic crystals, including technologically important ones such as silicon and diamond. Figure 1.7 shows the crystal construction in 2D, with the multi-atom basis pair placed regularly on spatially distributed Bravais lattice points.

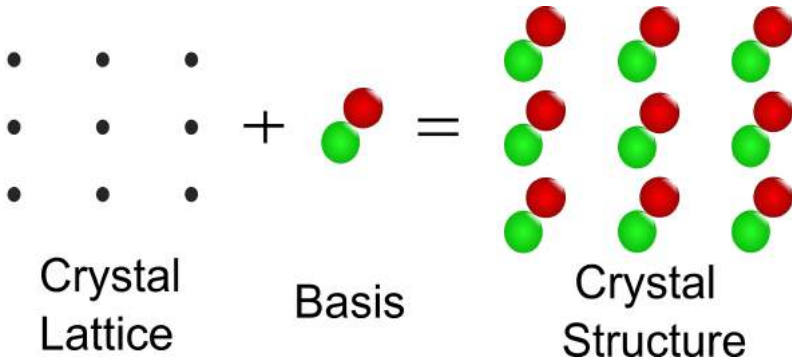


Fig. 1.7 Structure of a two-atom basis crystal. Each nodal site of the lattice contains a two-atom basis that defines the complete crystal structure upon translation through all possible lattice vectors.

One of the most fascinating 2D lattices, and one of intense contemporary study, is graphene, which consists entirely of carbon atoms in hexagonal arrangement on a 2D plane as shown in Fig. 1.8. The equilibrium distance between nearest carbon atoms is $\tilde{a} = 1.42 \text{ \AA}$, where the ‘ \sim ’ denotes a bond length (often the lattice constant and bond lengths differ for more complex lattices). Different edge configurations are possible in graphene, and the two most common are shown in the figure. Importantly, graphene is one of the monatomic structures that requires the addition of a basis atom to describe the full lattice. Its basis vectors, as shown in Fig. 1.9, are:

$$\begin{aligned}\vec{a}_1 &= \frac{3}{2}\tilde{a}\hat{x} + \frac{\sqrt{3}}{2}\tilde{a}\hat{y} \\ \vec{a}_2 &= \frac{3}{2}\tilde{a}\hat{x} - \frac{\sqrt{3}}{2}\tilde{a}\hat{y}.\end{aligned}\tag{1.4}$$

The vector that connects the primary and basis atoms within a unit cell is simply $\vec{a}_b = \tilde{a}\hat{x}$.

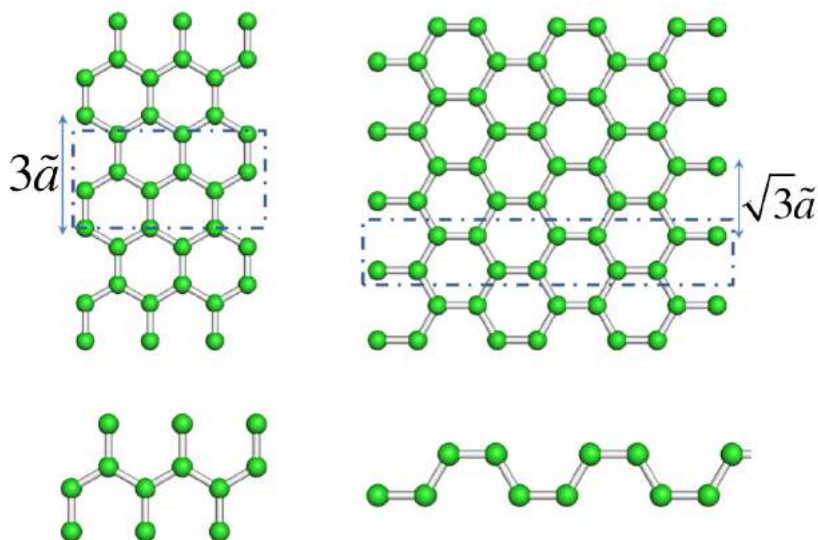


Fig. 1.8 Graphene nanoribbon crystal structure. The left structure is the armchair configuration; the right structure is zigzag. Dashed rectangles represent a graphene nanoribbon unit cell. The unit cell for each configuration is displayed below the crystal lattice structure.

1.3 Mathematical Description of the Lattice

The analysis of crystals can seem challenging in comparison to that of individual molecules because of the former's vast size. To overcome this challenge, we take advantage of a crystal lattice's *translational symmetry*. This approach requires a mathematical description that inverts space such that large entities become small.

We describe something large in terms of small things in the common way—with Fourier transforms. We start again with 1D chain of atoms and allow for the possibility that these atoms have a distributed mass density ρ . Perfect periodicity with lattice constant a (see Fig. 1.10) implies that:

$$\rho(x + ma) = \rho(x), \quad (1.5)$$

where m is any integer.

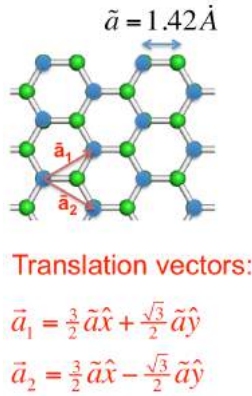


Fig. 1.9 Basis vectors for the graphene crystal structure.

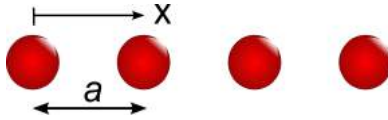


Fig. 1.10 Perfect periodic 1D chain of atoms with lattice constant a .

Each density function $\rho(x)$ and $\rho(x + ma)$ can be expanded in a Fourier series such that Eq. (1.5) becomes:

$$\begin{aligned} \rho(x) &= \sum_n \rho_n \exp \{iG_n x\} \\ &= \rho(x + ma) = \sum_n \rho_n \exp \{iG_n(x + ma)\} \\ &= \sum_n \rho_n \exp \{iG_n x\} \exp \{iG_n ma\}, \end{aligned} \quad (1.6)$$

$$\rightarrow \exp \{iG_n ma\} = 1 \rightarrow G_n ma = 2\pi \times \text{integer}, \quad (1.7)$$

where n and m are indexing integers. The last relation, Eq. (1.7), severely restricts the possible values of G . This restriction should not be surprising because the original density function, ρ , is strictly periodic and in the limit of point masses represents a series of delta functions. In fact, the series of real-space lattice points at $a, 2a, 3a, \dots$ for this simple 1D problem is simply the Bravais lattice vector defined by $\vec{R} = na\hat{x}$.

Extending to multiple dimensions, the restrictive relation between \vec{G} and \vec{R} is:

$$\vec{G}_n \cdot \vec{R}_m = 2\pi \times \text{integer}. \quad (1.8)$$

The vector \vec{G} thus becomes critically important in the description of lattices—the *reciprocal lattice vector*. In the interest of brevity and following the lead of Ziman, we will not be “concerned here with mathematically pathological functions, and may use naive Fourier theory quite freely” (Ziman, 1972). As such, we will simply state the relations between reciprocal lattice translation vectors \vec{b}_i and the direct lattice translation vectors \vec{a}_i in 3D:

$$\vec{G} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3, \quad (1.9)$$

where

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad (1.10)$$

and k_i are integers, and the denominator in Eq. (1.10) is the unit cell volume.

Once the \vec{b}_i vectors are known, the reciprocal space can be populated with discrete points. We will focus on 2D graphene here. Analysis of the primitive translational vectors in Eq. (1.4) in the context of Eq. (1.8) reveals that we must have $\vec{b}_1 \perp \vec{a}_2$ and $\vec{b}_2 \perp \vec{a}_1$ and that

$$\begin{aligned} \vec{b}_1 &= C_1 \left[\frac{\sqrt{3}}{2} \hat{x} + \frac{3}{2} \hat{y} \right] \\ \vec{b}_2 &= C_2 \left[\frac{\sqrt{3}}{2} \hat{x} - \frac{3}{2} \hat{y} \right]. \end{aligned} \quad (1.11)$$

The constants C_1 and C_2 must be equal to preserve the generality of Eq. (1.8), and given the magnitude of the vectors $|\vec{a}_i| = \sqrt{3}\tilde{a}$, we find:

$$\begin{aligned} C_1 = C_2 &= \frac{4\pi}{a3\sqrt{3}} \\ \rightarrow \vec{b}_1 &= \frac{2\pi}{\tilde{a}} \left[\frac{1}{3} \hat{x} + \frac{1}{\sqrt{3}} \hat{y} \right] \\ \rightarrow \vec{b}_2 &= \frac{2\pi}{\tilde{a}} \left[\frac{1}{3} \hat{x} - \frac{1}{\sqrt{3}} \hat{y} \right]. \end{aligned} \quad (1.12)$$

The resulting lattices, both direct (a) and reciprocal (b), for graphene are shown in Fig. 1.11, as well as the respective translational vectors and the so-called 1st Brillouin zone, which is hexagonal in shape. The reciprocal lattice's primitive cell (i.e., 1st Brillouin zone) is established by connecting lattice points with lines, which then define the shaded region of 2D space closest to a given lattice point.

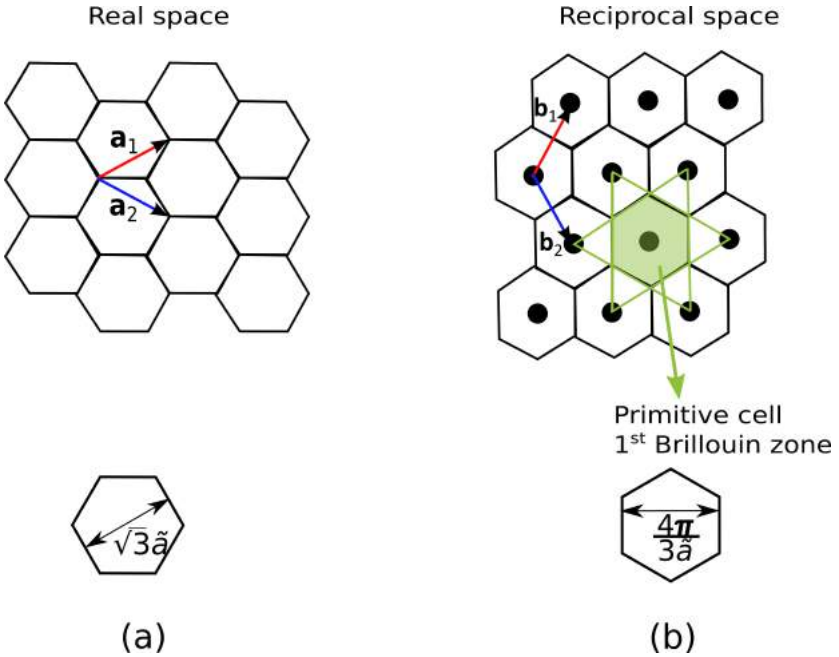


Fig. 1.11 (a) Direct graphene lattice. (b) Reciprocal graphene lattice. The primitive cell of the reciprocal lattice is the 1st Brillouin zone. Translation vectors of both lattices are also depicted.

Reciprocal space is often termed 'k-space', and we will use the terms interchangeably. Reciprocal space is also useful in defining directions in a crystal. For a given real-space lattice plane, the Miller indices $(k_1 k_2 k_3)$ are vector coordinates (see Eq. (1.12)) of the shortest reciprocal lattice vector normal to the plane. The Miller indices should not be confused with the primary directions in the real-space lattice, which are denoted by square brackets $[xyz]$.

1.4 Lattice Vibrations and Phonons

The description of lattice vibrations starts with the potential-energy/displacement relation of Eq. (1.2). When constructed as a linear chain of atoms, the individual potential energies from each compressed or expanded spring are summed to form the harmonic potential energy U^{harm} :

$$U^{\text{harm}} = \frac{1}{2}g \sum_n \{u[na] - u[(n+1)a]\}^2, \quad (1.13)$$

where the terms na and $(n+1)a$ designate the spatial positions of the atoms. The force on an individual atom (at, say, location na) can be calculated from the spatial derivative of displacement at that location:

$$F = m \frac{d^2 u(na)}{dt^2} = -\frac{\partial U^{\text{harm}}}{\partial u(na)} = -g \{2u(na) - u[(n-1)a] - u[(n+1)a]\}, \quad (1.14)$$

where the factor 2 appearing in $2u(na)$ is the result of the fact that location ‘ na ’ appears twice in the summation of Eq. (1.13) (once as $(n+1)a$ and then as na as the sum proceeds). The ‘ na ’ nomenclature becomes quite tedious in practice, and we therefore simplify the expression of Eq. (1.14) as:

$$m \frac{d^2 u_n}{dt^2} = -g \{2u_n - u_{n-1} - u_{n+1}\}. \quad (1.15)$$

The solution of Eq. (1.15) requires boundary conditions, and the simplest are the so-called Born-von Karman type in which the ends of the 1D chain are attached as in a loop (see Fig. 1.12). We note that this ‘loop’ does not add a new dimension to the problem, as the number of atoms N is assumed to be very large.

The Born-von Karman boundary conditions become:

$$\begin{aligned} u_N &= u_0 \\ u_{N+1} &= u_1. \end{aligned} \quad (1.16)$$

We assume a plane-wave solution for displacement at location n as:

$$u_n(t) \sim \exp\{i(Kna - \omega t)\}, \quad (1.17)$$

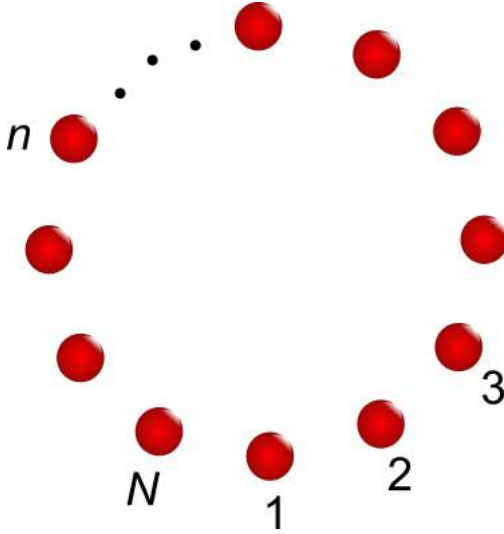


Fig. 1.12 1D chain of N atoms with the Born-von Karman boundary condition.

where K is the wavevector of the plane wave and is proportional to the inverse of wavelength. Application of Eq. (1.17) to the boundary conditions above yields:

$$\begin{aligned}
 u_{N+1} &\sim \exp \{i [K (N + 1) a - \omega t]\} \\
 u_1 &\sim \exp \{i [K a - \omega t]\} \\
 \rightarrow 1 &= \exp [i K N a] \rightarrow K N a = 2\pi n,
 \end{aligned} \tag{1.18}$$

where n is an indexing integer. The final relation in Eq. (1.18) is of crucial importance, for it restricts the possible values of the wavevector K that can ‘fit’ on the looped 1D chain. Of course, if the number of total atoms N is large, then many wavevectors are possible. Defining the wavelength as $\lambda_n = aN/n$, the set of allowed wavevectors becomes:

$$K_n = \frac{2\pi n}{aN} = \frac{2\pi}{\lambda_n}. \tag{1.19}$$

Finally, we note that the minimum size of a wave (wavelength) is $\lambda_{\min} = 2a$, for any shorter waves would not have atoms to sustain them. Another way of explaining this characteristic is that any smaller wavelengths would have nodal positions (in the standing wave sense) that could

be described by longer waves in which the nodal positions would exist on lattice sites, instead of between atoms. Consequently, the maximum unique wavevector is:

$$|K_{\max, \text{unique}}| = \frac{\pi}{a}. \quad (1.20)$$

This important restriction enables us to convert what is an infinite domain in real space (as $N \rightarrow \infty$) into a finite domain in reciprocal space ($K \in [-\pi/a, \pi/a]$), with the associated advantages of mathematical convenience. Importantly, this unique region of reciprocal space (or \mathbf{k} -space) coincides with the 1st Brillouin zone.

We now return to the equation of motion, Eq. (1.15), and its solution. Substitution of the plane-wave function of Eq. (1.17) for position na and incorporation of the discrete wavevectors K_j produces:

$$\begin{aligned} -m\omega_j^2 e^{i(K_j na - \omega_j t)} &= -g [2 - e^{-iK_j a} - e^{iK_j a}] e^{i(K_j na - \omega_j t)} \\ &= -2g (1 - \cos K_j a) e^{i(K_j na - \omega_j t)}. \end{aligned} \quad (1.21)$$

The resulting relationship between frequency and wavevector defines the *dispersion relation* of the lattice:

$$\omega_j(K_j) = \sqrt{\frac{2g(1 - \cos K_j a)}{m}} = 2\sqrt{\frac{g}{m}} \left| \sin\left(\frac{1}{2}K_j a\right) \right|. \quad (1.22)$$

The continuous form of this relation ($\omega(K)$, which we will use hereafter, dropping the subscript j) is sketched in Fig. 1.13. We note that the maximum frequency depends quite simply on the spring constant and atomic mass, as $\omega_{\max} = 2\sqrt{g/m}$.

The dispersion relation contains information pertinent to a wide range of material characteristics, from elastic constants to the scattering rates of phonons. We will discuss many of these in context throughout the remainder of the text. For now, we highlight the phase and group velocities:

$$\text{phase velocity: } c = \frac{\omega}{K}, \quad (1.23)$$

$$\text{group velocity: } v_g = \frac{\partial \omega}{\partial K}. \quad (1.24)$$

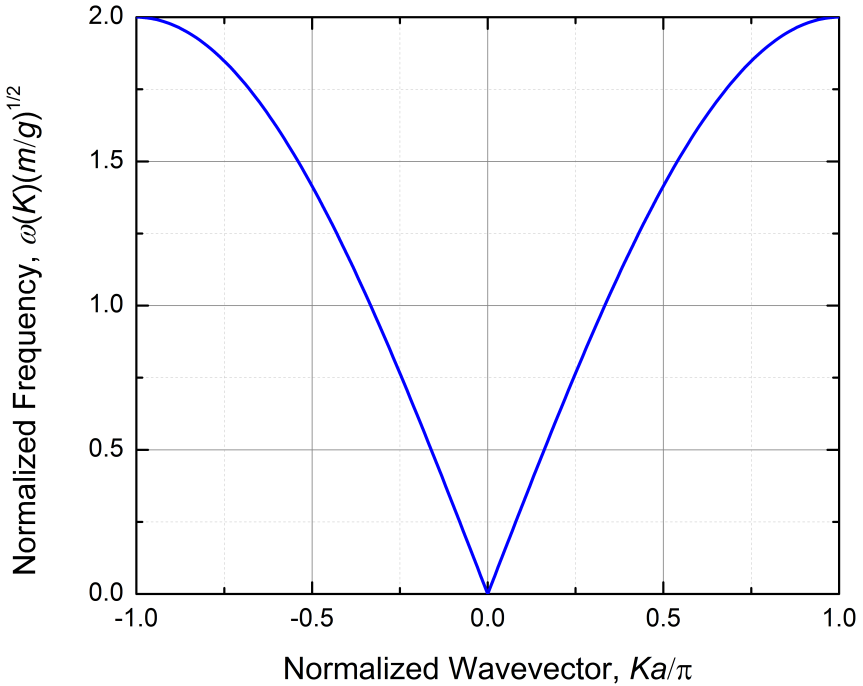


Fig. 1.13 Dispersion relation for a monatomic 1D chain of atoms.

Most of our interest will be given to the group velocity because it determines the rate of energy transport. Further, we will often focus on the long-wave limit ($K \rightarrow 0$), for which:

$$\begin{aligned} \lim_{K \rightarrow 0} \omega &= a \sqrt{\frac{g}{m}} |K| \\ \rightarrow \lim_{K \rightarrow 0} v_g &= a \sqrt{\frac{g}{m}} = \left| \frac{\omega}{K} \right| = c. \end{aligned} \quad (1.25)$$

In this limit, the group and phase velocities are equal, and they both are the same as the speed of sound in the solid. Therefore, the types of phonons that exhibit this behavior (other types are considered later) are termed *acoustic phonons*.

Thus far we have used strictly classical descriptions of mechanical vibrations to derive the vibrational spectrum of the lattice. However, to treat collections of vibrations (because a lattice can support many vibrational

modes at the same time), we must transition to a quantum description. Nevertheless, we can retain the results from the classical harmonic oscillator solution above to define each *normal mode* in terms of a wavevector K and frequency ω (i.e., the dispersion relation remains valid). A solution of the time-independent Schrödinger equation of quantum mechanics (see Eq. (1.31) in the next section) reveals that each mode can contain a set of energies described by:

$$\varepsilon_K = \left(N_K + \frac{1}{2}\right) \hbar\omega_K, \quad (1.26)$$

where N_K represents the number of phonons with wavevector K , and the terminology ω_K is intended to signify the inherent relationship between frequency and wavevector embodied by the dispersion relation (Eq. (1.22)). The $\frac{1}{2}$ term in Eq. (1.26) accounts for the so-called zero-point energy whose derivation is available elsewhere (Ashcroft and Mermin, 1976, Appendix L). The term N_K defines the average number of such excited modes of wavevector K , or the number of *phonons*, and is defined by Bose-Einstein statistics:

$$N_K = \frac{1}{\exp\left(\frac{\hbar\omega_K}{k_B T}\right) - 1}, \quad (1.27)$$

where k_B is Boltzmann's constant, and T is temperature. We will later use the symbol f_{BE}^0 as a synonym for N_K (in attempt to maintain some consistency while also identifying various symbols that are used in the literature for the occupation number).

The connection between the quantum energy of Eq. (1.26) and the classical vibration amplitude is often elusive to new learners and is therefore included here to connect with mechanical intuition. Classically, each vibrational mode contains a combination of potential and kinetic energy that can be shown to be, on average, equal in magnitude by the virial theorem (Ashcroft and Mermin, 1976) such that:

$$\bar{\varepsilon}_{\text{classical}} = \sum_{\text{lattice}} m |\dot{u}|^2, \quad (1.28)$$

where the “ $\dot{}$ ” denotes time differentiation. For a simple lattice of N atoms with one atom of mass m per unit cell, the summation can be transformed

to reciprocal space as:

$$\bar{\epsilon}_{\text{classical}} = \sum_K Nm\omega_K^2 |\tilde{u}_K|^2, \quad (1.29)$$

where $|\tilde{u}_K|$ is the amplitude of atomic displacement for a mode with wavevector K . Equating the summed term in Eq. (1.29) with the quantum version (Eq. (1.26)), the relationship between displacement amplitude and (quantized) energy becomes:

$$\begin{aligned} |\tilde{u}_K|^2 &= \frac{\epsilon_K}{Nm\omega_K^2} \\ &= \frac{(N_K + \frac{1}{2})\hbar}{Nm\omega_K}. \end{aligned} \quad (1.30)$$

This result should be intuitive, for it indicates that displacement amplitude increases with increasing occupation number and decreases with increasing frequency, both in the square-root sense. An illustration of phonon quantization, showing the relationship between allowed energies and atomic displacements, is shown in Fig. 1.14. For further details, the reader is referred to Ziman (1972).

Still remaining in our development is the extension of the foregoing principles of dispersion and energy to multiple dimensions and orientations of oscillations relative to the propagation direction (i.e., polarization). We defer these subjects to later chapters, when they can be developed in better context.

1.5 Free Electrons

Electronic behavior varies widely among different types of materials, from ‘free’ conduction in metals to virtually none in insulators. In this chapter we will consider only metals, and even then we will use the simplest approximation—free electron theory. Later chapters elucidate more complicated electronic structure.

The fundamental equation governing quantum particles is Schrödinger’s equation, whose time-independent form is:

$$\frac{-\hbar^2}{2m_e} \nabla^2 \Psi(\vec{r}) + \mathcal{V}(\vec{r})\Psi = E\Psi(\vec{r}), \quad (1.31)$$

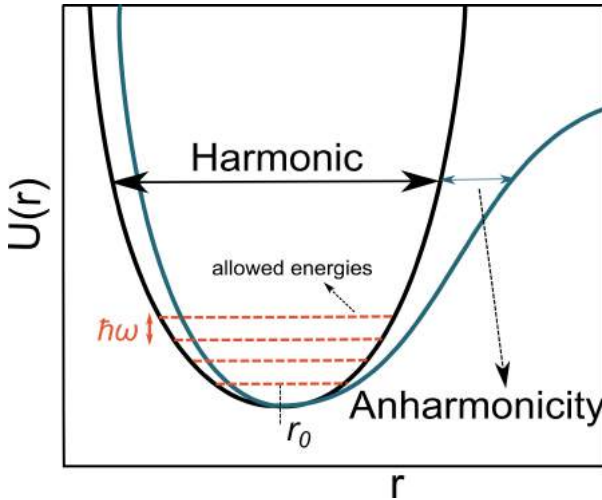


Fig. 1.14 Discrete energy levels depict phonon quantization. Successive energy levels are separated by $\hbar \omega$.

where Ψ is the electron wavefunction, and $\mathcal{V}(\vec{r})$ represents a potential energy function that commonly represents the periodic ion field in a crystal. However, $\mathcal{V}(\vec{r}) = 0$ is assumed to make electrons ‘free’ in the present simplification. The wavefunction determines the probability per unit volume P of finding an electron at position \vec{r} according to:

$$P = |\Psi(\vec{r})|^2 = \Psi(\vec{r})\Psi^*(\vec{r}), \tag{1.32}$$

where the “*” denotes complex conjugation. Once again, we assume a plane-wave solution (in this case, a steady-state form):

$$\Psi_k(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}}, \tag{1.33}$$

where V is volume and \vec{k} is the electron’s wavevector.¹ Substitution into the governing equation yields an expression for the energy eigenvalue E_k :

$$E_k = \frac{\hbar^2 k^2}{2m_e}, \tag{1.34}$$

¹We will use the lowercase symbol k for electrons, and the uppercase ω for phonons to signify the carrier type. The term \mathbf{k} -space is generic and applies to either.

where $k = \left| \vec{k} \right|$. Equation (1.34) relates electron energy and wavevector and is the dispersion relation for electrons, analogous to Eq. (1.22) for phonons. In this case, the functional relationship is parabolic, $E_k \sim k^2$. Such parabolic dispersion relations (or bands) are common in real materials, even for those with complicated electronic structures.

The parabolic ‘ $E - k$ ’ relation suggests a connection between wavevector and momentum. The usual Newtonian expressions for momentum p and energy become:

$$\begin{aligned} |p| &= m_e |v|; \quad E = \frac{m_e v^2}{2} \rightarrow v = \sqrt{\frac{2E}{m_e}} \\ \rightarrow |p| &= m_e \sqrt{\frac{2E}{m_e}} = \sqrt{2Em_e} = \sqrt{\hbar^2 k^2} = \hbar k \\ \rightarrow \vec{p} &= \hbar \vec{k}. \end{aligned} \quad (1.35)$$

The final result indicates that the wavevector can be considered a surrogate for momentum.

The momentum of electrons is restricted to certain allowed states, as it was for phonons. For the free electron gas, we can determine these values by considering an electron in a cube (the so-called ‘electron in a box’ problem). The wavefunction and its corresponding probability functional in Eq. (1.32) are assumed to be spatially periodic (see Fig. 1.15), such that:

$$\Psi(x + L) = \Psi(x); \quad \Psi(y + L) = \Psi(y); \quad \Psi(z + L) = \Psi(z). \quad (1.36)$$

Combining these periodic conditions with the plane-wave solution of Eq. 1.33 produces a set of allowable wavevectors:

$$\begin{aligned} e^{ik_x L} &= e^{ik_y L} = e^{ik_z L} = 1 \\ \rightarrow k_x &= \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}, \quad n_i = 1, 2, 3, \dots \end{aligned} \quad (1.37)$$

This result should be familiar, for it is the same as that for phonons in the linear chain (Eq. (1.19)) for $L = aN$, the chain length. Therefore, allowable wavevectors are separated by $2\pi/L$ in reciprocal space; this characteristic will be useful in the next chapter in deriving the so-called density of states.

An important difference exists, however, between the manner in which the allowed wavevectors are populated for electrons and phonons. The latter can populate a state with a limitless number whose average (which need

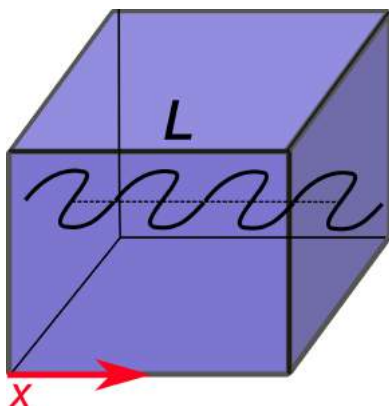


Fig. 1.15 Electron in a cube with a spatially periodic wavefunction.

not be an integer) is given by Eq. (1.27). Conversely, the electron occupation number of a given state is limited by the Pauli exclusion principle to be either 0 (not occupied) or 1 (occupied). Therefore, free electrons readily fill the reciprocal space until the number of carriers is exhausted.

Consider a material that contains N' free electrons in a volume of real space V . The ratio of these is the electron density $\eta_e = N'/V$. Because each allowed state occupies a reciprocal-space volume of $(2\pi/L)^3$, the number of electrons can be expressed in terms of a spherical ‘volume’ of \mathbf{k} -space as:

$$N' = 2 \frac{(4\pi k_F^3/3)}{(2\pi/L)^3} = \frac{k_F^3}{3\pi^2} V, \quad (1.38)$$

where k_F is called the Fermi wavevector and represents the largest occupied state at absolute zero temperature (the next chapter considers non-zero temperatures). The factor 2 in Eq. (1.38) accounts for the two electron spin states—up and down.

Other Fermi quantities can be easily derived from the Fermi wavevector:

$$\text{Fermi wavevector: } k_F = (3\pi^2 \eta_e)^{1/3}, \quad (1.39)$$

$$\text{Fermi energy: } E_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2 \eta_e)^{2/3}, \quad (1.40)$$

$$\text{Fermi velocity: } v_F = \frac{\hbar k_F}{m_e} = \frac{\hbar}{m_e} (3\pi^2 \eta_e)^{1/3}, \quad (1.41)$$

$$\text{Fermi temperature: } \theta_F = \frac{E_F}{k_B} = \frac{\hbar^2}{2m_e k_B} (3\pi^2 \eta_e)^{2/3}. \quad (1.42)$$

The Fermi energy E_F is the most commonly used, and as shown in Eq. (1.40), can be calculated from the electron density. The Fermi velocity v_F is also an important quantity because even though the electron velocities cover a very broad range, only states near the Fermi level are active in conduction because of the nearby availability of unoccupied states necessary to produce transport.

A sketch of the filled and empty energy levels is shown in Fig. 1.16. By convention, the zero energy datum is chosen to sit at the bottom of the conduction band, with non-conducting core electron states beneath. The electrons fill energies upward until they reach the Fermi energy and are contained in the solid by an energy barrier called the work function ϕ , which is the difference between the vacuum energy E_{vac} and Fermi energy E_F .

1.6 Example: 1D Atomic Chain with a Diatomic Basis

We choose a diatomic 1D chain of atoms as shown schematically in Fig. 1.17 to demonstrate a slightly more complicated situation than the monatomic chain of Section 1.4. The 2-atom basis produces an entirely separate phonon branch, as derived below.

For details of phonon analysis for linear chains, the reader is referred to Chapter 2 of Ziman (1972). We note that the definition of a here, which is the distance between unit cells, is a bit different from Ziman's, which does not span a full unit cell but rather the distance between atoms within a cell. Here we include the essential elements starting again with the Lagrangian mechanics relation, $\mathbf{F} = m\ddot{\mathbf{u}} = -\nabla U^{\text{harm}}$ (cf., Eq. (1.14)), where \mathbf{F} is the force on a particle of mass m with displacement \mathbf{u} , and again U^{harm} is the potential energy of the entire many-body system. Given the one-dimensional nature of the present formulation, we drop the spatial vector notation.

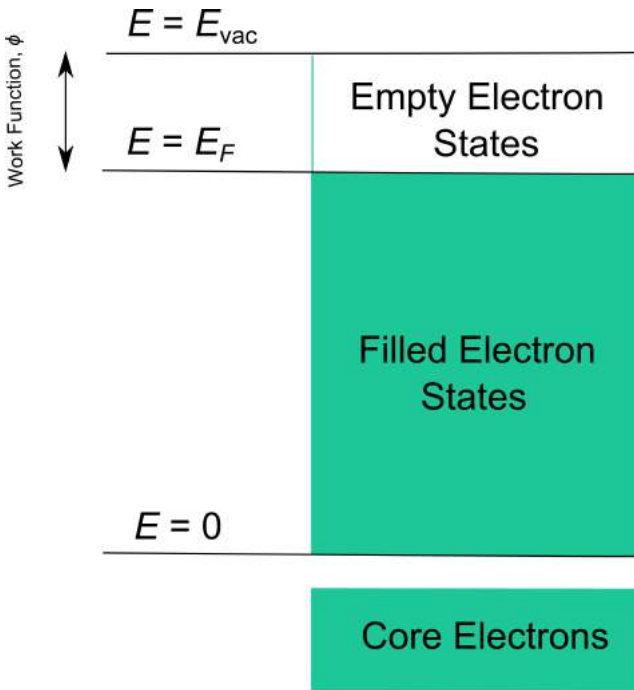


Fig. 1.16 Sketch of filled and empty electron energy states. The work function, ϕ , is defined as the difference between the Fermi energy, E_F , and the vacuum energy, E_{vac} .

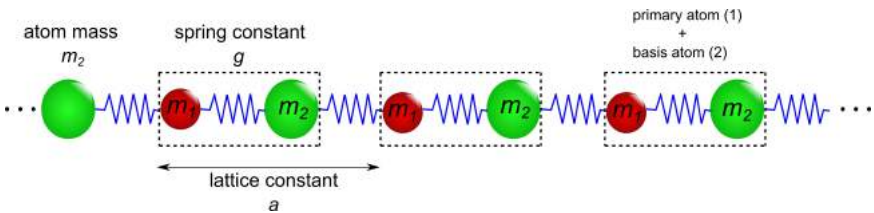


Fig. 1.17 Schematic of a 1D atomic chain with a two-atom basis.

In comparison to the monatomic chain, the index accounting for different atoms is more difficult when a basis atom is added (as well as any additional displacement dimensions not considered here); consequently, a matrix-based approach is required. To account for the discreteness of the

system, we represent each atom's displacement as $u_{n,\alpha}$ where α is the basis index (1 or 2) and n is the unit cell index. The equation of motion becomes (Ziman, 1972):

$$m_\alpha \ddot{u}_{n,\alpha} = - \sum_{m,\beta} \frac{\partial^2 U^{\text{harm}}}{\partial u_{n,\alpha} \partial u_{m,\beta}} u_{m,\beta} = - \sum_{m,\beta} \Phi_{n,\alpha}^{m,\beta} u_{m,\beta}, \quad (1.43)$$

where U^{harm} for this 2-atom basis is:

$$U^{\text{harm}} = \frac{1}{2}g \sum_n (u_{n,1} - u_{n,2})^2 + (u_{n,2} - u_{n+1,1})^2. \quad (1.44)$$

The matrix $\Phi_{n,\alpha}^{m,\beta}$ (hereafter called the 'force constants matrix') contains the interatomic force constants between each atom pair (i.e., (n, α) and (m, β)). Inspection of Eqs. (1.43) and (1.44) reveals:

$$\begin{aligned} \Phi_{n,1}^{n,1} &= \Phi_{n,2}^{n,2} = 2g \\ \Phi_{n,2}^{n,1} &= \Phi_{n,1}^{n,2} = \Phi_{n,1}^{n-1,2} = \Phi_{n,2}^{n+1,1} = -g. \end{aligned} \quad (1.45)$$

Recognizing the symmetry of the problem (i.e., that all unit cells are identical) and using a left-to-right numbering scheme, the force constants matrix becomes:

$$\Phi = \begin{bmatrix} 2g & -g \\ -g & 2g \end{bmatrix}. \quad (1.46)$$

From the translational symmetry of the chain, the unit cell indices n and m can be replaced by 0 and p , respectively, where p is simply an index that begins at 0 and increases in unit steps away from the cell of interest (i.e., 0). The Fourier transform of this matrix becomes the so-called dynamical matrix of lattice dynamics analysis (Young and Maris, 1989):

$$\begin{aligned} D_\alpha^\beta &= \frac{1}{\sqrt{m_\alpha m_\beta}} \Phi_{0,\alpha}^{p,\beta} e^{i\vec{K} \cdot \vec{r}_p} \\ &= \begin{pmatrix} \frac{2g}{m_1} & \frac{-g}{\sqrt{m_1 m_2}} (1 + e^{-iKa}) \\ \frac{-g}{\sqrt{m_1 m_2}} (1 + e^{+iKa}) & \frac{2g}{m_2} \end{pmatrix}, \end{aligned} \quad (1.47)$$

where \vec{r}_p is the distance between the unit cells of the pair of atoms under consideration and implied summation applies to the index p . The dynamical

matrix emerges as part of the governing equation of motion (Eq. (1.43)) cast in frequency space:

$$\omega^2 \tilde{u}_\alpha(K) = \frac{1}{\sqrt{m_\alpha m_\beta}} \Phi_{0\alpha i}^{p\beta j} e^{iK \cdot \vec{r}_p} \tilde{u}_\beta(K) = D_\alpha^\beta \tilde{u}_\beta(K), \quad (1.48)$$

where \tilde{u} is the amplitude of displacement. The so-called secular equation emerges from the foregoing expression and is used to extract the eigenvalues ω^2 :

$$\det |\mathbf{D} - \omega^2 \mathbf{I}| = 0, \quad (1.49)$$

where \mathbf{I} is the identity matrix (2 by 2 in this case). The solution of Eq. (1.49) provides a form of the dispersion relation:

$$\omega^4 - 2g \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \omega^2 + \frac{4g^2}{m_1 m_2} \sin^2 \left(\frac{Ka}{2} \right) = 0. \quad (1.50)$$

Using quadratic reduction, the foregoing result can be solved for ω^2 :

$$\omega(K)^2 = g \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm g \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4}{m_1 m_2} \sin^2 \left(\frac{Ka}{2} \right)}. \quad (1.51)$$

The ‘ \pm ’ term in Eq. (1.51) produces the peculiarity of having two possible branches. The lower branch (defined as having the lower frequency, represented by ω_-) is the acoustic branch and is equivalent to that derived for the monatomic chain (Eq. (1.22)). The upper branch (ω_+), called the *optical branch*, is new and represents generally out-of-phase vibrations between neighboring atoms (i.e., the displacements of neighboring atoms are nearly equal and opposite). The limiting forms at the Brillouin zone origin and edges for both branches are:

$$\lim_{K \rightarrow 0} \omega_-(K) = Ka \sqrt{\frac{g\mu}{2m_1 m_2}}; \quad \lim_{K \rightarrow 0} \omega_+(K) = \sqrt{\frac{2g}{\mu}}, \quad (1.52)$$

$$\omega_-\left(K = \frac{\pi}{a}\right) = \sqrt{\frac{2g}{m_2}}; \quad \omega_+\left(K = \frac{\pi}{a}\right) = \sqrt{\frac{2g}{m_1}}, \quad (1.53)$$

where $\mu = (1/m_1 + 1/m_2)^{-1}$, and m_2 is the heavier of the two masses.

The two branches of the dispersion are shown in Fig. 1.18. The curves reveal an energy band gap between the branches that grows with increasing contrast between the two atomic masses. Moreover, the shape of the optical branch takes a generally flat character, suggesting that the group velocity ($d\omega/dK$) is relatively small. Consequently, optical phonons are often neglected in the calculation of thermal conductivity, in favor of the acoustic branch.

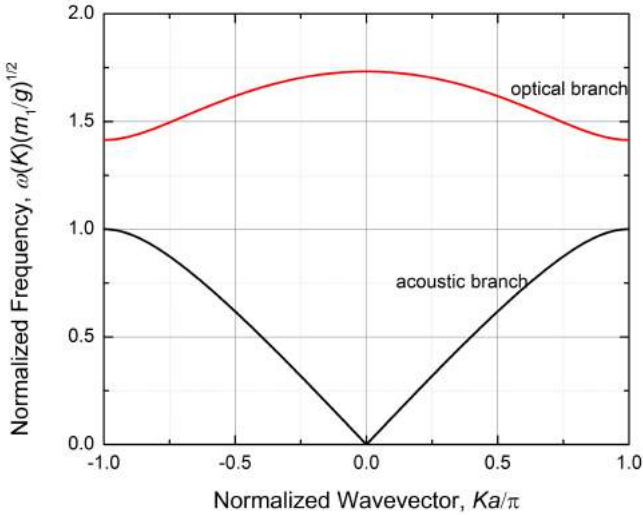


Fig. 1.18 Normalized frequency as a function of normalized wavevector for a diatomic 1D chain with $m_2 = 2m_1$.

Finally, we address a common source of confusion related to the application of the diatomic dispersion results to the case of $m_1 = m_2$ (i.e., the monatomic case). Figure 1.19 shows the dispersion curve for the range $K \in \{-\pi/a, \pi/a\}$. Notably, the solution still predicts the presence of an optical mode, and thus one might wonder whether the optical mode is simply an artifact of mathematics. However, careful inspection reveals that the condition $m_1 = m_2$ produces one-eighth of a full sine wave for the acoustic branch in the range $K \in \{0, \pi/a\}$ instead of the usual quarter sine wave (cf., Figs. 1.13 and 1.18). The reason for this change is that the diatomic analysis uses a lattice constant $a = 2\tilde{a}$ that is exactly twice as large as that

for the monatomic case ($a = \tilde{a}$) for this special case of $m_1 = m_2$. Therefore, the range of K sampled in Fig. 1.19 is only half that of Fig. 1.13. The missing portion of the dispersion curve is actually contained in the optical branch, as shown in Fig. 1.19, which spans $K \in \{0, 2\pi/a\}$ and shows the completion of the quarter sine wave by the ‘virtual’ optical branch. This result provides an example of the importance of defining the primitive unit cell, from which the 1st Brillouin zone derives, as the *smallest* symmetric region necessary to fill exactly all space through the translation vector \vec{R} .

1.7 Conclusion

This chapter has laid a foundation in crystallography and the fundamentals of phonons and electrons, albeit in a highly idealized and simplified form. Often the mathematics of these fundamentals can obscure more intuitive or at least more familiar understanding. For example:

- The speed of sound in silicon (Si) is approximately 6400 m/s. With its nearest neighbor distance of 0.235 nm and atomic mass of 28.0855 g/mol, it is a straightforward exercise to estimate the spring constant from the $K \rightarrow 0$ limit (Eq. (1.25)) as $g = 35$ N/m, which is remarkably similar to the actual value (Zhang *et al.*, 2007).
- Many metals have Fermi energies near $E_F = 5$ eV. The corresponding Fermi velocity is $v_F = \sqrt{2E_F/m_e} \approx 10^6$ m/s, which is roughly two orders of magnitude less than the speed of light, $c_0 = 2.99792458 \times 10^8$ m/s.

Lastly, we include here a brief glossary of some the concepts covered in this chapter:

- **Primitive Cell:** A region of space that is closer to one point than any others.
- **Bravais Lattice:** A distribution of points in space that defines a repeating pattern.
- **1st Brillouin Zone:** The primitive cell of the reciprocal lattice.
- **Miller Indices:** Coordinates (hkl) of the shortest reciprocal lattice vector normal to a given real-space plane.
- **Group Velocity:** The speed at which phonons carry energy in a lattice (see Eq. (1.24)).

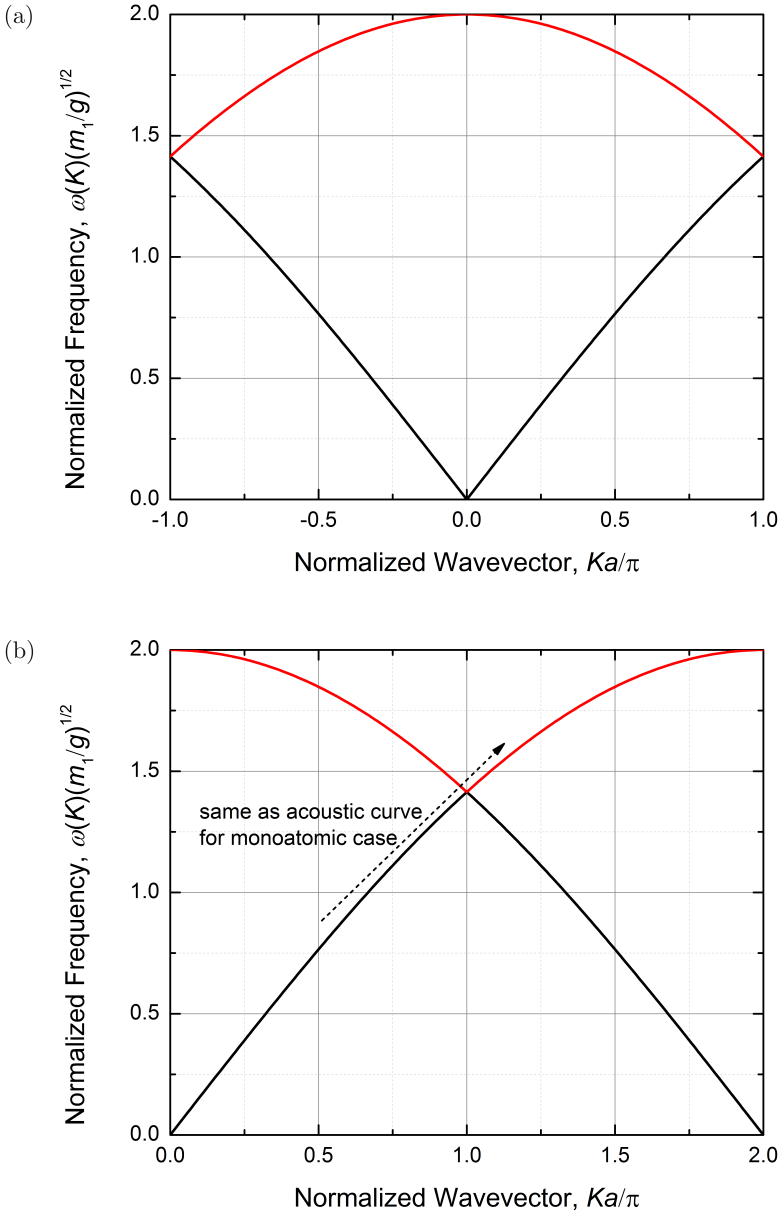


Fig. 1.19 Normalized frequency as a function of normalized wavevector for a diatomic 1D chain, for the special case of $m_1 = m_2$. (a) The usual range $Ka/\pi \in \{-1, 1\}$. (b) The range $Ka/\pi \in \{0, 2\}$.

- **Normal Mode:** A lattice wave that is characterized by a branch, wavevector, and frequency (and, later, polarization).
- **Phonon:** a quantized lattice vibration (i.e., one that can take on only a discrete energy, $\hbar\omega$).
- **Acoustic Phonons:** Phonons that determine the speed of sound in a solid and are characterized by $\omega \sim K$ as $K \rightarrow 0$.
- **Optical Phonons:** Phonons that have flat dispersion, low group velocity, and are characterized by non-zero ω as $K \rightarrow 0$.
- **Occupation Number:** The number of carriers with a given wavevector.

Example Problems

Problem 1.1: Graphene reciprocal lattice

The primitive lattice vectors (\vec{a}_1, \vec{a}_2) of graphene are given by:

$$\vec{a}_1 = \frac{3}{2}\tilde{a}\hat{x} + \frac{\sqrt{3}}{2}\tilde{a}\hat{y},$$

$$\vec{a}_2 = \frac{3}{2}\tilde{a}\hat{x} - \frac{\sqrt{3}}{2}\tilde{a}\hat{y},$$

where \tilde{a} is the C-C bond length. Calculate the reciprocal lattice vectors \vec{b}_1, \vec{b}_2 of graphene. Show that the primitive unit cell of the reciprocal lattice (also known as the 1st Brillouin zone) is a hexagon with a side length of $\frac{4\pi}{3\sqrt{3}\tilde{a}}$.

Solution

The primitive lattice vectors are:

$$\vec{a}_1 = \frac{3}{2}\tilde{a}\hat{x} + \frac{\sqrt{3}}{2}\tilde{a}\hat{y}, \quad \vec{a}_2 = \frac{3}{2}\tilde{a}\hat{x} - \frac{\sqrt{3}}{2}\tilde{a}\hat{y}, \quad \vec{a}_3 = c\hat{z}, \quad (1.54)$$

where c is an arbitrarily large constant (no periodicity exists in the z direction). The reciprocal lattice vectors are then given by:

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ &= \frac{2\pi}{\tilde{a}} \left(\frac{1}{3}\hat{x} + \frac{1}{\sqrt{3}}\hat{y} \right), \end{aligned} \quad (1.55)$$

$$\begin{aligned} \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ &= \frac{2\pi}{\tilde{a}} \left(\frac{1}{3}\hat{x} - \frac{1}{\sqrt{3}}\hat{y} \right), \end{aligned} \quad (1.56)$$

$$\begin{aligned} \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ &= \frac{2\pi}{c}\hat{z}, \end{aligned} \quad (1.57)$$

where $\vec{b}_3 \rightarrow 0$ as $c \rightarrow \infty$ indicating that the reciprocal lattice is two-dimensional. Figure 1.20 shows the process involved in construction of the reciprocal lattice. The Γ point of the reciprocal lattice is joined to its six nearest neighbors given by the points \vec{b}_1 (point A), \vec{b}_2 (point C), $\vec{b}_1 + \vec{b}_2$ (point B), $-\vec{b}_1$ (point D), $-\vec{b}_2$ (point F) and $-\vec{b}_1 - \vec{b}_2$ (point E). Perpendicular bisectors (red dotted lines in Fig. 1.20) are then drawn for each of these six line segments ΓA , ΓB , ΓC , ΓD , ΓE and ΓF . The region of intersection of these perpendicular bisectors forms the hexagonal Brillouin zone of graphene.

The side of the hexagon can be obtained from simple trigonometry. $\angle M\Gamma K = \frac{1}{2}\angle M\Gamma B = 30^\circ$. Thus $MK = \Gamma M/\sqrt{3} = |\vec{b}_1|/2\sqrt{3} = 2\pi/3\sqrt{3}\vec{a}$. One side of the hexagonal Brillouin zone is $2MK = 4\pi/3\sqrt{3}\vec{a}$.

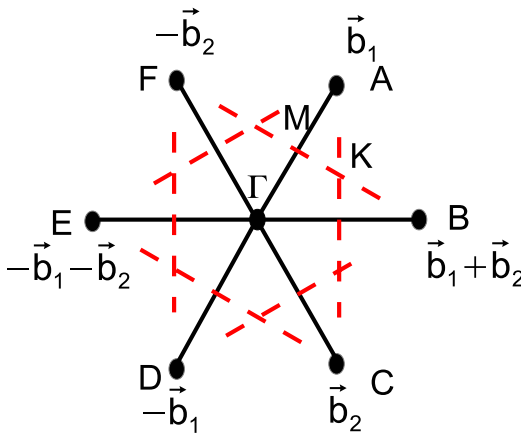


Fig. 1.20 Construction of the graphene Brillouin zone.

Problem 1.2: Dispersion relation for a 1D chain

- (a) Consider a monoatomic 1D chain with nearest neighbor interactions. Assume a spring constant $g = 25 \text{ N/m}$, atomic mass $m = 28 \text{ amu}$ and a lattice spacing of 5 \AA . Calculate the sound velocity and the maximum possible phonon frequency.
- (b) Now we generalize the monoatomic chain to include long-range interactions among atoms. Assume that the spring constant between two atoms separated by a distance of ja is given by g_j where j is an index that can take values $1, 2, 3$ and so on. Show that the new dispersion relation is given by:

$$\omega = 2 \sqrt{\sum_j \frac{g_j \sin^2(\frac{1}{2}jKa)}{m}}.$$

Solution

- (a) Sound velocity is given by:

$$c = a \sqrt{\frac{g}{m}} = 11594 \text{ m/s}, \quad (1.58)$$

where mass is converted to kg ($1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg}$). The maximum phonon frequency is given by:

$$\omega_{\max} = 2 \sqrt{\frac{g}{m}} = 4.63 \times 10^{13} \text{ rad/s}, \quad (1.59)$$

- (b) When interactions are considered between all pairs of atoms, the equation of motion for the atom at position na is given by:

$$\begin{aligned} m \frac{d^2 u(na)}{dt^2} &= \sum_{j=1}^{j=\infty} g_j (u[(n+j)a] - u(na)) - \sum_{j=1}^{j=\infty} g_j (u(na) - u[(n-j)a]) \\ &= \sum_{j=1}^{j=\infty} g_j (u[(n+j)a] - 2u(na) + u[(n-j)a]). \end{aligned} \quad (1.60)$$

Substituting the plane wave solution $u(na) = \exp(i(Kna - \omega t))$ into the above equation produces:

$$\begin{aligned}
 -m\omega^2 &= \sum_{j=1}^{j=\infty} g_j (\exp(ijKa) - 2 + \exp(-ijKa)) \\
 &= \sum_{j=1}^{j=\infty} -4g_j \sin^2\left(\frac{jKa}{2}\right). \tag{1.61}
 \end{aligned}$$

Thus the generalized dispersion relation is given by:

$$\omega = 2\sqrt{\sum_{j=1}^{j=\infty} \frac{g_j \sin^2(\frac{1}{2}jKa)}{m}}. \tag{1.62}$$

Problem 1.3: Kinetic energy of the free electron gas

Obtain an expression for the total kinetic energy of the free electron gas at $T = 0$ K. Express your answer in terms of the Fermi energy E_F and the total number of electrons N .

Solution

The following expressions for Fermi wavevector and Fermi energy were derived in the chapter:

$$k_F = (3\pi^2\eta_e)^{1/3}, \quad E_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2\eta_e)^{2/3}. \tag{1.63}$$

The volume of a spherical shell in \mathbf{k} -space with radius k and thickness dk is given by $4\pi k^2 dk$. The number of states in this shell is given by:

$$dN = 2 \frac{4\pi k^2 dk}{(2\pi/L)^3}, \tag{1.64}$$

where the factor 2 accounts for spin degeneracy. The energy of each state on the spherical shell of radius k is $\hbar^2 k^2 / 2m_e$. The total energy of electrons is obtained by integrating up to the maximum wavevector k_F .

$$\begin{aligned}
 E &= \int_0^{k_F} \left(\frac{\hbar^2 k^2}{2m_e} \right) \left(2 \frac{4\pi k^2 dk}{(2\pi/L)^3} \right) \\
 &= \frac{\hbar^2 L^3}{2m_e \pi^2} \int_0^{k_F} k^4 dk \\
 &= \frac{\hbar^2 L^3 k_F^5}{10m_e \pi^2} \\
 &= \frac{3}{5} \underbrace{\left(\frac{k_F^3 L^3}{3\pi^2} \right)}_N \underbrace{\left(\frac{\hbar^2 k_F^2}{2m_e} \right)}_{E_F} \\
 &= \frac{3}{5} N E_F.
 \end{aligned} \tag{1.65}$$

Problem 1.4: Phonon bandgap in a diatomic chain

Consider the diatomic chain (discussed in Section 1.6) with atomic masses m_1 and m_2 . Assume that the spring constant is g for all the bonds. At what point in the Brillouin zone is the bandgap (difference between the optical and acoustic branch frequencies) a minimum? Obtain an expression for the non-dimensional bandgap (normalized by $\sqrt{g/m_1}$) as a function of the mass ratio m_2/m_1 . Use the online Chapter 1 CDF tool² to observe the changes in shape of the acoustic and optical branches for varying mass ratio.

Solution

Observation of the acoustic and optical branches of a diatomic chain reveals that the bandgap is minimum at the edge of the Brillouin zone. The dispersion relation for a 1D diatomic chain of atoms is given by (see Eq. (1.51)):

$$\omega(K)^2 = g \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \pm g \sqrt{\left(\frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4}{m_1 m_2} \sin^2 \left(\frac{Ka}{2} \right)}. \tag{1.66}$$

²See http://nanohub.org/groups/cdf_tools_thermal_energy_course/wiki

The angular frequency at the edge of the Brillouin zone is obtained by substituting $K = \pi/a$:

$$\omega_- \left(K = \frac{\pi}{a} \right) = \sqrt{\frac{2g}{m_2}}, \quad \omega_+ \left(K = \frac{\pi}{a} \right) = \sqrt{\frac{2g}{m_1}}. \quad (1.67)$$

The non-dimensional bandgap is given by:

$$\frac{\omega_+ \left(K = \frac{\pi}{a} \right) - \omega_- \left(K = \frac{\pi}{a} \right)}{\sqrt{\frac{g}{m_1}}} = \sqrt{2} \left(1 - \sqrt{\frac{m_1}{m_2}} \right), \quad (m_2 > m_1). \quad (1.68)$$

From the above expression, the bandgap increases with increasing mismatch between the masses m_1 and m_2 . Figure 1.21 shows snapshots of the dispersion curves from the online Chapter 1 CDF tool. The optical branch flattens and the maximum frequency of the acoustic branch reduces for increasing m_2/m_1 .

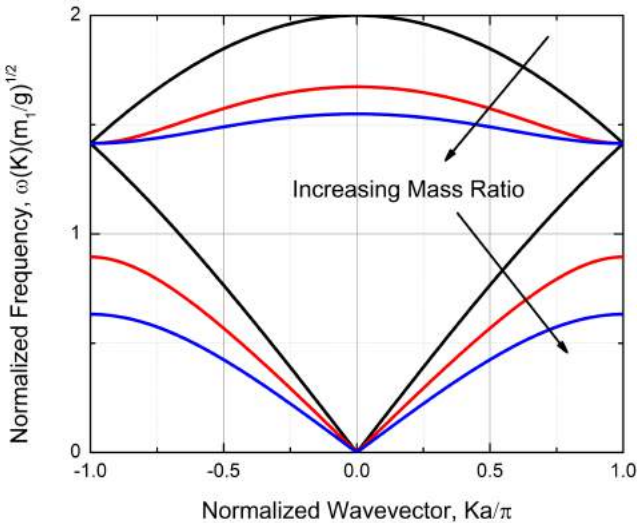


Fig. 1.21 Dispersion curves of the diatomic chain for increasing 2 1.

Chapter 2

Carrier Statistics

2.1 Introduction

Before proceeding further into details of nanoscale structure and energy transport, we first consider in this chapter an important distinction between *nanoscience* and *nanotechnology*. The former has been practiced for a century, ever since the nature of atomic structure was uncovered by the likes of Ernest Rutherford, Niels Böhr, and Marie Curie. The foundations of nanotechnology were similarly laid by researchers in the physical sciences, but nanotechnology is almost always characterized by a unique, *collective* behavior of an ensemble of nanoscale objects. In other words, nanotechnology encompasses phenomena that occur because of unique subcontinuum effects and that also can be directed towards a useful technological purpose.

The discipline of statistical mechanics provides the tools to achieve descriptions of large assemblies of nanoscale objects and is the primary subject of this chapter. Once again, we provide here only the basic essentials, while directing the motivated reader to more comprehensive coverage in topical books by, for example, Chandler (1987) and Laurendeau (2005).

2.2 Statistical Ensembles

A collection of energetic particles can be characterized by its number of particles N , volume V , and energy E . The collection can exist in a variety of states in which the foregoing variables may change upon application of a suitable perturbation. To analyze the diversity of states, we invoke the fundamental premise of statistical mechanics (Chandler, 1987):

During a measurement (e.g., of temperature), every possible state does in fact occur such that observed properties are averages of all possible states.

The statistics of any ensemble can be described by defining its allowed states, and each state can be represented by $\nu = (N, V, E)$. We define Ω_ν as the number of possible arrangements of the ensemble that can produce the state ν within dE of energy E . The fundamental *statistical assumption* that all states are equally probable then implies the probability that a particle will be in a state ν is:

$$P_\nu = \frac{1}{\Omega_\nu}. \quad (2.1)$$

The number of states also provides insight into the randomness that is possible in a given ensemble. Such disorder forms the essence of the thermodynamic property called entropy, which was derived by Boltzmann as:

$$S = k_B \ln(\Omega_\nu). \quad (2.2)$$

This result, when combined with the Maxwell relations (Laurendeau, 2005), produces a statistical definition for temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}, \quad (2.3)$$

or

$$\beta = \frac{1}{k_B T} = \left(\frac{\partial \ln \Omega_\nu}{\partial E} \right)_{N,V}, \quad (2.4)$$

where the term β is a common thermodynamic expression for the inverse of ‘thermal energy’ $k_B T$.

Various permutations and restrictions can be applied to an ensemble in order to change its state. Energy and particle number are the most important such properties for our purposes. If these properties are allowed to vary within an ensemble, then the probability of a state ν can be shown to be Laurendeau (2005):

$$P_\nu = \frac{\exp(-\beta E_\nu + \beta \mu N_\nu)}{\Xi}, \quad (2.5)$$

where

$$\Xi = \sum_\nu \exp(-\beta E_\nu + \beta \mu N_\nu), \quad (2.6)$$

and where μ is the electrochemical potential; the latter equation defines the ensemble’s partition function Ξ , which is essentially a normalizing factor

to ensure that the total probability sums to unity. Further, the quantification of ensemble statistics allows the calculation of averages through by taking ‘moments’ of probability. For example, an average energy can be calculated as:

$$\langle E \rangle = \sum_{\nu} P_{\nu} E_{\nu}. \quad (2.7)$$

An ensemble in which both the energy and number of particles are allowed to vary is termed the *grand canonical ensemble*. A given state will have N_1 particles each with energy E_1 , N_2 particles with energy E_2 , and so on. Their average total energy and particle numbers can be expressed using Eqs. (2.5)–(2.7) as:

$$\langle E \rangle = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\beta, \mu, V}, \quad (2.8)$$

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial (\beta \mu)} \right)_{\beta, V}. \quad (2.9)$$

The statistics of the particles of interest here can be described in this manner, noting that:

- Bose-Einstein statistics, which govern phonons and photons, allow integer occupation numbers $N_{\nu} = 0, 1, 2, 3, \dots$
- Fermi-Dirac statistics, which govern electrons, allow only binary occupation numbers $N_{\nu} = 0$ or 1 , as a result of the Pauli exclusion principle (Ashcroft and Mermin, 1976).
- Both of the above statistics converge at very high particle energies (relative to the thermal energy $k_B T$) to classical Maxwell-Boltzmann occupation statistics.

The resulting *average occupation numbers* $\langle N_{\nu} \rangle$, despite these differences, can be expressed in a general form as:

$$f_i^o = \frac{1}{e^{\frac{E_i - \mu}{k_B T}} + \gamma}, \quad (2.10)$$

$$\begin{aligned} \gamma &= 1 \text{ (Fermi-Dirac, } i = FD) \\ \gamma &= -1 \text{ (Bose-Einstein, } i = BE) \\ \gamma &= 0 \text{ (Maxwell-Boltzmann, } i = MB) \end{aligned}$$

where the equilibrium ‘distribution function’ f_i^o is synonymous with the average occupation number and is used hereafter. The Maxwell-Boltzmann distribution ($\gamma = 0$) represents the limit $(E_i - \mu) \gg k_B T$ for both Fermi-Dirac and Bose-Einstein distributions.

The electrochemical potential depends on the enumeration of carriers. It is zero for systems with an indefinite number of carriers (i.e., phonons and photons) (Pathria and Beale, 2011). The Helmholtz free energy can be expressed as $A = \mu N - pV$, and if N is unbounded, the equilibrium number of particles N must be determined by minimizing A with respect to N , which by definition requires $(\partial A / \partial N)_V = \mu = 0$. For phonons and thermal photons (which are both called ‘bosons’ because they follow Bose-Einstein statistics) μ is zero because these particles can be created or destroyed at random without a change in the electrochemical potential. For electrons in metals, which have a finite number of carriers, μ can be approximated in terms of the Fermi energy E_F and temperature as (Ashcroft and Mermin, 1976):

$$\mu \approx E_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 \right], \quad (2.11)$$

where the Fermi energy represents the highest occupied energy at absolute zero temperature and was expressed for a free-electron gas previously in Eq. (1.40) (See also Eq. (5.20) of Zhang (2007)).

As an example, consider a distribution of phonons from which we choose those with a particular frequency ω_ν . While the energy of each of these phonons has already been shown to be $\hbar\omega_\nu$, the actual number of such phonons at a given temperature must be determined from statistics. In accord with the energy of a given phonon mode derived in the previous chapter (see Eq. (1.26)), the average (or expected) energy of all phonons at this frequency is:

$$\begin{aligned} \langle E_\nu \rangle &= \hbar\omega_\nu \left\{ f_{BE}^o(\omega_\nu, T) + \frac{1}{2} \right\} \\ &= \hbar\omega_\nu \left\{ \left[\exp \left(\frac{\hbar\omega_\nu}{k_B T} \right) - 1 \right]^{-1} + \frac{1}{2} \right\}, \end{aligned} \quad (2.12)$$

where the $1/2$ term accounts for zero-point energy (i.e., energy at zero absolute temperature). Figure 2.1 shows the resulting variation of average energy for phonons at frequencies of $\omega_\nu = 10^{13}$ and $\omega_\nu = 10^{14}$ rad/s. The figure also contains a comparison with the classical energy $k_B T$ that arises

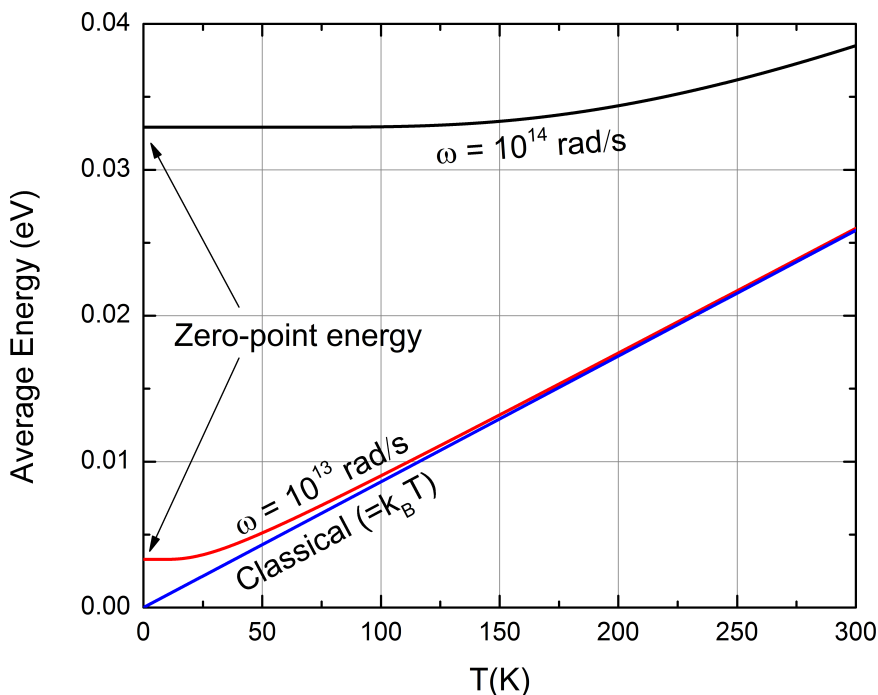


Fig. 2.1 Temperature-dependent energy of a classical harmonic oscillator and two quantum harmonic oscillators at $\omega = 10^{13}$ rad/s and $\omega = 10^{14}$ rad/s. The zero-point energy for quantum oscillators is on the y -axis.

from the equipartition theorem (Laurendeau, 2005). In this case, half of the ‘thermal energy’ $k_B T$ comes from the average kinetic energy in a single direction ($k_B T/2$), while the other half originates from the average potential energy in the bonds.

Clearly, temperature is intimately related to energy in both classical and quantum systems. For a simple (classical) harmonic oscillator, the relationship is direct: $\langle E_{\text{tot}} \rangle = k_B T$. For a quantum harmonic oscillator, the temperature dependence is contained within the occupation number: $\langle E_{\text{tot}} \rangle = \hbar\omega [f_{BE}^o(\omega, T) + 1/2]$. To complicate matters further, an atomic lattice can support many harmonic oscillators (according to the dispersion relation), and we need to sum (average) over all of their frequencies to find temperature. The results of Fig. 2.1 suggest that phonons oscillating at frequencies of $\omega = 10^{13}$ rad/s (and lower) can be approximated by classical statistics for all except cryogenic temperatures (i.e., below liquid nitrogen

temperature, 77 K), whereas phonons at $\omega = 10^{14}$ rad/s require quantum statistics, even well above room temperature. The general guideline for assessing whether a classical approximation is appropriate is to evaluate $\chi = \frac{\hbar\omega}{k_B T}$. For example, at room temperature:

$$\frac{\hbar \times 10^{13} \text{ rad/s}}{k_B T} = 0.25 \quad (\chi < 1, \text{ classical approximation is reasonable})$$

$$\frac{\hbar \times 10^{14} \text{ rad/s}}{k_B T} = 2.5 \quad (\chi > 1, \text{ classical approximation is not reasonable}).$$

2.3 Phonon Density of States

The need to quantify the number of states around a certain energy or wavevector is common in the integral analysis of phonons. The associated quantity is called the *density of states* and describes the number of allowable phonon states per unit ‘volume’ (i.e., length in 1D, area in 2D, true volume in 3D) per unit energy or wavevector, depending on context. Recalling the restriction on allowable wavevectors from the looped 1D chain example (see Eq. (1.19)), we notice that allowable wavevectors are separated by a \mathbf{k} -space increment of $2\pi/L$, where $L = aN$ (N is the number of primitive unit cells; for cells with a single atom per unit cell N is therefore the number atoms). We find a similar result for 2D and 3D lattices for which each allowable wavevector occupies a \mathbf{k} -space ‘volume’ of $(2\pi/L)^d$, where d is dimensionality.

The number of states is calculated by forming the ratio of a smooth (i.e., circular in 2D, spherical in 3D) \mathbf{k} -space ‘volume’ to that of an individual state, as shown in Fig. 2.2. One subtlety of the foregoing development is that \mathbf{K} can take both positive and negative values, and therefore with K defined as the absolute magnitude of \mathbf{K} (i.e., $K = |\mathbf{K}|$), one allowable wavevector exists for each increment of π/L in the 1D \mathbf{k} -space (which, by definition, is strictly positive) as a special case. Therefore, the number of allowed phonon states from 0 to K (which, recall, is the absolute magnitude of \mathbf{K}) for 1-, 2-, and 3-dimensional systems is:

$$N_{1D} = \frac{2K}{2\pi/L}, \quad (2.13)$$

$$N_{2D} = \frac{\pi K^2}{4\pi^2/L^2}, \quad (2.14)$$

$$N_{3D} = \frac{4\pi K^3/3}{8\pi^3/L^3}. \quad (2.15)$$

Once this number of allowed modes or phonons is known, the density of such states (per unit wavevector and real-space ‘volume’) can be expressed as:

$$D_{1D}(K) = \frac{1}{L} \frac{dN_{1D}}{dK} = \frac{1}{\pi}, \quad (2.16)$$

$$D_{2D}(K) = \frac{1}{L^2} \frac{dN_{2D}}{dK} = \frac{K}{2\pi}, \quad (2.17)$$

$$D_{3D}(K) = \frac{1}{L^3} \frac{dN_{3D}}{dK} = \frac{K^2}{2\pi^2}. \quad (2.18)$$

The density of states is often described with respect to phonon frequency instead of wavevector. This transformation is made quite readily using the chain rule and the definition of phonon group velocity ($v_g(\omega) = d\omega/dK$):

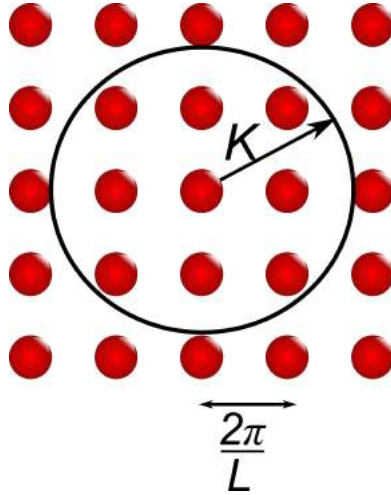
$$D_{1D}(\omega) = \frac{1}{L} \frac{dN_{1D}}{d\omega} = \frac{1}{L} \frac{dN_{1D}}{dK} \frac{dK}{d\omega} = \frac{1}{v_g(\omega)\pi}, \quad (2.19)$$

$$D_{2D}(\omega) = \frac{1}{L^2} \frac{dN_{2D}}{d\omega} = \frac{1}{L^2} \frac{dN_{2D}}{dK} \frac{dK}{d\omega} = \frac{K(\omega)}{2\pi v_g(\omega)}, \quad (2.20)$$

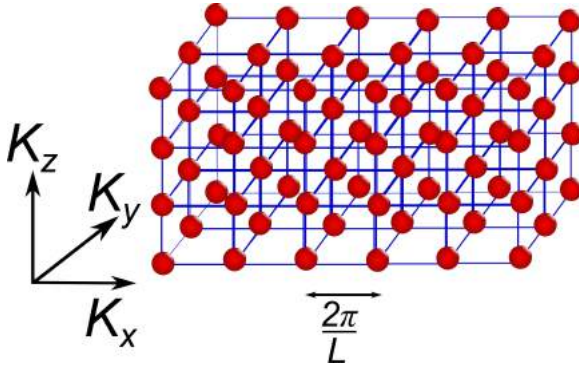
$$D_{3D}(\omega) = \frac{1}{L^3} \frac{dN_{3D}}{d\omega} = \frac{1}{L^3} \frac{dN_{3D}}{dK} \frac{dK}{d\omega} = \frac{K(\omega)^2}{2\pi^2 v_g(\omega)}, \quad (2.21)$$

where, as we have shown previously (see Eq. (1.22)), the phonon group velocity generally depends on frequency (and thus the wavevector through the dispersion relation).

At this point in the development, the $K(\omega)$ relations above are often simplified for phonon transport through the Debye approximation, which assumes linear dispersion $\omega = v_{g,\text{ave}}K$ and places an upper bound ω_D on frequency in order to match the total number of possible phonon states.



(a)



(b)

Fig. 2.2 \mathbf{k} -space in 2D and 3D. Minimum separation between allowable wavevectors is $\frac{2\pi}{L}$. \mathbf{k} -space spherical ‘volume’ (circular area for 2D) is depicted in the figure.

The resulting density of states for a bulk material becomes:

$$D_{3D, \text{Debye}}(\omega) = \frac{\omega^2}{2\pi^2 v_{g, \text{ave}}^3}, \quad \text{for } \omega < \omega_D = v_{g, \text{ave}} (6\pi^2 \eta_a)^{1/3}, \quad (2.22)$$

where $v_{g, \text{ave}}$ is an appropriately averaged phonon velocity among the acoustic polarizations and η_a is the number of unit cells per unit volume of real space. For now, we will refrain from making this approximation.

2.4 Electron Density of States

Electron states are similarly restricted, as shown in Section 1.5 for the particle-in-box problem. The result, Eq. (1.37), in combination with the parabolic dispersion of Eq. (1.34) provides us with analogues to the foregoing analysis of phonons.

The electron density of states is almost always expressed per unit energy E as $D(E)$ (this convention allows us to distinguish it from the phonon density of states, which is usually described in terms of frequency ω , cf. Eq. (2.21)). Given the quantum relation $E = \hbar\omega$ between energy and frequency, the density of states per unit energy is closely related to that given above for phonon density of states per unit frequency. Accordingly, the electronic density of states can be expressed as $D(E) = 2D(\omega)/\hbar$, where the factor of 2 accounts for spin degeneracy. The resulting expressions in each dimensionality follow:

$$D_{1D}(E) = \frac{2m_e}{\pi\hbar^2k(E)}, \quad (2.23)$$

$$D_{2D}(E) = \frac{m_e}{\pi\hbar^2}, \quad (2.24)$$

$$D_{3D}(E) = \frac{m_e k(E)}{\pi^2\hbar^2}, \quad (2.25)$$

where m_e is the electron rest mass, and we have made use of the momentum relation $m_e v_g = \hbar k$.

The same result can be derived by integrating over \mathbf{k} -space using Dirac delta functions for allowable states (Lundstrom, 2009):

$$\begin{aligned} D(E) &= \frac{1}{L^d} \sum_{k'} \delta[E(k) - E(k')], \\ &= \frac{2}{(2\pi)^d} \int_{k'} \delta\left(\frac{\hbar^2 k^2}{2m_e} - \frac{\hbar^2 k'^2}{2m_e}\right) d\vec{k}' \\ &= \frac{2m_e}{\pi\hbar\sqrt{2m_e E}} \quad (1D) \\ &= \frac{m}{\pi\hbar^2} \quad (2D) \\ &= \frac{m_e\sqrt{2m_e E}}{\pi^2\hbar^3} \quad (3D), \end{aligned} \quad (2.26)$$

where in this set of equations we have made the parabolic band approximation for $k(E)$, namely:

$$E = \frac{\hbar^2 k^2}{2m_e} \quad \text{or} \quad k(E) = \frac{\sqrt{2m_e E}}{\hbar}. \quad (2.27)$$

Figure 2.3 shows a parabolic electron band with two ranges of \mathbf{k} -space. The allowed states are equally distributed in \mathbf{k} -space, but corresponding mapping of energies from allowed \mathbf{k} -states shows a higher density of states at low energies (and low wavevectors), where the band is flattest.

A schematic of the resulting electron density of states appears in Fig. 2.4. The curves for confined structures (quantum wells, wires, and dots) contain multiple ‘bands’ that build upon each other and generally follow the overall \sqrt{E} trend of the curve for a bulk conductor.

For greater depth, the reader is referred to the nanoHUB’s ‘CNTbands’ tool (Seol *et al.*, 2011a), which calculates the geometry, band structure, and density of states of single-walled carbon nanotubes. As an example, Fig. 2.5 shows results for a (12, 12) CNT.

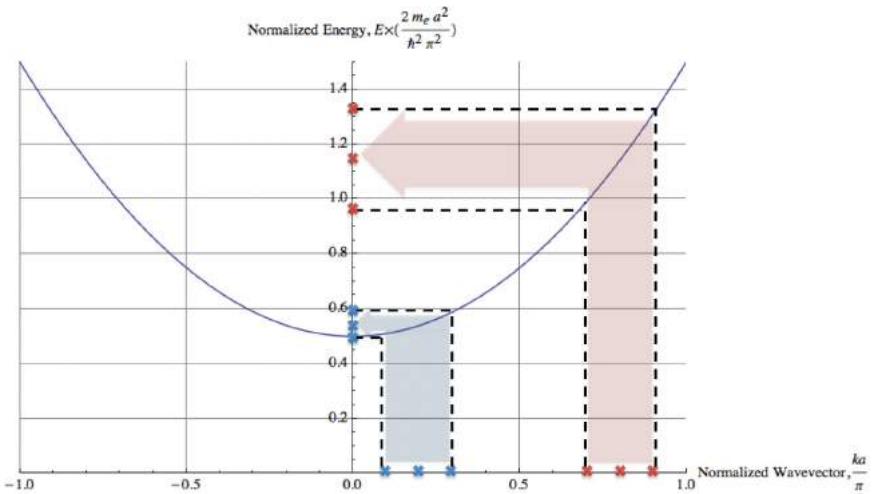


Fig. 2.3 Parabolic electron energy band (with normalized band edge at $E_{c,\text{norm}} = 0.5$) and corresponding allowable k -states at low and high wavevectors.

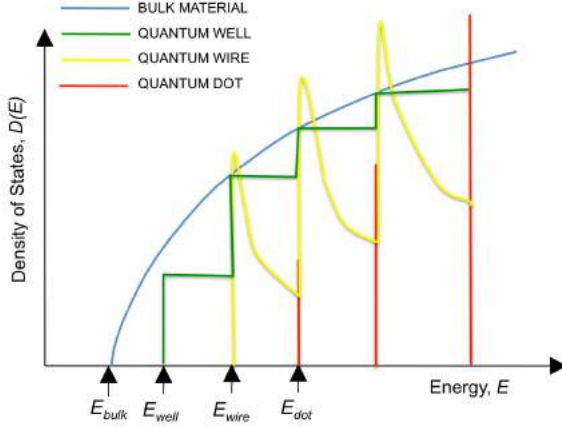


Fig. 2.4 Electron density of states for 0D (quantum dot), 1D (quantum wire), 2D (quantum well), and 3D (bulk) materials. Bulk material density of states follows a \sqrt{E} dependence, whereas confined material densities of states present discontinuities due to multiple band-folding from confined dimensions.

2.5 Example: Derivation of Planck's Law

This section provides a brief derivation of Planck's law of blackbody radiation from basic statistical principles, as an example of a 'boson' thermal field. For more information, the reader is referred to the textbook by Rybicki and Lightman (2008). The reader might also find interest in the historical development of early research in radiation physics as surveyed by Barr (1960).

2.5.1 Photon Gas in a Box

First, consider a cubic box with each side of length L filled with electromagnetic (EM) radiation (a so-called 'photon gas') that forms standing waves whose allowable wavelengths are restricted by the size of the box. We will assume that the waves do not interact and therefore can be separated into the three orthogonal Cartesian directions such that the allowable wavelengths are:

$$\lambda_i = \frac{2L}{n_i}, \quad (2.28)$$

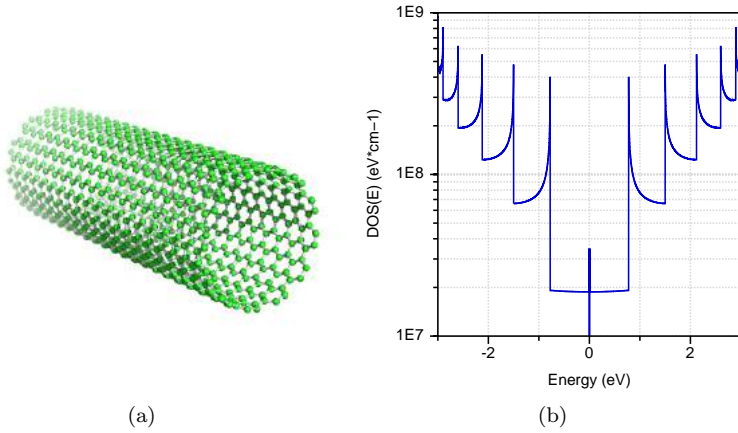


Fig. 2.5 Geometry and density of states of a (12,12) single-walled carbon nanotube (SWCNT). Refer to <https://nanohub.org/resources/cntbands-ext> for the online tool.

where n_i is an integer greater than zero, and i represents one of the three Cartesian directions— x , y , or z .

From quantum mechanics, the energy of a given mode (i.e., an allowable set n_x, n_y, n_z) can be expressed as:

$$E(N) = \left(N + \frac{1}{2}\right) \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2}, \quad (2.29)$$

where h is Planck's constant (6.626×10^{-34} J s). The number N represents the number of such modes, or photons, with the set of quantum numbers $\{n_x, n_y, n_z\}$. Importantly, unlike electrons, an unlimited number of modes, or photons, of a given energy can exist; thus, photons are governed by Bose-Einstein statistics, for which the average $\langle N \rangle = f_{BE}^o$ according to Eq. (2.9).

2.5.2 Statistical Mechanics of the Photon Gas

To derive the energy density in this photon gas, we first need to know the relative probability with which a given energy state $E(N)$ is occupied at a given temperature. Here, we turn to statistical mechanics, which reveals this probability as:

$$P_N = \frac{\exp(-\beta E(N))}{Z(\beta)}, \quad (2.30)$$

where β is the inverse of thermal energy, or $\beta = (k_B T)^{-1}$, and $Z(\beta)$ is the partition function that normalizes the probability as:

$$Z(\beta) = \sum_{N=0}^{\infty} \exp(-\beta E(N)) = \frac{1}{1 - \exp(-\beta \varepsilon)}, \quad (2.31)$$

where $\varepsilon = \frac{hc}{2L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{hc}{\lambda}$ is the energy of a single photon, and the latter equality derives from the relationship between the wavelength λ and the n_i indices of the EM waves in the box. This wavelength is related to the speed of light c and frequency ν through the familiar relation

$$\frac{c}{\lambda} = \nu \Rightarrow \varepsilon = h\nu. \quad (2.32)$$

Again from statistical mechanics (and specifically Bose-Einstein statistics), the average energy within a given mode can be expressed as

$$\langle E(N) \rangle = -\frac{d \ln Z}{d\beta} = \frac{\varepsilon}{\exp(\beta \varepsilon) - 1}, \quad (2.33)$$

where the zero point energy is neglected.

2.5.3 Energy Density of the Photon Gas

Now that we have an expression for the average energy of a given mode, we can sum (integrate) over all modes to find the total specific energy within the photon gas. This energy can be expressed as an integral over all energies:

$$\begin{aligned} u &= \int_0^{\infty} \langle E \rangle D(\varepsilon) d\varepsilon \\ &= \int_0^{\infty} \frac{\varepsilon}{\exp(\beta \varepsilon) - 1} D(\varepsilon) d\varepsilon, \end{aligned} \quad (2.34)$$

where $D(\varepsilon)$ is the density of states that gives the number of allowed modes per unit volume and per unit energy within an interval between ε and $\varepsilon + d\varepsilon$. This function can be derived from the allowable wavelengths and n indices as:

$$D(\varepsilon) d\varepsilon = \frac{8\pi}{h^3 c^3} \varepsilon^2 d\varepsilon. \quad (2.35)$$

The total energy per unit volume (or ‘specific’ energy) can now be expressed as

$$u = \int_0^\infty \frac{8\pi}{h^3 c^3} \frac{\varepsilon^3}{\exp(\beta\varepsilon) - 1} d\varepsilon, \quad (2.36)$$

where the integrand is the spectral energy density u' . This function can be expressed in terms of an energy, wavelength, or frequency spectral basis through the relation $\varepsilon = hc/\lambda$ such that different forms of u' are commonly used. However, they are each integrands in expressions that are used to calculate the overall energy density as:

$$\frac{U}{L^3} = u(T) = \int_0^\infty u'(\varepsilon, T) d\varepsilon = \int_0^\infty u'(\lambda, T) d\lambda = \int_0^\infty u'(\nu, T) d\nu. \quad (2.37)$$

The corresponding expressions for spectral energy density follow:

$$u'(\varepsilon, T) = \frac{8\pi}{h^3 c^3} \frac{\varepsilon^3}{\exp\left(\frac{\varepsilon}{k_B T}\right) - 1}, \quad (2.38)$$

$$u'(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}, \quad (2.39)$$

$$u'(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \quad (2.40)$$

$$u'(\omega, T) = \frac{(\hbar\omega)^3}{\pi^2 \hbar^2 c^3} \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}. \quad (2.41)$$

2.5.4 Blackbody Emission Intensity

Now assume that a small hole is cut into the box as shown in Fig. 2.6. All radiation emanating from this hole will be moving at the speed of light c . Also, the radiation will be uniformly distributed throughout the hemisphere of solid angles (2π steradians), and one half of the energy will be oriented such that it can move outward through the hole.

The spectral radiation intensity is defined as the rate of energy emitted per unit area per unit solid angle and per unit wavelength. The rate of energy emitted per area is simply the product of the energy density derived

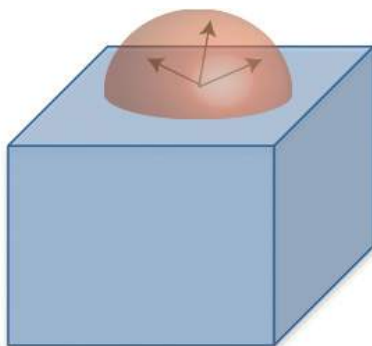


Fig. 2.6 Blackbody emission from a small hole in a box.

above and the speed of light (i.e., the distance swept by a ray per unit of time). Therefore, the spectral intensity becomes:

$$I(\lambda, T) = \frac{1}{2} \left[\frac{u'(\lambda, T)c}{2\pi} \right] = \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}. \quad (2.42)$$

Similarly, the spectral intensity (per unit frequency ν instead of wavelength) is:

$$I(\nu, T) = \frac{1}{2} \left[\frac{u'(\nu, T)c}{2\pi} \right] = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}. \quad (2.43)$$

And finally, the intensity per unit angular frequency $\omega = 2\pi\nu$ is:

$$I(\omega, T) = \frac{1}{2} \left[\frac{u'(\omega, T)c}{2\pi} \right] = \frac{\hbar\omega^3}{4\pi^3 c^2} \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}. \quad (2.44)$$

This distribution is plotted for different temperatures in Fig. 2.7.

The foregoing analysis of electromagnetic transport with photons highlights the convergence of statistical distributions and energy states. The results emphasize particularly well the spectral behavior of transport and its interrelationship with temperature. Subsequent chapters will demonstrate similar concepts for phonons and electrons.

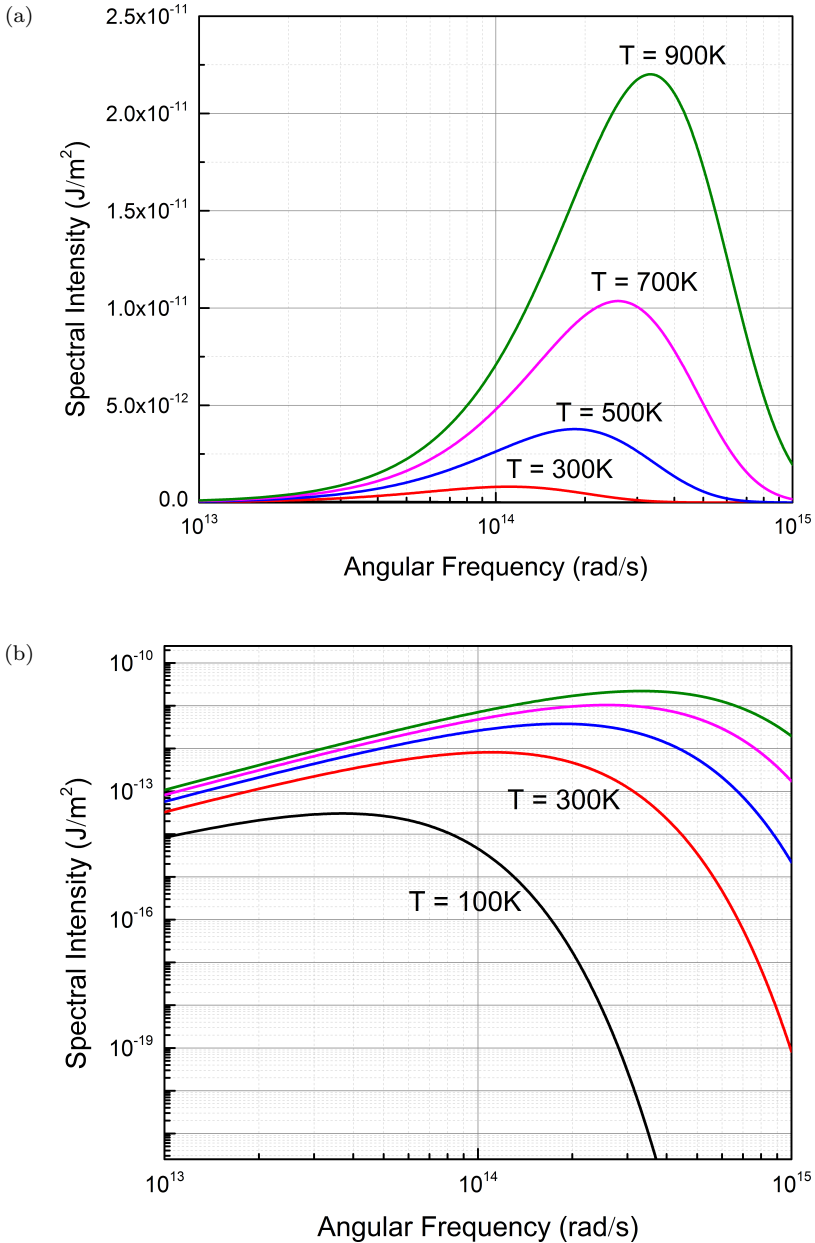


Fig. 2.7 Spectral intensity (per unit angular frequency ω) as a function of angular frequency at different temperatures. The frequency at maximum spectral intensity increases with increasing temperature, according to Wien's displacement law (Modest, 2003).

Example Problems

Problem 2.1: Getting a feel for the numbers (note: this problem has been adapted from Kaviany (2008))

- The maximum energies of acoustic and optical phonons in graphene are 0.16 eV and 0.21 eV respectively. Determine f_{BE}^o at $T = 300$ and 3000 K, for these two energies.
- The Fermi energy of aluminum is 11.7 eV. Assuming that the chemical potential is equal to the Fermi energy, determine f_{FD}^o for $E = 1, 11.5$ and 20 eV. Calculate the occupation numbers at $T = 1$ and 3000 K.
- The average thermal speed of monoatomic gas molecules is given by $\sqrt{8k_B T / (\pi m)}$. Determine the average speed, kinetic energy and the Maxwell-Boltzmann energy distribution function f_{MB}^o (at the average energy) for argon gas at $T = 300$ K.
- The surface temperature of the sun can be approximated to be about 5700 K. Determine f_{BE}^o for photons emitted from the sun at $\lambda = 100$ nm (UV), $\lambda = 600$ nm (visible) and $\lambda = 900$ nm (IR).

Solution

- (a) The Bose-Einstein distribution is given by:

$$f_{BE}^o = \frac{1}{\exp(E/k_B T) - 1}. \quad (2.45)$$

At $T = 300$ K, $k_B T = 0.026$ eV. Thus, $f_{BE}^o = 0.002$ for $E = 0.16$ eV and $f_{BE}^o = 0.0003$ for $E = 0.21$ eV. At $T = 3000$ K, $k_B T = 0.258$ eV. Thus, $f_{BE}^o = 1.164$ for $E = 0.16$ eV and $f_{BE}^o = 0.796$ for $E = 0.21$ eV. The occupation numbers increase with increasing temperature (see Fig. 2.8a). Also note that f_{BE}^o can be greater than 1 because the Pauli exclusion principle does not apply for bosons.

- (b) The Fermi-Dirac distribution is given by:

$$f_{FD}^o = \frac{1}{\exp((E - \mu)/k_B T) + 1}. \quad (2.46)$$

At $T = 1$ K, $k_B T = 8.63 \times 10^{-5}$ eV. Thus $f_{FD}^o = 1$ for $E = 1$ eV, $f_{FD}^o = 1$ for $E = 11.5$ eV and $f_{FD}^o = 0$ for $E = 20$ eV.

At $T = 3000$ K, $k_B T = 0.258$ eV. Thus $f_{FD}^o = 1$ for $E = 1$ eV, $f_{FD}^o = 0.68$ for $E = 11.5$ eV and $f_{FD}^o = 0$ for $E = 20$ eV. The Fermi-Dirac distribution changes from 1 to 0 in a small energy window (of the order of $k_B T$) around the electrochemical potential (see Fig. 2.8b).

- (c) From the given expression, the average thermal speed of argon atoms ($m = 40$ amu. = 6.64×10^{-26} kg) at $T = 300$ K is 398.8 m/s. Thus the average kinetic energy is:

$$E = \frac{1}{2} m_{Ar} v^2 = 0.033 \text{ eV}. \quad (2.47)$$

The Maxwell-Boltzmann distribution is given by $f_{MB}^o = \exp(-E/k_B T) = 0.28$.

- (d) For a given wavelength λ , the energy of a photon is $E = hc/\lambda$. Thus $E = 12.42$ eV for $\lambda = 100$ nm, $E = 2.07$ eV for $\lambda = 600$ nm and $E = 1.38$ eV for $\lambda = 900$ nm. Also $k_B T = 0.49$ eV at $T = 5700$ K. Thus $f_{BE}^o = 9.82 \times 10^{-12}$ for $\lambda = 100$ nm, $f_{BE}^o = 0.0148$ for $\lambda = 600$ nm and $f_{BE}^o = 0.063$ for $\lambda = 900$ nm.

Problem 2.2: Working with the Bose-Einstein distribution function

- (a) The energy levels of a quantum harmonic oscillator are given by:

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega,$$

where $n = 0, 1, 2, \dots$. Obtain an expression for the partition function Ξ (you will need to sum an infinite geometric series) defined by ($\mu = 0$ for phonons):

$$\Xi = \sum_n \exp(-\beta E_n).$$

- (b) Obtain an expression for the average energy $\langle E \rangle$ defined by:

$$\langle E \rangle = -\frac{\partial \ln \Xi}{\partial \beta}.$$

Show that the average energy of the mode with frequency ω can be written as $\hbar \omega (f_{BE}^o + \frac{1}{2})$, where f_{BE}^o denotes the Bose-Einstein distribution function.

Solution

(a) The partition function Ξ is given by:

$$\begin{aligned}\Xi &= \sum_n \exp(-\beta E_n) \\ &= \sum_{n=0}^{n=\infty} \exp(-\beta(n+1/2)\hbar\omega) \\ &= \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)}.\end{aligned}\tag{2.48}$$

(b) The average energy $\langle E \rangle$ is given by:

$$\begin{aligned}\langle E \rangle &= -\frac{\partial \ln \Xi}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta} \left(-\frac{\beta\hbar\omega}{2} - \ln(1 - \exp(-\beta\hbar\omega)) \right) \\ &= \frac{\hbar\omega}{2} + \frac{\hbar\omega \exp(-\beta\hbar\omega)}{1 - \exp(-\beta\hbar\omega)} \\ &= \hbar\omega \left(\frac{1}{\exp(\beta\hbar\omega) - 1} + \frac{1}{2} \right) \\ &= \hbar\omega \left(f_{BE}^o + \frac{1}{2} \right).\end{aligned}\tag{2.49}$$

Problem 2.3: Phonon DOS in graphene

The dispersion relation for graphene (excluding optical branches), which is a two-dimensional material, is shown in Fig. 2.9. Graphene has three acoustic branches commonly known as the LA, TA and ZA modes. The LA and TA modes can be approximated by a linear dispersion relation while the ZA mode, which represents out-of-plane vibrations, is more closely represented by a quadratic dispersion relation near the Brillouin zone center (see Appendix). Obtain an expression for the phonon density of states $D(\omega)$ at three different frequencies ω_1 , ω_2 , and ω_3 as indicated in Fig. 2.9.

Solution

The DOS for the LA mode is given by:

$$\begin{aligned}
 D_{LA}(\omega) &= \frac{1}{L^2} \frac{dN}{dK} \frac{dK}{d\omega} \\
 &= \frac{1}{v_{g1} L^2} \frac{L^2 K}{2\pi} \quad \left(N = \frac{\pi K^2}{(2\pi/L)^2}, \frac{d\omega}{dK} = v_{g1} \right) \\
 &= \frac{\omega}{2\pi v_{g1}^2}. \tag{2.50}
 \end{aligned}$$

Similarly, the DOS for the linear TA mode is given by:

$$D_{TA}(\omega) = \frac{\omega}{2\pi v_{g2}^2}. \tag{2.51}$$

The DOS for the quadratic ZA mode is given by:

$$\begin{aligned}
 D_{ZA}(\omega) &= \frac{1}{L^2} \frac{dN}{dK} \frac{dK}{d\omega} \\
 &= \frac{1}{2cK L^2} \frac{L^2 K}{2\pi} \quad \left(N = \frac{\pi K^2}{(2\pi/L)^2}, \frac{d\omega}{dK} = 2cK \right) \\
 &= \frac{1}{4\pi c}. \tag{2.52}
 \end{aligned}$$

All three modes are present at ω_1 . Thus,

$$\begin{aligned}
 D_{\text{tot}}(\omega_1) &= D_{LA}(\omega_1) + D_{TA}(\omega_1) + D_{ZA}(\omega_1) \\
 &= \frac{\omega_1}{2\pi v_{g1}^2} + \frac{\omega_1}{2\pi v_{g2}^2} + \frac{1}{4\pi c}. \tag{2.53}
 \end{aligned}$$

Only the LA and TA modes are active at ω_2 :

$$\begin{aligned}
 D_{\text{tot}}(\omega_2) &= D_{LA}(\omega_2) + D_{TA}(\omega_2) \\
 &= \frac{\omega_2}{2\pi v_{g1}^2} + \frac{\omega_2}{2\pi v_{g2}^2}. \tag{2.54}
 \end{aligned}$$

Only the LA mode is active at ω_3 :

$$\begin{aligned}
 D_{\text{tot}}(\omega_3) &= D_{LA}(\omega_3) \\
 &= \frac{\omega_3}{2\pi v_{g1}^2}. \tag{2.55}
 \end{aligned}$$

Problem 2.4: Phonon frequency at maximum intensity

Wien's displacement law for electromagnetic radiation relates the photon wavelength at which the energy distribution is maximum to the temperature. In this problem we derive a similar relation for phonons, except in frequency space. Assume a 3D material with a single phonon branch having a constant group velocity v_g (Debye approximation).

- Show that the dominant phonon frequency (frequency at which the spectral energy distribution is maximum) ω_{\max} as a function of temperature T is given by $\hbar\omega_{\max} = Ck_B T$ where C is a constant of proportionality. Neglect the zero-point energy in your analysis.
- Use the online Chapter 2 CDF tool¹ to observe the spectral phonon energy distribution as a function of temperature.
- Verify the relation you obtained for the maximum phonon frequency by tabulating the maximum points in the curve for a few different temperatures. Also obtain the constant C .

2.5.4.1 Solution

Under the Debye approximation, the density of states $D(\omega)$ is given by:

$$D(\omega) = \frac{\omega^2}{2\pi^2 v_g^3}. \quad (2.56)$$

The spectral energy density $u(\omega, T)$ is then given by:

$$\begin{aligned} u(\omega, T) &= \underbrace{\hbar\omega}_{\text{energy}} \underbrace{\frac{\omega^2}{2\pi^2 v_g^3}}_{\text{DOS}} \underbrace{\frac{1}{\exp(\hbar\omega/k_B T) - 1}}_{\text{occupation}} \\ &= \frac{\hbar}{2\pi^2 v_g^3} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1}. \end{aligned} \quad (2.57)$$

At a given temperature, spectral energy density is a maximum when $\frac{\partial u}{\partial \omega} = 0$. Thus,

$$3\omega^2(\exp(\hbar\omega/k_B T) - 1) - \omega^3 \exp(\hbar\omega/k_B T) \frac{\hbar}{k_B T} = 0. \quad (2.58)$$

¹See http://nanohub.org/groups/cdf_tools_thermal_energy_course/wiki

Defining $x^* = \hbar\omega/k_B T$, we arrive at the following implicit equation for x^* .

$$3(1 - \exp(-x^*)) = x^*. \quad (2.59)$$

- The above equation can be solved numerically (using WolframAlpha² for example) to obtain $x^* = 2.82$. Thus $\hbar\omega_{\max} = 2.82 k_B T$. The frequency at which the spectral energy distribution is a maximum increases linearly with temperature. In other words, the peak wavelength is inversely proportional to temperature.
- Figure 2.10 shows snapshots from the online Chapter 2 CDF tool where the spectral energy distribution is plotted for three different temperatures. The peak of the curves moves to the right for increasing temperature.
- Use the online tool to tabulate ω_{\max} for a few different temperatures and confirm the linear relationship between ω_{\max} and T .

²See [http://www.wolframalpha.com/input/?1=solve+3\(1-exp\(-x\)\)+%3D+x](http://www.wolframalpha.com/input/?1=solve+3(1-exp(-x))+%3D+x)

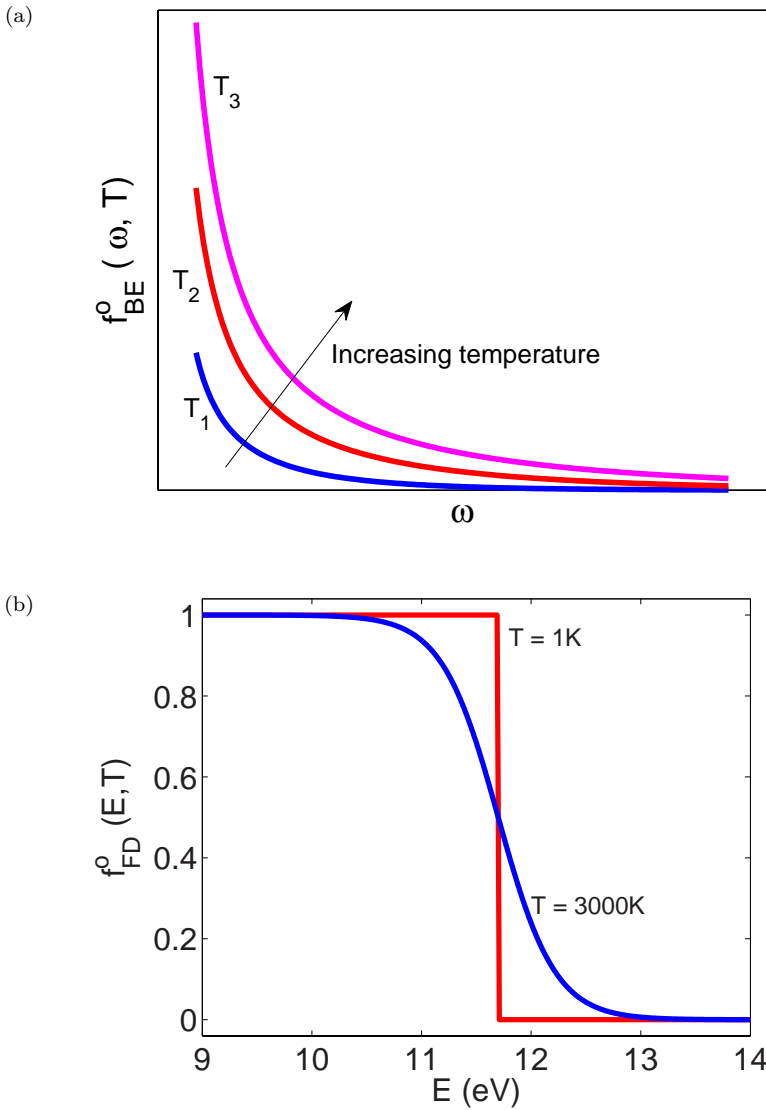


Fig. 2.8 (a) Bose-Einstein distribution function. (b) Fermi-Dirac distribution function.

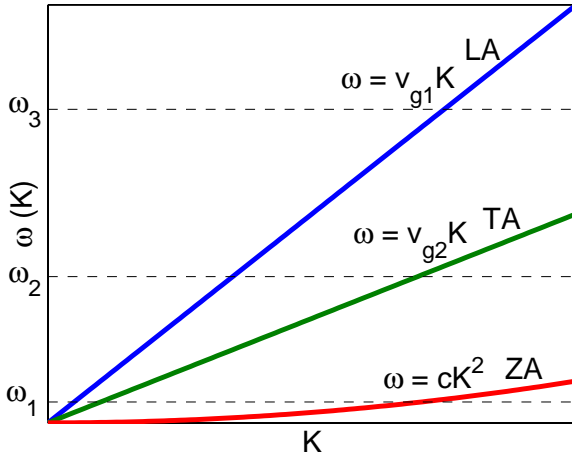


Fig. 2.9 Graphene dispersion relation.

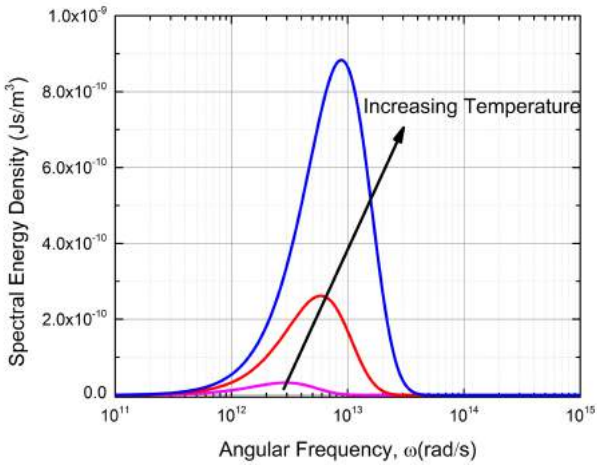


Fig. 2.10 Spectral energy distribution for three different temperatures.

Chapter 3

Basic Thermal Properties

3.1 Introduction

The energy density analysis discussed in Section 2.5.3 provided important insights about the inter-relationship between carrier energy and carrier statistics for photons. A similar analysis for phonons and electrons (and their respective energy levels and statistics) will provide the basis for the property known as internal energy. This property should be familiar to those who have studied classical or statistical thermodynamics, as should the related quantity called specific heat. For a given collection of carriers, knowledge of its internal energy and dependence on temperature (which derives from its statistics) allows explicit calculation of volumetric specific heat as:

$$c_v = \frac{\partial u(T)}{\partial T}, \quad (3.1)$$

where the normalizing quantity (i.e., the ‘amount’ of the ensemble by which $u(T)$ is normalized) can be either volume or mass. In Eq. (2.37) from the previous chapter, volume is the normalizing quantity for $u(T)$.

The specific heat quantifies the ability of a set of energy carriers to store thermal energy relative to the temperature rise required to store this energy. At the same time, these carriers can move within a material or control volume and while doing so transport thermal energy. Consequently, the average speed with which the carriers move combined with the amount of energy that they carry provides the foundation of the important thermal transport property known as thermal conductivity. We develop these concepts in the present chapter for the carriers of most interest here—phonons and electrons.

3.2 Specific Heat

The most general expression for the extensive (i.e., not specific, or intensive) internal energy U is:

$$U = \sum_{\mathbf{k}} \sum_p E_{i,p}(\mathbf{k}) f_i^o [E_{i,p}(\mathbf{k}), T], \quad (3.2)$$

where we have neglected zero-point energy. The foregoing equation is the summation form of the integral expression (Eq. (2.34)) used in the derivation of Planck's law for photons, in which the concept of density of states was employed somewhat obsequiously to convert sums to integrals. This duality between summative and integral forms of quantities will persist throughout subsequent analysis both because of various preferences that have evolved in different communities of theorists and because sometimes the summative form is more analytically convenient than the integral form and *vice versa*, depending on context. Here, we seek first to relieve some of the common confusion associated with the dual forms.

We first recognize that \mathbf{k} -space summation is often cumbersome. A general conversion from summation to integration of a function F in \mathbf{k} -space is:

$$\lim_{L \rightarrow \infty} \frac{1}{L^d} \sum_{\mathbf{k}} F(\mathbf{k}) = \int F(\mathbf{k}) \frac{d\mathbf{k}}{(2\pi)^d}, \quad (3.3)$$

where $F(\mathbf{k})$ is a generic function in a \mathbf{k} -space of dimension d (which matches the real-space dimension of a given problem). This conversion derives from the fact that each allowable states \mathbf{k} -space volume is $(2\pi/L)^d$. Applied to Eq. (3.2), the internal energy can be expressed in integral form as:

$$u = \frac{U}{L^d} = \sum_p \int \frac{E_{i,p}(\mathbf{k}) f_i^o [E_{i,p}(\mathbf{k}), T]}{(2\pi)^d} d\mathbf{k}. \quad (3.4)$$

And then using Eq. (3.1), specific heat can be expressed as:

$$c_v = \frac{\partial u}{\partial T} = \sum_p \int \frac{E_{i,p}(\mathbf{k})}{(2\pi)^d} \frac{\partial f_i^o}{\partial T} d\mathbf{k}, \quad (3.5)$$

where

$$\frac{\partial f_i^o}{\partial T} = (f_i^o)^2 e^{(E_i - \mu)/k_B T} \left(\frac{E_i - \mu}{k_B T^2} \right). \quad (3.6)$$

For many (most, really) problems, the d -dimensional \mathbf{k} -space integral remains cumbersome, and therefore, the concept of density of states is used to convert the multi-dimensional integral to a single dimension (either energy or frequency). We apply this process to different carrier types in the following subsections.

3.2.1 Acoustic Phonon Specific Heat

The \mathbf{k} -space integral in Eq. (3.5) explicitly calls for knowledge of the energy-wavevector relation ($E_{i,p}(\mathbf{k})$). For phonons, this relation is typically expressed in terms of frequency and wavevector through the dispersion relation. In Chapter 1, we derived the dispersion relation for an acoustic phonon branch in the idealized one-dimensional atomic chain (Eq. (1.22)). In higher dimensions, an atom can move in more than one direction, as shown in Fig. 3.1. These extra dimensions create additional phonon ‘branches’ whose dispersion is generally similar to the longitudinal branch (see Fig. 1.13), except that the effective spring constant g differs, resulting in a different maximum phonon frequency at the edge of the Brillouin zone. Further, three-dimensional crystals with appropriate lattice symmetry relative to the propagation direction of interest can exhibit *degeneracy* such that the two transverse branches have identical dispersion relations.

The curvature of the acoustic phonon dispersion relation and associated factors that cause real materials to deviate from the ideal sine function of Eq. (1.22) has motivated the use of a simplified dispersion model. The most prominent among these is the Debye approximation (Debye, 1912), which approximates the sine function as a line through the ω - K origin:

$$\omega(K) \approx v_{g,ave} K. \quad (3.7)$$

This approximation, however, cannot be applied blindly because doing so would fail to account for the finite number of allowable phonon states as discussed in Section 2.3. The Debye frequency represents the maximum allowable frequency such that the number of states (N) in a given branch matches the number of allowed wavevectors.

To determine the number of independent wavevectors in a Brillouin zone, the following statement from Ziman (1972, p. 25) is crucial:

[T]here are exactly as many allowed wave-vectors in a Brillouin zone as there are unit cells in a block of crystal.

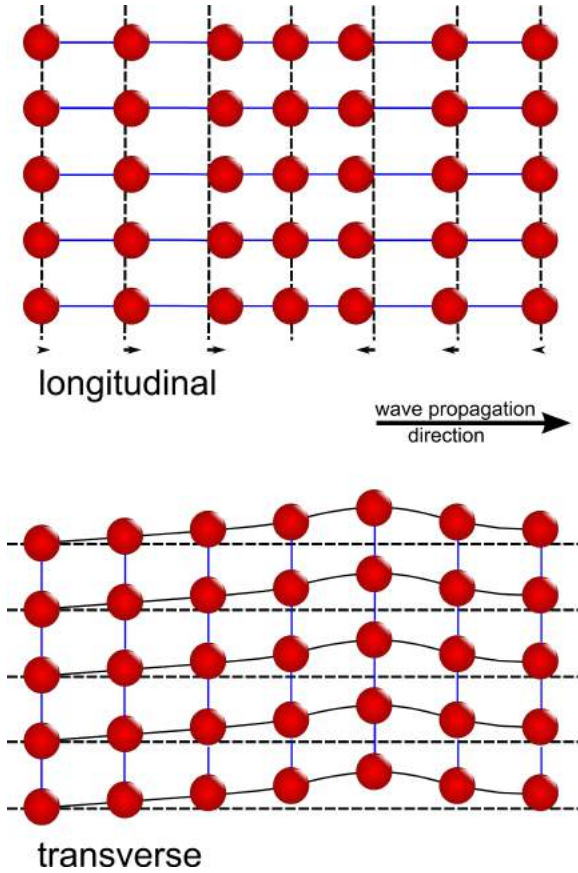


Fig. 3.1 Longitudinal and transverse phonon branches. Atoms vibrate along the wave propagation direction in the longitudinal mode. In the transverse mode, atoms vibrate perpendicular to the wave propagation direction.

The number of allowed states in each dimensionality as a function of the magnitude of the wavevector K was given previously (Eq. (2.13)–(2.15)). Setting the number of states to equal the number of unit cells in the crystal, the Debye wavevectors are:

$$K_{D,1D} = \pi\eta_a, \quad (3.8)$$

$$K_{D,2D} = (4\pi\eta_a)^{1/2}, \quad (3.9)$$

$$K_{D,3D} = (6\pi^2\eta_a)^{1/3}, \quad (3.10)$$

where η_a is the number of unit cells per unit ‘volume’ of the given dimensionality (i.e., length for 1D, area for 2D, and true volume for 3D). Substituting the Debye dispersion relation gives the Debye frequency:

$$\omega_{D,1D} = v_{g,\text{ave}}\pi\eta_a, \quad (3.11)$$

$$\omega_{D,2D} = v_{g,\text{ave}}(4\pi\eta_a)^{1/2}, \quad (3.12)$$

$$\omega_{D,3D} = v_{g,\text{ave}}(6\pi^2\eta_a)^{1/3}. \quad (3.13)$$

A common tabulated representation of the Debye frequency for bulk (3D) materials is the Debye temperature:

$$\theta_D = \frac{\hbar\omega_{D,3D}}{k_B} = \frac{\hbar v_{g,\text{ave}}(6\pi^2\eta_a)^{1/3}}{k_B}. \quad (3.14)$$

One subtle point of clarification is important here, because the foregoing Debye quantities are often expressed in terms of the atomic density instead of the unit cell density. The former is substantially easier to calculate because it can be derived easily from knowledge of a crystal’s mass density and constituent atomic mass(es). Of course, the two are equivalent for crystals with one atom per unit cell (i.e., with no basis atoms). In contrast, as described in Section 1.6 the presence of basis atoms produces entirely new phonon branches (cf., the optical branch in the 1D diatomic chain example). If our intention is to approximate *both* acoustic and optical branches with the linear-dispersion Debye approximation, then we would replace the unit cell density η_a in the foregoing equations with $n \times \eta_a$, where n represents the number of atoms per unit cell.

This approximation may be reasonable with the understanding that the Debye wavevector will extend substantially beyond the edge of the Brillouin zone boundary, as shown in Fig. 3.2, to include the extension of the optical branch into the ‘second’ Brillouin zone. However, as we will see in the subsequent section, an entirely different model for specific heat is often most appropriate for optical phonons, in which case the unit cell density alone should be used in calculating Debye metrics. For readers seeking further details, Ashcroft and Mermin (1976, pp. 462–463) clarify this issue particularly well.

The general results for phonon density of states in frequency space (Eqs. (2.19)–(2.21)) become, under the Debye approximation:

$$D_{D,1D}(\omega) = \frac{1}{v_{g,\text{ave}}\pi}, \quad (3.15)$$

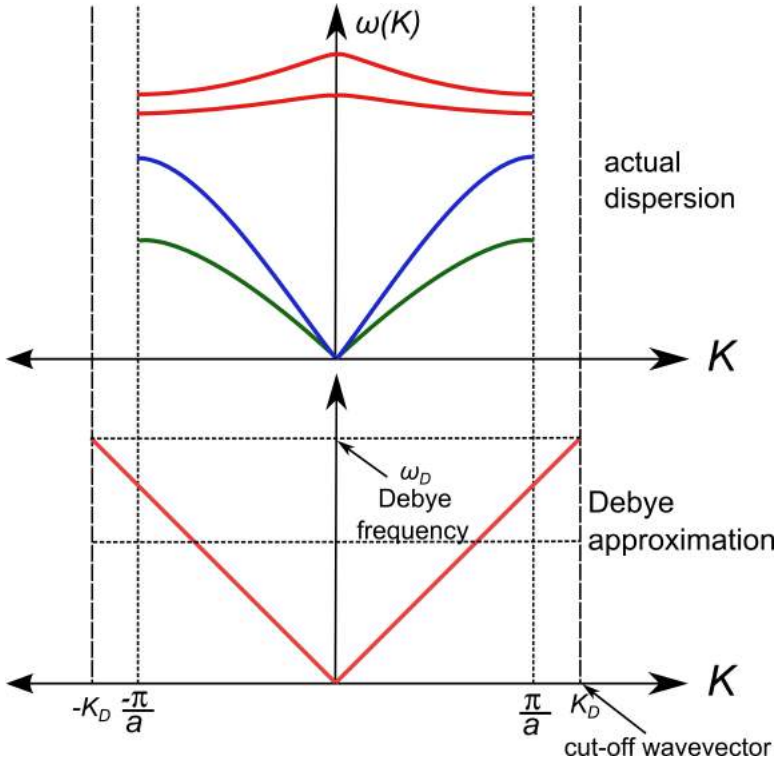


Fig. 3.2 Debye's linear approximation to the phonon dispersion. The Debye cutoff wavevector, K_D , is chosen such that it contains allowed wavevectors equalling the number of ions in the crystal. Debye quantities such as the Debye cutoff wavevector, K_D , and the associated Debye cutoff frequency, ω_D , are depicted.

$$D_{D,2D}(\omega) = \frac{\omega}{2\pi v_{g,ave}^2}, \quad (3.16)$$

$$D_{D,3D}(\omega) = \frac{\omega^2}{2\pi^2 v_{g,ave}^3}, \quad (3.17)$$

where these results are applicable for $\omega < \omega_D$. For most of the foregoing Debye quantities, the average group velocity plays an important role. Often, the long-wavelength velocity $\left[\frac{\partial\omega}{\partial K}\right]_{K=0}$ is used. This approximation is most suitable for low-temperature conditions in which the phonon population is dominated by low frequencies. However, even in such cases, the single value of $v_{g,ave}$ implies \mathbf{k} -space symmetry in the applicable directions. Further, in some prior work, a single group velocity is defined as an amalgam of

the transverse and longitudinal branches. Instead of enumerating all of the possible representations for group velocity here, the reader is cautioned to scrutinize the definition of group velocity for any work that employs the Debye approximation.

Given the foregoing assumptions (and particularly re-emphasizing the \mathbf{k} -space symmetry), we can calculate the canonical Debye specific heat for acoustic phonons in 3D (bulk) materials from the general expression (Eq. (3.5)):

$$\begin{aligned}
 c_{v,D,3D} &= \sum_p \int \frac{E_{i,p}(K)}{(2\pi)^d} \frac{\partial f_i^o}{\partial T} d\mathbf{k} \stackrel{3D}{=} \sum_p \int \frac{\hbar v_{g,\text{ave}} K}{(2\pi)^3} \frac{\partial f_i^o}{\partial T} d\mathbf{k} \\
 &= \sum_p \int_0^{K_D} \frac{\hbar v_{g,\text{ave}} K}{(2\pi)^3} \frac{\partial f_{BE}^o}{\partial T} 4\pi K^2 dK \\
 &= \sum_p \int_0^{\omega_D} \hbar \omega \frac{\partial f_{BE}^o}{\partial T} D_{D,3D}(\omega) d\omega \\
 &= \sum_p \int_0^{\omega_D} \frac{\hbar \omega^3}{2\pi^2 v_{g,\text{ave}}^3} \frac{\partial f_{BE}^o}{\partial T} d\omega \\
 &= 9\eta_a k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}, \tag{3.18}
 \end{aligned}$$

where $x \equiv \frac{\hbar \omega}{k_B T}$, and the last equality derives from (a) the definition of the temperature derivative of the distribution function (Eq. (3.6)), (b) the definition of group velocity in terms of unit cell density and Debye temperature (Eq. (3.14)) and (c) the assumption that the three acoustic phonon branches can be combined through a single Debye group velocity (thus eliminating the branch summation by multiplying the integral by a factor of 3). This latter approximation should be taken with caution; again, the definition of the group velocity must be appropriate to the assumptions invoked.

The final Debye specific heat expression in Eq. (3.18) is a much-celebrated result, despite the fact that the integral is not generally reducible to an analytic expression. Often, the extreme temperature limits can be used to determine limiting expressions for low and high temperatures *relative to the Debye temperature*. For the low-temperature limit:

$$c_{v,D,3D\text{low}} \approx 234\eta_a k_B \left(\frac{T}{\theta_D} \right)^3 \quad (T \ll \theta_D). \tag{3.19}$$

This result indicates that, at low temperatures, the acoustic phonon specific heat increases as T^3 for a 3D material, and we will find below that the factor of 3 derives from the dimensionality of the material (e.g., the temperature dependence for 2D materials is T^2). Conversely, for very high temperatures (relative to θ_D), the result becomes independent of temperature:

$$c_{v,D,3D\text{high}} \approx 3\eta_a k_B \quad (T \gg \theta_D). \quad (3.20)$$

The temperature-independence of the latter result is caused by the capping of energy states imposed by the maximum phonon energy associated with θ_D . In effect, any increases in temperature must be accommodated by increasing the phonon populations of states that are already well occupied at or below θ_D , as opposed to the situation at very low temperatures for which empty states can be filled when temperature increases. The high-temperature result is called the “Law of Dulong and Petit” (Ashcroft and Mermin, 1976).

3.2.2 Optical Phonon Specific Heat

Clearly, the Debye specific heat model is well suited for phonon branches that exhibit a linear-like behavior through the origin of the dispersion curve (e.g., acoustic branches with shapes like quarter sine waves). However, this model is dubious for optical phonons, which exhibit relatively flat dispersion curves that intercept the frequency (energy) axis at non-zero values (see Fig. 1.18). Einstein (1906) proposed a general model for phonon specific heat that assumes such flat dispersion behavior by assigning a single phonon frequency to each branch. While the intention was to apply this model for all branches, later developments, such as the Debye model (Debye, 1912) described above, revealed clearly that this model is best applied to optical phonon branches only.

The derivation of the Einstein model for specific heat generally follows that of Section 3.2.1. It differs in the assumption that all phonons in the branch of interest oscillate at a single frequency ω_E , leading to the definition of the Einstein temperature θ_E :

$$\theta_E = \frac{\hbar\omega_E}{k_B}. \quad (3.21)$$

For convenience, we retain the summation form throughout the derivation. Using this dispersion relation (i.e., $\omega = \text{constant} = \omega_E$) in the general integral expression for internal energy U (Eq. (3.2)) results in:

$$U = \sum_{\mathbf{k}} \sum_p \hbar\omega_E f_{BE}^o(\omega_E, T). \quad (3.22)$$

Because the frequency does not depend on wavevector in the Einstein approximation, the entire argument can be brought out of the summation. Then after differentiating with respect to temperature and dividing by volume (i.e., L^d), the Einstein specific heat becomes:

$$\begin{aligned}
 c_{v,E} &= \frac{\hbar\omega_E}{L^d} \frac{\partial f_{BE}^o(\omega_E, T)}{\partial T} \sum_{\mathbf{k}} \sum_p 1 \\
 &= \sum_p \eta_a \hbar\omega_E (f_{BE}^o)^2 e^{(\hbar\omega_E)/k_B T} \left(\frac{\hbar\omega_E}{k_B T^2} \right) \\
 &= \sum_p \eta_a k_B \frac{\chi_E^2 e^{\chi_E}}{(e^{\chi_E} - 1)^2}, \tag{3.23}
 \end{aligned}$$

where η_a is the number of allowable states (i.e., unit cells) per unit real ‘volume’, and $\chi_E = (\hbar\omega_E)/(k_B T) = \theta_E/T$.

For many problems, the Einstein temperature will be much higher than the real temperature, such that the optical phonon states are sparsely occupied, or $\chi_E \gg 1$. In this limit, Eq. (3.23) gives $c_{v,E} \approx 0$. In such cases, the Debye analysis for only the acoustic branches suffices to characterize the total phonon specific heat. Conversely, for very high temperatures ($\chi_E \ll 1$), we find from $\lim_{\chi_E \rightarrow 0} \frac{\chi_E^2 e^{\chi_E}}{(e^{\chi_E} - 1)^2} = 1$ that:

$$c_{v,E} = \sum_p \eta_a k_B \quad (T \gg \theta_E). \tag{3.24}$$

Thus, in spite of the differences with the Debye model, the Einstein result reduces to the Debye model’s high-temperature limit (i.e., the Law of Dulong and Petit, see Eq. (3.20)), assuming three phonon branches (i.e., $p = 3$).

A comparison of the Debye and Einstein models is shown in Fig. 3.3, in which both the low-temperature differences and high-temperature convergence are clearly apparent. However, we emphasize that the high-temperature limit for the Einstein model typically requires unusually high temperatures because optical phonon frequencies of most materials correspond to much higher energies than the equivalent thermal energy, i.e., $\omega_E \gg k_B T/\hbar$. However, each of these models can be accurate for all temperatures in the correct context. The important point to remember is that the Debye model is appropriate for acoustic phonons, while the Einstein model (particularly Eq. (3.23)) should be used for optical phonons.

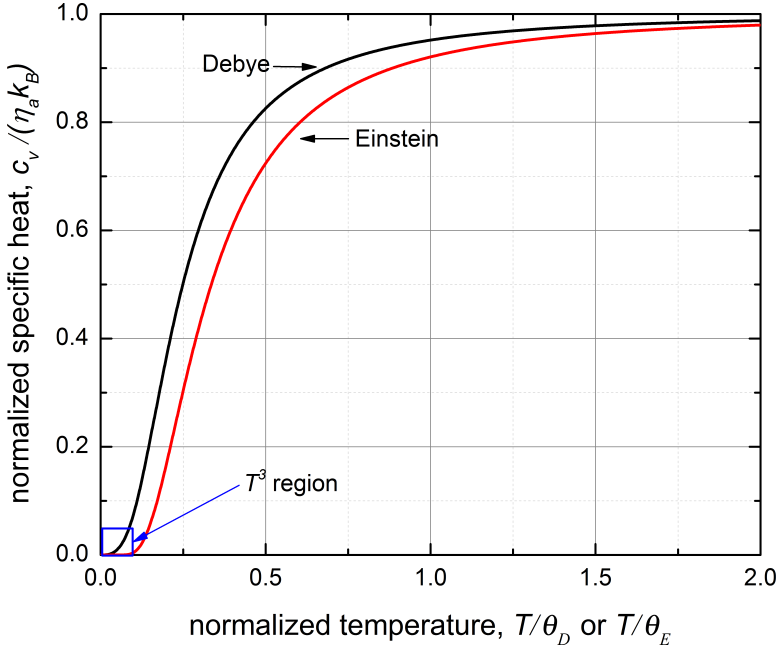


Fig. 3.3 Comparison of specific heat dependence on temperature, as predicted by the Debye and the Einstein model. The specific heats, derived from both the models, converge at low and high temperatures.

3.2.3 Electron Specific Heat

The analysis of specific heat for electrons begins with a subtle modification of the internal energy expression of Eq. (3.2):

$$U_e = 2 \sum_{\mathbf{k}} \sum_p E_{i,p}(\mathbf{k}) f_{FD}^o [E_{i,p}(\mathbf{k}), T], \quad (3.25)$$

where the pre-factor ‘2’ accounts for spin degeneracy, and the summation over p relates to electronic bands instead of phonon branches. Once again, mathematical convenience dictates the replacement of the \mathbf{k} -space summation with an integral by invoking the electron density of states (Eq. (2.22)) and expressing the energy on a volumetric basis:

$$u_e = \int_0^\infty E f_{FD}^o(E, T) D(E) dE, \quad (3.26)$$

where the factor ‘2’ has now been absorbed into the density of states (cf., Eq. (2.22)).

Another subtlety of the analysis for electrons derives from the Pauli exclusion principle, which dictates that some energy states must be occupied even at absolute zero temperature. The highest such occupied energy is the Fermi energy, E_F , which can be defined in terms of the integral form of electron density η_e :

$$\eta_e = \int_0^{\infty} f_{FD}^o(E, T) D(E) dE = \int_0^{E_F} D(E) dE, \quad (3.27)$$

where the latter equality derives from the fact that the Fermi-Dirac function is unity below the Fermi energy and zero above it at zero absolute temperature. In order to keep the derivation more general, we will refrain from deriving an explicit expression for E_F , because doing so would require us to assume a specific form of $D(E)$.

To assist in deriving the electron specific heat, an alternative specific internal energy u^* can be defined to simplify the subsequent integral analysis:

$$u^* \equiv u_e - E_F \eta_e \quad (3.28)$$

$$\begin{aligned} &= \int_0^{\infty} E f_{FD}^o(E, T) D(E) dE - \int_0^{\infty} E_F f_{FD}^o(E, T) D(E) dE \\ &= \int_0^{\infty} (E - E_F) f_{FD}^o(E, T) D(E) dE. \end{aligned} \quad (3.29)$$

This contrivance is useful because the subtracted term in Eq. (3.28) is a constant, resulting in a null temperature derivative. Using Eq. (3.27) this constant term can be expressed as an integral involving the distribution function and density of states. The final equality (Eq. (3.29)) contains the difference $(E - E_F)$, which also appears in the distribution function $f_{FD}^o(E, T)$ through the common and broadly valid assumption of equality between the electrochemical potential μ (which exhibits a significant temperature dependence only at extremely high temperatures for which the thermal energy approaches the Fermi energy; see Eq. (2.11)) and the Fermi energy E_F (which is by definition a constant) (Kittel, 2007).

The electron specific heat can now be expressed by the temperature derivative of u^* :

$$c_{v,e} = \frac{\partial u}{\partial T} = \frac{\partial u^*}{\partial T} = \int_0^{\infty} (E - E_F) \frac{\partial f_{FD}^o}{\partial T} D(E) dE. \quad (3.30)$$

The temperature derivative of the Fermi-Dirac distribution function is non-negligible only in a small region about the Fermi energy. Therefore, the

density of states term can be replaced with an integral pre-factor of $D(E_F)$, resulting in:

$$c_{v,e} \approx D(E_F) \int_0^\infty (E - E_F) \frac{\partial f_{FD}^o}{\partial T} dE = k_B^2 T D(E_F) \int_{-\frac{E_F}{k_B T}}^\infty \frac{x^2 e^x}{(e^x + 1)^2} dx, \quad (3.31)$$

where $x = (E - E_F)/(k_B T)$. Finally, recognizing that typically $E_F \gg k_B T$, the lower bound of the integral can be approximated as $-\infty$, enabling analytical evaluation:

$$c_{v,e} \approx \frac{\pi^2}{3} k_B^2 T D(E_F). \quad (3.32)$$

Substituting the density of states for three-dimensional free-electron metals (see Eq. (2.22)), the specific heat becomes:

$$\begin{aligned} c_{v,e} &\approx \frac{m k_B^2 \sqrt{2m E_F}}{3 \hbar^3} T \\ &= \frac{\pi^2 k_B^2 \eta_e}{2 E_F} T, \end{aligned} \quad (3.33)$$

where the latter equality derives from the definition of the Fermi energy for a parabolic band (Eq. (1.40)). A distinguishing feature of the final result is the linear temperature dependence, which can be used to assess the relative contributions of electrons ($\sim T^1$) and phonons ($\sim T^3$) in metals at low temperatures (i.e., well below the Debye and Fermi temperatures).

3.2.4 Specific Heat for Low-Dimensional Structures

The specific heat integral in \mathbf{k} -space (Eq. (3.5)) can be converted to frequency space generally (i.e., without invoking a dispersion assumption such as the Debye approximation) for phonons through the use of the density of states:

$$\begin{aligned} c_v &= \frac{\partial u}{\partial T} = \sum_p \int \frac{E_{i,p}(\mathbf{k})}{(2\pi)^d} \frac{\partial f_{BE}^o}{\partial T} d\mathbf{k} \\ &= \sum_p \int \hbar \omega D_{dD}(\omega) \frac{\partial f_{BE}^o}{\partial T} d\omega, \end{aligned} \quad (3.34)$$

where d represents the dimensionality of the problem (i.e., “ $dD = 1D$ ” for $d = 1$).

Then, applying the Debye model's density of states, a general expression for the Debye specific heat of acoustic phonons becomes:

$$c_{v,D} = d \times \eta_a k_B \sum_p \left(\frac{T}{\theta_{D,p}} \right)^d \int_0^{\theta_{D,p}/T} \frac{x^{d+1} e^x dx}{(e^x - 1)^2}. \quad (3.35)$$

This result reinforces the memorable result that the specific heat for low temperatures is proportional to temperature raised to the power of the dimensionality for temperatures well below the Debye temperature, as shown in Fig. 3.4. The results indicate that the power law relationship $c_v \sim T^d$ holds well up to $T \approx 0.1\theta_D$. Consequently, the temperature dependence of specific heat (a property that is relatively easy to measure) provides a means of assessing the effective dimensionality of the medium under study.

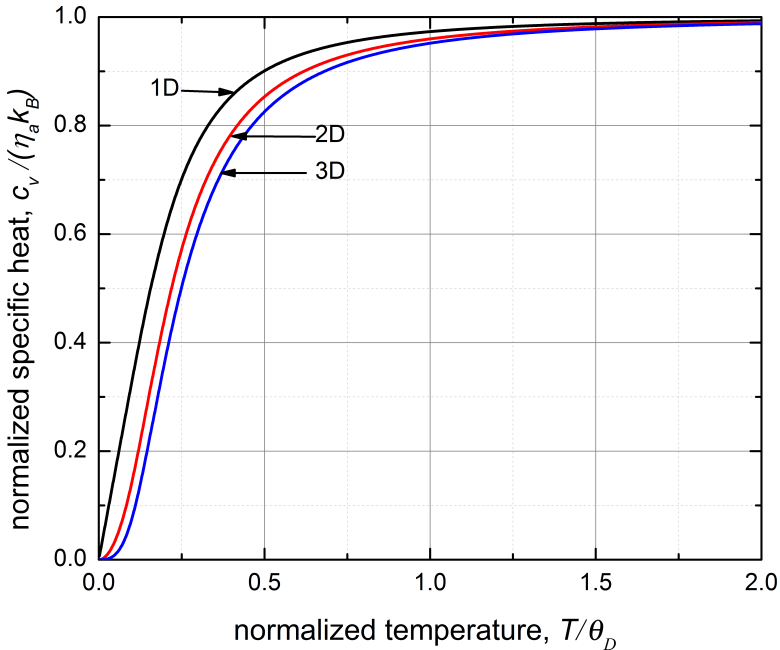


Fig. 3.4 Variation of specific heat with temperature for low-dimensional structures, as predicted by the Debye model. Notice the T^d dependence of specific heat at low temperatures, where d is the dimensionality of the medium.

3.3 Thermal Conductivity from Kinetic Theory

The foregoing expressions for specific heat serve important roles in determining a second prominent thermal property—thermal conductivity. Various approaches are available to derive the latter quantity, and here we offer the most common and intuitive derivation. The subsequent chapters consider other derivation approaches that are generally more rigorous and versatile.

Kinetic theory covers broadly the behavior of particles in an ensemble and can be used to derive many thermophysical properties (Vincenti and Kruger, 1967). The basic theory treats particles as independent entities that can collide, or scatter, with each other or with other objects such as defects and boundaries. As such, the approach is somewhat agnostic to the type of particle, as long as its velocity and ability to carry a property (such as thermal energy) are known.

Figure 3.5 shows this scenario schematically. An energy-carrying particle (e.g., electron or phonon in the present context) sits at the vertical position $z + \Lambda_z$ within a field of particles with average intensive internal energy u that depends on position z . The particles move in three dimensions randomly and experience a collision one time for every distance Λ traveled, on average. The distance Λ is termed the *mean free path*, or scattering length. In the case of the particle highlighted in Fig. 3.5, the vertical (z) component of its distance traveled before its next collision is Λ_z , as its direction makes a polar angle θ with the z axis.

The heat flux rate (per unit area) can be expressed in terms of the z -components of the particle velocity and mean free path:

$$q_z'' = \frac{1}{2} v_z [u(z - \Lambda_z) - u(z + \Lambda_z)], \quad (3.36)$$

where the $\frac{1}{2}$ term derives from the fact that only half the particles move up from $z - \Lambda_z$ or down from $z + \Lambda_z$, and v_z is the z -component of the particle's velocity. The energy difference in Eq. (3.36) can be expanded as a Taylor series:

$$u(z + \Lambda_z) = u(z - \Lambda_z) + \left. \frac{\partial u}{\partial z} \right|_z (2\Lambda_z) + \vartheta (\Lambda_z^2). \quad (3.37)$$

Using $\Lambda_z = \Lambda \cos \theta$ and $v_z = v \cos \theta$, the heat flux becomes:

$$q_z'' \approx -v_z \Lambda_z \frac{\partial u}{\partial z} = -(\cos^2 \theta) v \Lambda \frac{\partial u}{\partial z}. \quad (3.38)$$

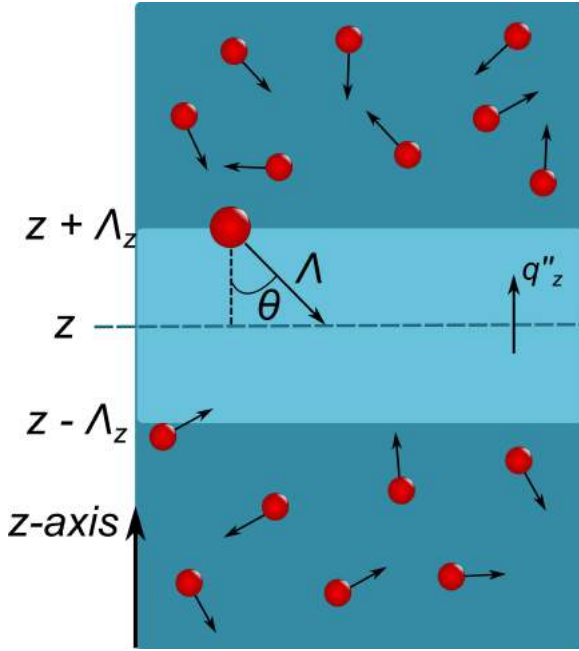


Fig. 3.5 A schematic depicting the kinetic theory of thermal conductivity. An atom at $z + \Lambda_z$ travels a distance equivalent to its mean free path, Λ (Λ_z in the z -direction), before experiencing a collision. This atomic motion results in a heat flux, along the z -direction, which is a function of the particle velocity and the particle mean free path.

The foregoing steps assumed a specific direction of motion, but the actual directions within the ensemble are randomized. Therefore, an average heat flux must be defined by integrating over all possible directions through the three-dimensional solid angle $d\Omega = \sin\theta d\theta d\psi$, where ψ is the azimuthal angle:

$$\begin{aligned} \langle q''_z \rangle &= -v\Lambda \frac{\partial u}{\partial z} \left[\frac{1}{2\pi} \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta d\theta d\psi \right] \\ &= -\frac{1}{3}v\Lambda \frac{\partial u}{\partial z}. \end{aligned} \quad (3.39)$$

Assuming that the scattering processes are frequent enough to establish local thermodynamic equilibrium (which is *not* the case for predominantly ballistic transport), the chain rule can be applied to convert the energy

gradient to a temperature gradient:

$$\frac{\partial u}{\partial z} = \frac{\partial u}{\partial T} \frac{\partial T}{\partial z}. \quad (3.40)$$

Importantly, the first term on the right side is the previously developed specific heat (Eq. 3.1), and the average heat flux can be expressed as:

$$\langle q_z'' \rangle = -\frac{1}{3}v\Lambda \frac{\partial u}{\partial T} \frac{\partial T}{\partial z} = -\underbrace{\frac{1}{3}c_v v\Lambda}_{\kappa} \frac{\partial T}{\partial z}, \quad (3.41)$$

where the final form matches that of the classical Fourier's law, $q_z'' = -\kappa(\partial T/\partial z)$. The foregoing derivation therefore relates a material's thermal conductivity κ to the specific heat, velocity, and mean free path of thermal energy carriers:

$$\kappa = \frac{1}{3}c_v v\Lambda. \quad (3.42)$$

Some important issues and caveats concerning this expression follow:

- Thermal conductivity inherits the temperature dependence of the specific heat, velocity, and mean free path. We have considered elements of the first two, the last remains for the subsequent two chapters.
- The derivation above was somewhat casual regarding the variability of carrier velocity, which depends on the distribution function and occupation statistics. We will consider these issues further in the next chapter.
- For very small materials, any or all of the three components can be influenced substantially by the size of the domain under study, its lattice and defect structure, and its temperature.

Example Problems

Problem 3.1: Graphene ZA branch specific heat

In this chapter, we obtained integral expressions for the specific heat of branches that can be approximated with a linear dispersion (Debye model) and constant dispersion (Einstein model). The ZA branch of graphene, which represents out-of-plane vibrations (see Appendix), is however closely approximated near the Brillouin zone center by a quadratic dispersion relation of the form $\omega = CK^2$ where C is a constant.

- Determine the maximum cutoff wavevector K_Q and the corresponding cutoff frequency ω_Q in terms of the unit cell density η_a .
- Obtain an integral expression for the specific heat of the ZA branch as a function of temperature.

The low temperature specific heat of graphene shows a linear dependence on temperature (see Fig. 3.6) which then becomes quadratic for temperatures greater than 100 K. Can you explain this behavior based on your knowledge of the dispersion relation of graphene (see Chapter 2 Examples for a plot) and the expression you have just obtained in this problem?

Solution

- The cutoff wavevector K_Q is found by equating the number of states in \mathbf{k} -space within a circle of radius K_Q to the total number of unit cells N .

$$\frac{\pi K_Q^2}{\left(\frac{2\pi}{L}\right)^2} = N, \quad K_Q = (4\pi\eta_a)^{1/2}, \quad (3.43)$$

where η_a is the number of unit cells per unit area. The cutoff frequency ω_Q is then obtained from the dispersion relation:

$$\omega_Q = 4C\pi\eta_a. \quad (3.44)$$

- The specific heat $c_{v,ZA}$ is given by:

$$c_{v,ZA} = \int_0^{\omega_Q} \hbar\omega \frac{\partial f_{BE}^o}{\partial T} D_{Q,2D}(\omega) d\omega, \quad (3.45)$$

where $D_{Q,2D}(\omega)$ is the two-dimensional density of states under the quadratic dispersion model:

$$\begin{aligned}
 D_{Q,2D}(\omega) &= \frac{1}{L^2} \frac{dN}{d\omega} \\
 &= \frac{1}{L^2} \frac{dN}{dK} \frac{dK}{d\omega} \\
 &= \frac{1}{L^2} \frac{d}{dK} \left(\frac{\pi K^2}{(2\pi/L)^2} \right) \frac{1}{2CK} \\
 &= \frac{1}{4\pi C}.
 \end{aligned} \tag{3.46}$$

Thus the DOS of the ZA branch is a constant. Substituting the above expression into the integral in Eq. (3.45), and using the derivative of the Bose-Einstein distribution function, we obtain:

$$\begin{aligned}
 c_{v,ZA} &= \frac{1}{4\pi C} \int_0^{\omega_Q} \hbar\omega \frac{\exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T) - 1)^2} \frac{\hbar\omega}{k_B T^2} d\omega \\
 &= \eta_\alpha k_B \left(\frac{T}{\theta_Q} \right) \int_0^{\theta_Q/T} \frac{x^2 e^x}{(e^x - 1)^2} dx,
 \end{aligned} \tag{3.47}$$

where $x = \hbar\omega/k_B T$ and $\theta_Q = \hbar\omega_Q/k_B$ (analogous to the Debye temperature θ_D). For temperatures much less than θ_Q , the upper limit of the integral in Eq. (3.47) can be taken to be ∞ , and the specific heat is proportional to T . This result explains the linear dependence of the specific heat of graphene at low temperatures. At higher temperatures, the ZA branch becomes fully populated and the linear LA and TA modes contribute to specific heat. This explains the quadratic dependence at higher temperatures (see Section 3.2.4).

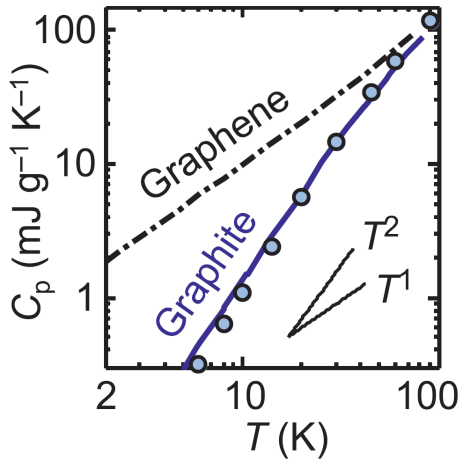


Fig. 3.6 Temperature dependence of the specific heat of graphene and graphite. Figure originally published by Pop *et al.* (2012). Used with permission.

Problem 3.2: Specific heat of metals

Figure 3.7 shows experimental measurements of the heat capacity of potassium at low temperatures. The following temperature dependence is observed:

$$c_v/T = 2.08 + 2.57T^2,$$

where c_v/T has units of mJ/mol K² and T is in K.

- Provide analytical expressions for the y-intercept and slope of the graph. Hint: Neglect any optical phonon contribution to specific heat as the experimental data are provided for low temperatures.
- Assuming that the conduction electron density in potassium is $1.34 \times 10^{22} \text{ cm}^{-3}$, determine the Fermi energy of potassium. Note that the experimental data are expressed per mole of potassium, while the heat capacity expressions derived in this chapter are per unit volume. Assume the density and atomic mass of potassium are 0.862 g/cc and 39 amu respectively.
- Potassium has a body-centered cubic (BCC) structure (1 atom per primitive unit cell) with an atomic density of 1.33×10^{22}

atoms/cm³. Determine the Debye temperature of potassium assuming that the three acoustic branches are replaced by a single branch of uniform group velocity.

Solution

- (a) Specific heat c_v can be expressed as a sum of electron and phonon contributions:

$$\begin{aligned} c_v &= c_{v,e} + c_{v,p} \\ &= \frac{\pi^2 k_B^2 \eta_e}{2E_F} T + \frac{234 \eta_a k_B}{\theta_D^3} T^3. \end{aligned} \quad (3.48)$$

Hence,

$$\frac{c_v}{T} = \underbrace{\frac{\pi^2 k_B^2 \eta_e}{2E_F}}_{y\text{-intercept}} + \underbrace{\frac{234 \eta_a k_B}{\theta_D^3}}_{\text{slope}} T^2. \quad (3.49)$$

- (b) Using the experimental data and the result from part (a),

$$2.08 \text{ mJ/mol K}^2 = 4.59 \times 10^{-5} \text{ J/cc K}^2 = \frac{\pi^2 k_B^2 \eta_e}{2E_F}. \quad (3.50)$$

Substituting $k_B = 1.3806 \times 10^{-23} \text{ J/K}$, $\eta_e = 1.34 \times 10^{22} \text{ cm}^{-3}$, we obtain $E_F = 2.74 \times 10^{-19} \text{ J} = 1.71 \text{ eV}$.

- (c) From the slope of the given graph and the result in part (a),

$$2.57 \text{ mJ/mol K}^4 = 5.68 \times 10^{-5} \text{ J/cc K}^4 = \frac{234 \eta_a k_B}{\theta_D^3}. \quad (3.51)$$

Substituting $\eta_a = 1.33 \times 10^{22} \text{ atoms/cm}^3$, we obtain $\theta_D = 91.1 \text{ K}$.

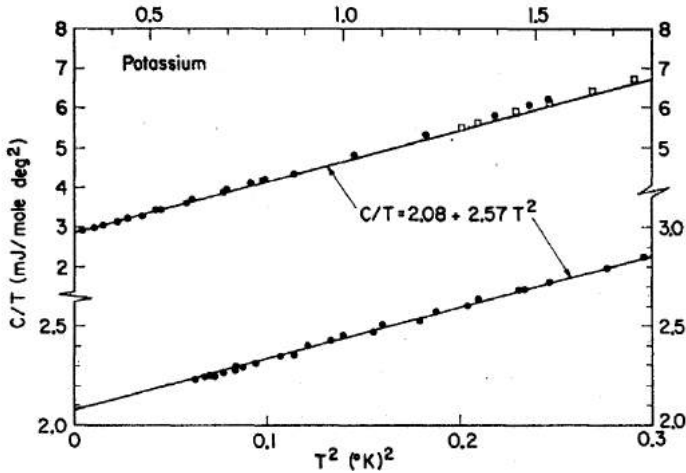


Fig. 3.7 Temperature dependence of the specific heat of potassium and sodium. Figure originally published by [Lien and Phillips (1964)]. Used with permission.

Problem 3.3: Thermal conductivity from kinetic theory

In this chapter, we derived the thermal conductivity of a three-dimensional material from kinetic theory. Perform a similar analysis for one- and two-dimensional materials to obtain the following generalized expression:

$$\kappa = \frac{1}{d} c_v v \Lambda,$$

where d is the dimension and can take the values 1, 2 or 3. Also derive an integral expression for the thermal conductivity and observe the temperature dependence at low temperatures. Assume that the velocity and mean free path are independent of temperature and carrier energy.

Solution

The following expression for heat flux q_z'' was obtained in the chapter:

$$q_z'' \approx -v_z \Lambda_z \frac{\partial u}{\partial z} = -v_z \Lambda_z \frac{\partial u}{\partial T} \frac{\partial T}{\partial z} = -c_v v_z \Lambda_z \frac{\partial T}{\partial z}. \quad (3.52)$$

In 1D, $v_z = v$, $\Lambda_z = \Lambda$.

$$q_z'' = -c_v v \Lambda \frac{\partial T}{\partial z}. \quad (3.53)$$

In 2D, $v_z = v \cos \theta$, $\Lambda_z = \Lambda \cos \theta$. We average the heat flux over an angle of π radians.

$$\begin{aligned} q_z'' &= -c_v v \Lambda \frac{\partial T}{\partial z} \frac{1}{\pi} \int_0^\pi \cos^2 \theta d\theta \\ &= -\frac{1}{2} c_v v \Lambda \frac{\partial T}{\partial z}. \end{aligned} \quad (3.54)$$

In 3D, the heat flux is averaged over a solid angle of 2π steradians.

$$\begin{aligned} q_z'' &= -c_v v \Lambda \frac{\partial T}{\partial z} \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta d\psi \\ &= -\frac{1}{3} c_v v \Lambda \frac{\partial T}{\partial z}. \end{aligned} \quad (3.55)$$

From Eqs. (3.53)–(3.55), thermal conductivity κ in d dimensions is given by,

$$\kappa = \frac{1}{d} c_v v \Lambda. \quad (3.56)$$

Substituting the low temperature result for specific heat c_v , we find:

$$\kappa = \eta_a k_B v \Lambda \left(\frac{T}{\theta_D} \right)^d \int_0^\infty \frac{x^{d+1} e^x dx}{(e^x - 1)^2}. \quad (3.57)$$

Note that the Debye approximation is used in the above expression for specific heat. Also we have neglected multiple phonon polarizations. At low temperatures, the thermal conductivity shows the same temperature dependence as the specific heat and scales as T^d .

Problem 3.4: Specific heat of a diatomic chain

Consider the diatomic chain studied in Chapter 1 with atomic masses m_1 , m_2 ($m_2 > m_1$) and a uniform atom spacing of a . Also assume a uniform spring constant g between all adjacent atoms. In this problem, we calculate the specific heat of the diatomic chain using the Debye model for the acoustic branch and the Einstein model for the optical branch. Assume that the constant frequency ω_E in the Einstein model is an average of the minimum and maximum frequencies of the optical branch.

- (a) Show that the ratio of Einstein and Debye temperatures can be expressed in terms of the mass ratio m_2/m_1 as follows:

$$\frac{\theta_E}{\theta_D} = \frac{1}{\pi} \left(\sqrt{\frac{m_1}{m_2}} + \sqrt{\frac{m_2}{m_1}} + \sqrt{1 + \frac{m_2}{m_1}} \right).$$

- (b) Calculate the normalized acoustic and optical phonon specific heats (normalized by $\eta_a k_B$) at normalized temperatures of $T/\theta_D = 0.2$, 1 and 2. Assume a mass ratio $m_2/m_1 = 2$. Also provide an intuitive explanation of your numerical results.
- (c) Use the online Chapter 3 CDF tool¹ to evaluate the acoustic and optical contributions to the total specific heat as a function of temperature. Also observe how these contributions change with varying mass ratio. Again, provide a physical explanation for the trend in the curves with varying mass ratio.

Solution

- (a) The Einstein frequency ω_E is calculated by taking an average of the minimum and maximum frequencies of the optical branch. See Section 1.6 for derivations of the minimum ($\omega_+(K = \pi/a)$) and maximum ($\omega_+(K = 0)$) frequencies.

$$\begin{aligned} \omega_E &= \frac{1}{2}(\omega_+(K = 0) + \omega_+(K = \pi/a)) \\ &= \frac{1}{2} \left(\sqrt{\frac{2g}{\mu}} + \sqrt{\frac{2g}{m_1}} \right) \\ &= \sqrt{\frac{g}{2}} \left(\frac{\sqrt{m_1 + m_2} + \sqrt{m_2}}{\sqrt{m_1 m_2}} \right). \end{aligned} \quad (3.58)$$

¹See http://nanohub.org/groups/cdf_tools_thermal_energy_course/wiki

The Debye frequency ω_D is just the product of the group velocity of the acoustic branch at the Brillouin zone center and the Debye cutoff wavevector K_D . In 1D, $K_D = \pi\eta_a = \pi/a$ since the unit cell density is $1/a$. See Section 1.6 for a derivation of the group velocity of the acoustic branch at the center of Brillouin zone.

$$\begin{aligned}\omega_D &= v_g(K=0)K_D \\ &= a\sqrt{\frac{g\mu}{2m_1m_2}}\frac{\pi}{a} \\ &= \pi\sqrt{\frac{g}{2(m_1+m_2)}}.\end{aligned}\quad (3.59)$$

From Eqs. (3.58) and (3.59), the ratio of Einstein and Debye temperatures is given by:

$$\frac{\theta_E}{\theta_D} = \frac{\omega_E}{\omega_D} = \frac{1}{\pi} \left(\sqrt{\frac{m_1}{m_2}} + \sqrt{\frac{m_2}{m_1}} + \sqrt{1 + \frac{m_2}{m_1}} \right). \quad (3.60)$$

- (b) The specific heat of the acoustic branch is given by (see Section 3.2.4):

$$c_{v,D} = \eta_a k_B \left(\frac{T}{\theta_D} \right) \int_0^{\theta_D/T} \frac{x^2 e^x dx}{(e^x - 1)^2}. \quad (3.61)$$

For $T/\theta_D = 0.1, 1$ and 2 , $c_{v,D}/\eta_a k_B = 0.328, 0.973$ and 0.993 respectively (the integral was evaluated numerically). Observe that the specific heat is very close to the Dulong and Petit limit of $c_{v,D} = \eta_a k_B$ for temperatures higher than the Debye temperature. The specific heat of the optical branch is given by (see Section 3.2.2):

$$c_{v,E} = \eta_a k_B \frac{\chi_E^2 e^{\chi_E}}{(e^{\chi_E} - 1)^2}, \quad (3.62)$$

where $\chi_E = \theta_E/T$. For $m_2/m_1 = 2$, $\theta_E/\theta_D = 1.226$ (using the result derived in part (a) of this problem). Hence $\theta_E/T = 1.226\theta_D/T$. For $T/\theta_D = 0.1, 1$ and 2 , $\chi_E = 12.26, 1.226$ and 0.613 respectively. Thus $c_{v,E}/\eta_a k_B = 0.0007, 0.884$ and 0.969 for $T/\theta_D = 0.1, 1$ and 2 respectively. Note that the optical phonon

Table 3.1 Acoustic and optical phonon specific heats of a diatomic chain with $m_2/m_1 = 2$.

$\frac{T}{\theta_D}$	$\frac{c_{v,D}}{\eta_a k_B}$	$\frac{c_{v,E}}{\eta_a k_B}$	$\frac{c_{v,D}}{c_{v,D} + c_{v,E}} \times 100\%$
0.1	0.328	0.0007	99.78%
1	0.973	0.884	52.4%
2	0.993	0.969	50.61%

specific heat is almost zero for $T/\theta_D = 0.1$. This is because the high frequency optical mode is negligibly populated at such low temperatures. The optical phonon specific heat also approaches the Dulong and Petit law for high temperatures.

Table 3.1 shows a summary of the results calculated. At low temperatures, the heat capacity of the acoustic branch dominates that of the optical branch. For temperatures above the Debye temperature, $c_{v,D}/c_{v,E} \approx 1$ indicating that both the acoustic and optical modes contribute equally to specific heat.

- (c) Figure 3.8 shows snapshots from the online Chapter 3 CDF tool where the acoustic and optical contributions to the total specific heat are plotted as a function of temperature. Clearly the acoustic branch dominates the specific heat at low temperatures, and the fractional contributions tend to 0.5 for very high temperatures. As the mass ratio increases, the Einstein frequency moves farther from the Debye frequency. Hence the temperature at which the acoustic and optical contributions become equal also increases with increasing mass ratio.

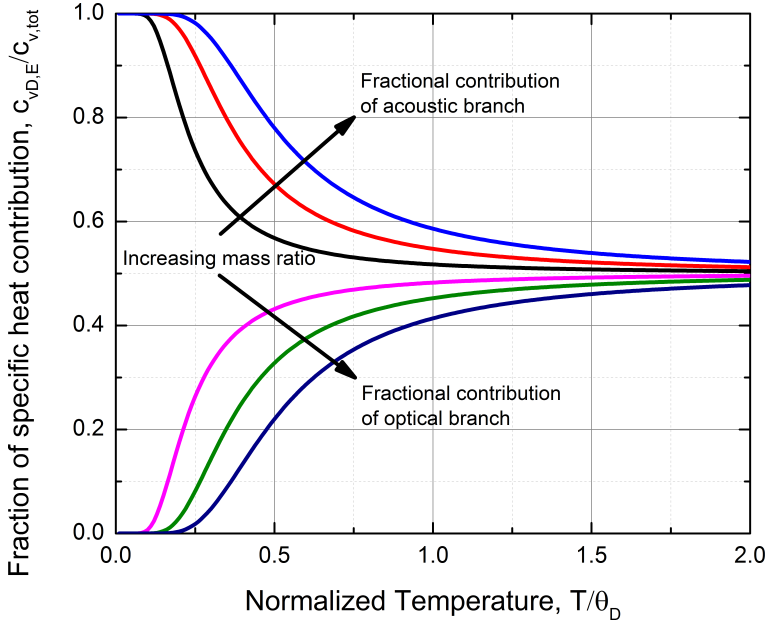


Fig. 3.8 Acoustic and optical contributions to specific heat.