

The Oxford Solid State Basics

STEVEN H. SIMON

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Preface to the 2016 Reprint

The 2016 reprint of this book is a “bug-fix” release — changes are limited to corrections of small errors and typos, and occasional (always very small) added explanatory material. While there have been numerous requests to add a chapter on this-or-that subject, there has not been much consensus on what subjects need to be added, so I concluded that it is probably best not to add any new material in hopes of keeping the book as streamlined as possible. (That said, I did add one short paragraph in chapter 18 about light emitting diodes in honor of the 2014 Nobel prize).

A large number of the errors in the book were in exercises that were not properly vetted before being released into the wild. Hopefully most of the problems with these exercises are fixed in this reprint. A few additional exercises are added as well. Those that are new or have been substantially changed have been marked with the symbol “&” to indicate where things differ from the original printing.

Thanks are due to a number of people. First, to those who have chosen to use this book for teaching. Second, to those who have read this book and have posted positive reviews on the web or otherwise recommended its use to others. Third, to those who have contacted me and pointed out typos or other problems to be fixed. Finally, to those who have generally supported me and made my efforts possible. I apologize for not mentioning all of you by name — you know who you are.

Oxford, United Kingdom
January 2016

Preface after Teaching this Course

Although things were a bit bumpy the first few times I taught this course, I learned a lot from the experience, and hopefully I have now managed to smooth out many of the rough parts. The good news is that the course has been viewed mostly as a success, even by the tough measure of student reviews. I would particularly like to thank the student who wrote on his or her review that I deserve a raise—and I would like to encourage my department chair to post this review on his wall and refer to it frequently.

If you can think of ways that this book could be further improved (correction of errors or whatnot) please let me know. The next generation of students will certainly appreciate it and that will improve your Karma. ☺

Oxford, United Kingdom
April 2013

Preface

¹This gibe against solid state physics can be traced back to the Nobel Laureate Murray Gell-Mann, discoverer of the quark, who famously believed that there was nothing interesting in any endeavor but particle physics. Interestingly he now studies complexity—a field that mostly arose from condensed matter.

When I was an undergraduate I thought solid state physics (a sub-genre of condensed matter physics) was perhaps the worst subject that any undergraduate could be forced to learn—boring and tedious, “squalid state” as it was commonly called.¹ How much would I really learn about the universe by studying the properties of crystals? I managed to avoid taking this course altogether. My opinion at the time was not a reflection of the subject matter, but rather was a reflection of how solid state physics was taught.

Given my opinion as an undergraduate, it is a bit ironic that I have become a condensed matter physicist. But once I was introduced to the subject properly, I found that condensed matter was my favorite subject in all of physics—full of variety, excitement, and deep ideas. Sadly, a first introduction to the topic can barely scratch the surface of what constitutes the broad field of condensed matter.

Last year, when I was told that a new course was being prepared to teach condensed matter physics to third year Oxford undergraduates, I jumped at the opportunity to teach it. I felt that it *must* be possible to teach a condensed matter physics course that is just as interesting and exciting as any other course that an undergraduate will ever take. It must be possible to convey the excitement of real condensed matter physics to the undergraduate audience. I hope I will succeed in this task. You can judge for yourself.

The topics I was asked to cover are not atypical for a solid state physics course. Some of these topics are covered well in standard solid state physics references that one might find online, or in other books. The reason I am writing this book (and not just telling students to go read a standard reference) is because condensed matter/solid state is an enormous subject—worth many years of lectures—and one needs a guide to decide what subset of topics are most important (at least in the eyes of an Oxford examination committee). The material contained here gives depth in some topics, and glosses over other topics, so as to reflect the particular topics that are deemed important at Oxford as well as to reflect the subjects mandated by the UK Institute of Physics.

I cannot emphasize enough that there are many many extremely good books on solid state and condensed matter physics already in existence. There are also many good resources online (including the rather infamous “Britney Spears’ guide to semiconductor physics”—which is tongue-in-cheek about Britney Spears, but is actually a very good reference about semiconductors). Throughout this book, I will try to point you to other good references appropriately.

So now we begin our journey through condensed matter. Let us go then, you and I...

Oxford, United Kingdom
January 2011

About this Book

This book is meant to be a first introduction to solid state and condensed matter physics for advanced undergraduate students. There are several main prerequisites for this course. First, the students should be familiar with basic quantum mechanics (we will sometimes use bra and ket notation). Secondly, the students should know something about thermodynamics and statistical mechanics. Basic mechanics and basic electromagnetism are also assumed. A very strong student might be capable of handling the material without all of the prerequisites, but the student would have to be willing to do some extra work on the side.

At the end of each chapter I give useful references to other books. A full list of all the books cited, along with proper reference and commentary, is provided in Appendix B.

Most chapters also have exercises included at the end. The exercises are marked with * if they are harder (with multiple *s if they are much harder). Exercises marked with ‡ are considered to be fundamental to the core syllabus (at least at Oxford).

A sample exam is provided (with solutions) in Appendix A. The current Oxford syllabus covers this entire book with the exception of Chapter 18 on device physics and Chapter 23 on the Hubbard model (interactions and magnetism).

Acknowledgments

Needless to say, I pilfered a fair fraction of the intellectual content of this book from parts of other books (mostly mentioned in Appendix B). The authors of these books put great thought and effort into their writing. I am deeply indebted to these giants who have come before me. Additionally, I have stolen many ideas about how this book should be structured from the people who have taught the condensed matter courses at Oxford in years past. Most recently this includes Mike Glazer, Andrew Boothroyd, and Robin Nicholas. I also confess to having stolen (with permission) many examples and exercises from the Oxford course or from old Oxford exams.

I am also very thankful to all the people who have helped me proof-read, correct, and otherwise tweak this book. Among others, this includes Mike Glazer, Alex Hearmon, Simon Davenport, Till Hackler, Paul Stubley, Stephanie Simmons, Katherine Dunn, Joost Slingerland, Radu Coldea, Stanislav Zavjalov, Nathaniel Jowitt, Thomas Elliott, Ali Khan, Andrew Boothroyd, Jeremy Dodd, Marianne Wait, Seamus O'Hagan, Simon Clark, Joel Moore, Natasha Perkins, Christiane Riedinger, Deyan Mihaylov, Philipp Karkowski, William Bennett, Francesca Mosely, Bruno Balthazar, Richard Fern, Dmitry Budker, Rafe Kennedy, Sabine Müller, Carrie Leonard-McIntyre, and Nick Jelley (and I apologize if I have left anyone's name off this list). I am also very grateful for the hospitality of the Aspen Center for Physics, the Nordic Institute for Theoretical Physics, National University of Ireland Maynooth, the Galileo Galilei Institute for Theoretical Physics, 139 Edgeview Lane, and the Economy Section of United Airlines Transatlantic where major parts of this book were written.

Finally, I thank my father for helping proofread and improve these notes... and for a million other things.

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About Condensed Matter Physics

1

This chapter is my personal take on why this topic is interesting. You might want to read it to figure out why you should think this book is interesting if that isn't otherwise obvious.

1.1 What Is Condensed Matter Physics

Quoting Wikipedia:

Condensed matter physics is the field of physics that deals with the macroscopic and microscopic physical properties of matter. In particular, it is concerned with the “condensed” phases that appear whenever the number of constituents in a system is extremely large and the interactions between the constituents are strong. The most familiar examples of condensed phases are solids and liquids, which arise from the electromagnetic forces between atoms.

The use of the term “condensed matter”, being more general than just the study of solids, was coined and promoted by Nobel laureate Philip W. Anderson.

Condensed matter physics is by far the largest single subfield of physics. The annual meeting of condensed matter physicists in the United States attracts over 6000 physicists each year! Topics included in this field range from the very practical to the absurdly abstract, from down-to-earth engineering to mathematical topics that border on string theory. The commonality is that all of these topics relate to the fundamental properties of matter.

1.2 Why Do We Study Condensed Matter Physics?

There are several very good answers to this question

(1) **Because it is the world around us**

Almost all of the physical world that we see is in fact condensed matter. We might ask questions such as

- why are metals shiny and why do they feel cold?

- why is glass transparent?
- why is water a fluid, and why does fluid feel wet?
- why is rubber soft and stretchy?

These questions are all in the domain of condensed matter physics. In fact almost every question you might ask about the world around you, short of asking about the sun or stars, is probably related to condensed matter physics in some way.

(2) **Because it is useful**

Over the last century our command of condensed matter physics has enabled us humans to do remarkable things. We have used our knowledge of physics to engineer new materials and exploit their properties to change our world and our society completely. Perhaps the most remarkable example is how our understanding of solids enabled new inventions exploiting semiconductor technology, which enabled the electronics industry, which enabled computers, iPhones, and everything else we now take for granted.

(3) **Because it is deep**

The questions that arise in condensed matter physics are as deep as those you might find anywhere. In fact, many of the ideas that are now used in other fields of physics can trace their origins to condensed matter physics.

A few examples for fun:

- The famous Higgs boson, which was recently observed at CERN, is no different from a phenomenon that occurs in superconductors (the domain of condensed matter physicists). The Higgs mechanism, which gives mass to elementary particles is frequently called the “Anderson–Higgs” mechanism, after the condensed matter physicist Phil Anderson¹ who described much of the same physics before Peter Higgs, the high-energy theorist.
- The ideas of the renormalization group (Nobel Prize to Kenneth Wilson in 1982) was developed simultaneously in both high-energy and condensed matter physics.
- The ideas of topological quantum field theories, while invented by string theorists as theories of quantum gravity, have been discovered in the laboratory by condensed matter physicists!
- In the last few years there has been a mass exodus of string theorists applying black-hole physics (in N -dimensions!) to phase transitions in real materials. The very same structures exist in the lab that are (maybe!) somewhere out in the cosmos!

That this type of physics is deep is not just my opinion. The Nobel committee agrees with me. During this course we will discuss the work of no fewer than fifty Nobel laureates! (See the index of scientists at the end of this book.)

¹The same guy who coined the term “condensed matter”.

(4) Because reductionism doesn't work

`begin{rant}` People frequently have the feeling that if you continually ask “what is it made of” you learn more about something. This approach to knowledge is known as *reductionism*. For example, asking what water is made of, someone may tell you it is made from molecules, then molecules are made of atoms, atoms of electrons and protons, protons of quarks, and quarks are made of who-knows-what. But none of this information tells you anything about why water is wet, about why protons and neutrons bind to form nuclei, why the atoms bind to form water, and so forth. Understanding physics inevitably involves understanding how many objects all interact with each other. And this is where things get difficult very quickly. We understand the Schroedinger equation extremely well for one particle, but the Schroedinger equations for four or more particles, while in principle solvable, in practice are never solved because they are too difficult—even for the world’s biggest computers. Physics involves figuring out what to do then. How are we to understand how quarks form a nucleus, or how electrons and protons form an atom if we cannot solve the many particle Schroedinger equation?

Even more interesting is the possibility that we understand very well the microscopic theory of a system, but then we discover that macroscopic properties *emerge* from the system that we did not expect. My personal favorite example is when one puts together many electrons (each with charge $-e$) one can sometimes find new particles emerging, each having one third the charge of an electron!² Reductionism would never uncover this—it misses the point completely. `end{rant}`

(5) Because it is a laboratory

Condensed matter physics is perhaps the best laboratory we have for studying quantum physics and statistical physics. Those of us who are fascinated by what quantum mechanics and statistical mechanics can do often end up studying condensed matter physics which is deeply grounded in both of these topics. Condensed matter is an infinitely varied playground for physicists to test strange quantum and statistical effects.

I view this entire book as an extension of what you have already learned in quantum and statistical physics. If you enjoyed those courses, you will likely enjoy this as well. If you did not do well in those courses, you might want to go back and study them again, because many of the same ideas will arise here.

²Yes, this really happens. The Nobel Prize in 1998 was awarded to Dan Tsui, Horst Stormer, and Bob Laughlin, for discovery of this phenomenon known as the fractional quantum Hall effect.

1.3 Why Solid State Physics?

Being that condensed matter physics is so huge, we cannot possibly study all of it in one book. Instead we will focus on just one particular subfield, known as “solid state physics”. As the name suggests, this is the

³Perhaps this is not surprising considering how many solid objects there are in the world.

⁴This stems from the term “solid state electronics” which describes any electronic device where electrons travel within a solid. This is in comparison to the old vacuum tube-based electronic systems where the electrons actually traveled *in vacuo*. The old-style tubes have been replaced in almost every application—with very few exceptions. One interesting exception is that many audiophiles and musicians prefer sound amplification using tubes rather than solid state electronics. What they prefer is that the tubes amplify sound with a characteristic distortion that the musicians somehow find appealing. For a pure amplification without distortion, solid state devices are far better.

study of matter in its solid state (as compared to being in a liquid state, a gas state, a superfluid state, or some other state of matter). There are several reasons why we choose to focus on the solid state. First of all, solid state physics is by far the biggest single subfield of condensed matter physics.³ Secondly, solid state physics is the most successful and most technologically useful subfield of condensed matter physics. Not only do we know far more about solids than we know about other types of matter, but also solids are far more useful than other types of matter. Almost all materials that have found their way to industrial application are in their solid state. Paramount among these materials are the solids known as semiconductors which are the basis of the entire electronics industry. Indeed, frequently the electronics industry is even called the “solid state” industry.⁴ More importantly, however, the physics of solids provides a paradigm for learning other topics in physics. The things we learn in our study of solids will form a foundation for study of other topics both inside the field of condensed matter, and outside of it.

Part I

Physics of Solids without Considering Microscopic Structure: The Early Days of Solid State

Specific Heat of Solids: Boltzmann, Einstein, and Debye

2

Our story of condensed matter physics starts around the turn of the last century. It was well known (and you should remember from your prior study of statistical physics) that the heat capacity¹ of a monatomic (ideal) gas is $C_v = 3k_B/2$ per atom, with k_B being Boltzmann's constant. The statistical theory of gases described why this is so.

As far back as 1819, however, it had also been known that for many solids the heat capacity is given by²

$$\begin{aligned} C &= 3k_B \text{ per atom} \\ \text{or } C &= 3R \end{aligned}$$

which is known as the *law of Dulong–Petit*,³ where R is the ideal gas constant. While this law is not always correct, it frequently is close to true. For example, see Table 2.1 of heat capacities at room temperature and pressure. With the exception of diamond, the law $C/R = 3$ seems to hold extremely well at room temperature, although at lower temperatures all materials start to deviate from this law, and typically C drops rapidly below some temperature (and for diamond when the temperature is raised, the heat capacity increases towards $3R$ as well, see Fig. 2.2).

In 1896 Boltzmann constructed a model that accounted for this law fairly well. In his model, each atom in the solid is bound to neighboring atoms. Focusing on a single particular atom, we imagine that atom as

²Here I do not distinguish between C_p (at constant pressure) and C_v (at constant volume) because they are very close to the same. Recall that $C_p - C_v = VT\alpha^2/\beta_T$, where β_T is the isothermal compressibility and α is the coefficient of thermal expansion. For a solid, α is relatively small.

³Both Pierre Dulong and Alexis Petit were French chemists. Neither is remembered for much else besides this law.

Table 2.1 Heat capacities of some solids at room temperature and pressure.

Material	C/R
Aluminum (Al)	2.91
Antimony (Sb)	3.03
Copper (Cu)	2.94
Gold (Au)	3.05
Silver (Ag)	2.99
Diamond (C)	0.735

¹We will almost always be concerned with the heat capacity C per atom of a material. Multiplying by Avogadro's number gives the *molar heat capacity* or heat capacity per mole. The *specific heat* (denoted often as c rather than C) is the heat capacity per unit mass. However, the phrase “specific heat” is also used loosely to describe the molar heat capacity, since they are both intensive quantities (as compared to the total heat capacity which is extensive—i.e., proportional to the amount of mass in the system). We will try to be precise with our language, but one should be aware that frequently things are written in non-precise ways and you are left to figure out what is meant. For example, really we should say C_v per atom = $3k_B/2$ rather than $C_v = 3k_B/2$ per atom, and similarly we should say C per mole = $3R$. To be more precise I really would have liked to title this chapter “Heat Capacity per Atom of Solids” rather than “Specific Heat of Solids”. However, for over a century people have talked about the “Einstein Theory of Specific Heat” and “Debye Theory of Specific Heat”, and it would have been almost scandalous to not use this wording.

being in a harmonic well formed by the interaction with its neighbors. In such a classical statistical mechanical model, the heat capacity of the vibration of the atom is $3k_B$ per atom, in agreement with Dulong–Petit. (You should be able to show this with your knowledge of statistical mechanics and/or the equipartition theorem; see Exercise 2.1).

Several years later in 1907, Einstein started wondering about why this law does not hold at low temperatures (for diamond, “low” temperature appears to be room temperature!). What he realized is that quantum mechanics is important!

Einstein’s assumption was similar to that of Boltzmann. He assumed that every atom is in a harmonic well created by the interaction with its neighbors. Further, he assumed that every atom is in an identical harmonic well and has an oscillation frequency ω (known as the “Einstein” frequency).

The quantum-mechanical problem of a simple harmonic oscillator is one whose solution we know. We will now use that knowledge to determine the heat capacity of a single one-dimensional harmonic oscillator. This entire calculation should look familiar from your statistical physics course.

2.1 Einstein’s Calculation

In one dimension, the energies of the eigenstates of a single harmonic oscillator are

$$E_n = \hbar\omega(n + 1/2) \quad (2.1)$$

with ω the frequency of the harmonic oscillator (the “Einstein frequency”). The partition function is then⁴

$$\begin{aligned} Z_{1D} &= \sum_{n \geq 0} e^{-\beta\hbar\omega(n+1/2)} \\ &= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh(\beta\hbar\omega/2)}. \end{aligned}$$

The expectation of energy is then (compare to Eq. 2.1)

$$\langle E \rangle = -\frac{1}{Z_{1D}} \frac{\partial Z_{1D}}{\partial \beta} = \frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) = \hbar\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right) \quad (2.2)$$

where n_B is the Bose⁵ occupation factor

$$n_B(x) = \frac{1}{e^x - 1}.$$

This result is easy to interpret. The mode ω is an excitation that is excited on average up to the n_B^{th} level, or equivalently there is a “boson” orbital which is “occupied” by n_B bosons.

Differentiating the expression for energy we obtain the heat capacity for a single oscillator,

$$C = \frac{\partial \langle E \rangle}{\partial T} = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}.$$

⁴We will very frequently use the standard notation $\beta = 1/(k_B T)$.

⁵Satyendra Bose worked out the idea of Bose statistics in 1924, but could not get it published until Einstein lent his support to the idea.

Note that the high-temperature limit of this expression gives $C = k_B$ (check this if it is not obvious!).

Generalizing to the three-dimensional case,

$$E_{n_x, n_y, n_z} = \hbar\omega[(n_x + 1/2) + (n_y + 1/2) + (n_z + 1/2)]$$

and

$$Z_{3D} = \sum_{n_x, n_y, n_z \geq 0} e^{-\beta E_{n_x, n_y, n_z}} = [Z_{1D}]^3$$

resulting in $\langle E_{3D} \rangle = 3\langle E_{1D} \rangle$, so correspondingly we obtain

$$C = 3k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}.$$

Plotted, this looks like Fig. 2.1.

Note that in the high-temperature limit $k_B T \gg \hbar\omega$ we recover the law of Dulong–Petit: $3k_B$ heat capacity per atom. However, at low temperature ($T \ll \hbar\omega/k_B$) the degrees of freedom “freeze out”, the system gets stuck in only the ground-state eigenstate, and the heat capacity vanishes rapidly.

Einstein’s theory reasonably accurately explained the behavior of the heat capacity as a function of temperature with only a single fitting parameter, the Einstein frequency ω (sometimes this frequency is quoted in terms of the Einstein temperature $\hbar\omega = k_B T_{Einstein}$). In Fig. 2.2 we show Einstein’s original comparison to the heat capacity of diamond.

For most materials, the Einstein frequency ω is low compared to room temperature, so the Dulong–Petit law holds fairly well (being relatively high temperature compared to the Einstein frequency). However, for diamond, ω is high compared to room temperature, so the heat capacity is lower than $3R$ at room temperature. The reason diamond has such a high Einstein frequency is that the bonding between atoms in diamond is very strong and the atomic mass of the carbon atoms that comprise diamond is relatively low, hence a high $\omega = \sqrt{\kappa/m}$ oscillation frequency, with κ a spring constant and m the mass. These strong bonds also result in diamond being an exceptionally hard material.

Einstein’s result was remarkable, not only in that it explained the temperature dependence of the heat capacity, but more importantly it told us something fundamental about quantum mechanics. Keep in mind that Einstein obtained this result 19 years before the Schrodinger equation was discovered!⁶

2.2 Debye's Calculation

Einstein’s theory of specific heat was extremely successful, but still there were clear deviations from the predicted equation. Even in the plot in his first paper (Fig. 2.2) one can see that at low temperature the experimental data lie above the theoretical curve.⁷ This result turns out to be rather important! In fact, it was known that at low temperatures

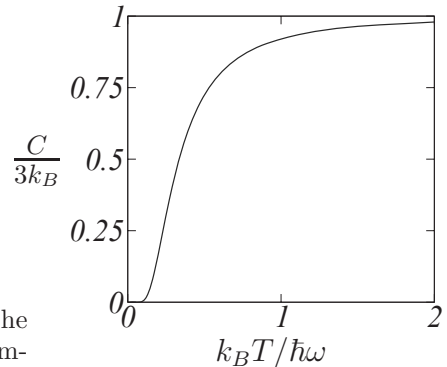


Fig. 2.1 Einstein heat capacity per atom in three dimensions.

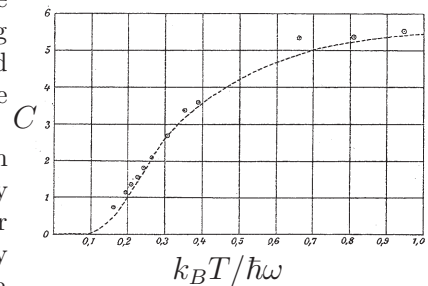


Fig. 2.2 Plot of molar heat capacity of diamond from Einstein’s original paper. The fit is to the Einstein theory. The y axis is C in units of cal/(K-mol). In these units, $3R \approx 5.96$. The fitting parameter $T_{Einstein} = \hbar\omega/k_B$ is roughly 1320K. Figure from A. Einstein, *Ann. Phys.*, **22**, 180, (1907), Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

⁶Einstein was a pretty smart guy.

⁷Although perhaps not obvious, this deviation turns out to be real, and not just experimental error.

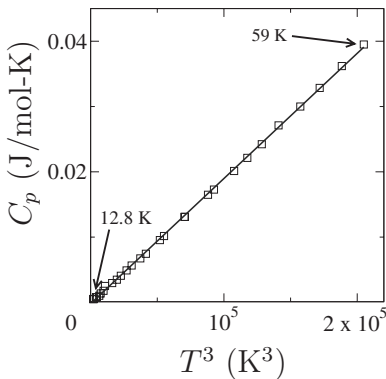


Fig. 2.3 Heat capacity of diamond is proportional to T^3 at low temperature. Note that the temperatures shown in this plot are far far below the Einstein temperature and therefore correspond to the very bottom left corner of Fig. 2.2. Data from Desnoyehs and Morrison, *Phil. Mag.*, **3**, 42 (1958).

⁸We will discuss magnetism in part VII.

⁹Peter Debye later won a Nobel Prize in chemistry for something completely different.

¹⁰Max Planck did not like his own calculation of the quantization of light. He later referred to it as “an act of desperation”. It seems that he viewed it mostly as a way to fudge the calculation to get an answer in agreement with experiment rather than being the revolutionary beginning of the new field of quantum physics.

¹¹Sound in fluids is longitudinal only.

¹²It is not too hard to keep track of the fact that the transverse and longitudinal velocities are different. Note also that we assume the sound velocity to be the same in every direction, which need not be true in real materials. It is not too hard to include such anisotropy in Debye’s theory as well. See Exercise 2.6.

most materials have a heat capacity that is proportional to T^3 . See for example, Fig. 2.3. (Metals also have a very small additional term proportional to T which we will discuss later in Section 4.2. Magnetic materials may have other additional terms as well.⁸ Non-magnetic insulators have only the T^3 behavior). At any rate, Einstein’s formula at low temperature is exponentially small in T , not agreeing at all with the actual experiments.

In 1912 Peter Debye⁹ discovered how to better treat the quantum mechanics of oscillations of atoms, and managed to explain the T^3 dependence of the specific heat. Debye realized that oscillation of atoms is the same thing as sound, and sound is a wave, so it should be quantized the same way as Planck¹⁰ had quantized light waves in 1900. Besides the fact that the speed of light is much faster than that of sound, there is only one minor difference between light and sound: for light, there are two polarizations for each wavevector $\mathbf{k}$, whereas for sound there are three modes for each $\mathbf{k}$ (a longitudinal mode, where the atomic motion is in the same direction as $\mathbf{k}$ and two transverse modes where the motion is perpendicular to $\mathbf{k}$; light has only the transverse modes¹¹). For simplicity of presentation here we will assume that the transverse and longitudinal modes have the same velocity, although in truth the longitudinal velocity is usually somewhat greater than the transverse velocity.¹²

We now repeat essentially what was Planck’s calculation for light. This calculation should also look familiar from your statistical physics course. First, however, we need some preliminary information about waves:

2.2.1 Periodic (Born–von Karman) Boundary Conditions

Many times in this course we will consider waves with periodic or “Born–von Karman” boundary conditions. It is easiest to describe this first in one dimension. Here, instead of having a one-dimensional sample of length L with actual ends, we imagine that the two ends are connected together making the sample into a circle. The periodic boundary condition means that, any wave in this sample e^{ikr} is required to have the same value for a position r as it has for $r + L$ (we have gone all the way around the circle). This then restricts the possible values of k to be

$$k = \frac{2\pi n}{L}$$

for n an integer. If we are ever required to sum over all possible values of k , for large enough L we can replace the sum with an integral obtaining

$$\sum_k \rightarrow \frac{L}{2\pi} \int_{-\infty}^{\infty} dk.$$

A way to understand this mapping is to note that the spacing between allowed points in k space is $2\pi/L$, so the integral $\int dk$ can be replaced by a sum over k points times the spacing between the points.¹³

In three dimensions, the story is extremely similar. For a sample of size L^3 , we identify opposite ends of the sample (wrapping the sample up into a hypertorus!) so that if you go a distance L in the x , y or z direction, you get back to where you started.¹⁴ As a result, our $\mathbf{k}$ values can only take values

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3)$$

for integer values of n_i , so here each $\mathbf{k}$ point now occupies a volume of $(2\pi/L)^3$. Because of this discretization of values of $\mathbf{k}$, whenever we have a sum over all possible $\mathbf{k}$ values we obtain

$$\sum_{\mathbf{k}} \rightarrow \frac{L^3}{(2\pi)^3} \int d\mathbf{k}$$

with the integral over all three dimensions of $\mathbf{k}$ -space (this is what we mean by the bold $d\mathbf{k}$). One might think that wrapping the sample up into a hypertorus is very unnatural compared to considering a system with real boundary conditions. However, these boundary conditions tend to simplify calculations quite a bit, and most physical quantities you might measure could be measured far from the boundaries of the sample anyway and would then be independent of what you do with the boundary conditions.

2.2.2 Debye's Calculation Following Planck

Debye decided that the oscillation modes of a solid were waves with frequencies $\omega(\mathbf{k}) = v|\mathbf{k}|$ with v the sound velocity—and for each $\mathbf{k}$ there should be three possible oscillation modes, one for each direction of motion. Thus he wrote an expression entirely analogous to Einstein's expression (compare to Eq. 2.2)

$$\begin{aligned} \langle E \rangle &= 3 \sum_{\mathbf{k}} \hbar \omega(\mathbf{k}) \left(n_B(\beta \hbar \omega(\mathbf{k})) + \frac{1}{2} \right) \\ &= 3 \frac{L^3}{(2\pi)^3} \int d\mathbf{k} \hbar \omega(\mathbf{k}) \left(n_B(\beta \hbar \omega(\mathbf{k})) + \frac{1}{2} \right) \end{aligned}$$

Each excitation mode is a boson of frequency $\omega(\mathbf{k})$ and is occupied on average $n_B(\beta \hbar \omega(\mathbf{k}))$ times.

By spherical symmetry, we may convert the three-dimensional integral to a one-dimensional integral

$$\int d\mathbf{k} \rightarrow 4\pi \int_0^\infty k^2 dk$$

(recall that $4\pi k^2$ is the area of the surface of a sphere¹⁵ of radius k) and we also use $k = \omega/v$ to obtain

$$\langle E \rangle = 3 \frac{4\pi L^3}{(2\pi)^3} \int_0^\infty \omega^2 d\omega (1/v^3) (\hbar \omega) \left(n_B(\beta \hbar \omega) + \frac{1}{2} \right) \quad (2.3)$$

¹³In your previous courses you may have used particle-in-a-box boundary conditions where instead of plane waves $e^{i2\pi n r/L}$ you used particle in a box wavefunctions of the form $\sin(n\pi r/L)$. This gives you instead

$$\sum_k \rightarrow \frac{L}{\pi} \int_0^\infty dk$$

which will inevitably result in the same physical answers as for the periodic boundary condition case. All calculations can be done either way, but periodic Born–von Karman boundary conditions are almost always simpler.

¹⁴Such boundary conditions are very popular in video games, such as the classic time-wasting game of my youth, *Asteroids* (you can find it online). It may also be possible that our universe has such boundary conditions—a notion known as the *doughnut universe*. Data collected by Cosmic Microwave Background Explorer (led by Nobel Laureates John Mather and George Smoot) and its successor the Wilkinson Microwave Anisotropy Probe appear consistent with this structure.

¹⁵Or to be pedantic, $\int d\mathbf{k} \rightarrow \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_0^\infty k^2 dk$ and performing the angular integrals gives 4π .

It is convenient to replace $nL^3 = N$ where n is the density of atoms. We then obtain

$$\langle E \rangle = \int_0^\infty d\omega g(\omega)(\hbar\omega) \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right) \quad (2.4)$$

where the *density of states* is given by¹⁶

$$g(\omega) = L^3 \left[\frac{12\pi\omega^2}{(2\pi)^3 v^3} \right] = N \left[\frac{12\pi\omega^2}{(2\pi)^3 n v^3} \right] = N \frac{9\omega^2}{\omega_d^3} \quad (2.5)$$

where

$$\omega_d^3 = 6\pi^2 n v^3. \quad (2.6)$$

This frequency will be known as the *Debye frequency*, and in the next section we will see why we chose to define it this way with the factor of 9 removed.

The meaning of the density of states¹⁷ here is that the total number of oscillation modes with frequencies between ω and $\omega + d\omega$ is given by $g(\omega)d\omega$. Thus the interpretation of Eq. 2.4 is simply that we should count how many modes there are per frequency (given by g), then multiply by the expected energy per mode (compare to Eq. 2.2), and finally we integrate over all frequencies. This result, Eq. 2.3, for the quantum energy of the sound waves is strikingly similar to Planck's result for the quantum energy of light waves, only we have replaced $2/c^3$ by $3/v^3$ (replacing the two light modes by three sound modes). The other change from Planck's classic result is the $+1/2$ that we obtain as the zero-point energy of each oscillator.¹⁸ At any rate, this zero-point energy gives us a contribution which is temperature independent.¹⁹ Since we are concerned with $C = \partial\langle E \rangle / \partial T$ this term will not contribute and we will separate it out. We thus obtain

$$\langle E \rangle = \frac{9N\hbar}{\omega_d^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} + T \text{ independent constant.}$$

By defining a variable $x = \beta\hbar\omega$ this becomes

$$\langle E \rangle = \frac{9N\hbar}{\omega_d^3 (\beta\hbar)^4} \int_0^\infty dx \frac{x^3}{e^x - 1} + T \text{ independent constant.}$$

The nasty integral just gives some number²⁰—in fact the number is $\pi^4/15$. Thus we obtain

$$\langle E \rangle = 9N \frac{(k_B T)^4}{(\hbar\omega_d)^3} \frac{\pi^4}{15} + T \text{ independent constant.}$$

¹⁶Although it now appears that the number of atoms N and the atomic density n are relevant parameters of the problem, in fact, these two factors cancel and only the original L^3 matters for our results in this section! The reason we have introduced such canceling factors here is because writing our results this way prepares us for the next section (Sec. 2.2.3) where N becomes an important physical parameter different from L^3 !

¹⁷We will encounter the concept of density of states many times, so it is a good idea to become comfortable with it!

¹⁸Planck should have gotten this energy as well, but he didn't know about zero-point energy—in fact, since it was long before quantum mechanics was fully understood, Debye didn't actually have this term either.

¹⁹The contribution of the zero-point energy is temperature independent and also infinite. Handling infinities like this is something that gives mathematicians nightmares, but physicists do it happily when they know that the infinity is not really physical. We will see in Section 2.2.3 how this infinity gets properly cut off by the Debye frequency.

²⁰If you wanted to evaluate the nasty integral, the strategy is to reduce it to the famous Riemann zeta function. We start by writing

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx \frac{x^3 e^{-x}}{1 - e^{-x}} = \int_0^\infty dx x^3 e^{-x} \sum_{n=0}^\infty e^{-nx} = \sum_{n=1}^\infty \int_0^\infty dx x^3 e^{-nx}$$

The integral can be evaluated and the expression can then be written as $3! \sum_{n=1}^\infty n^{-4}$. The resultant sum is a special case of the famous Riemann zeta function defined as $\zeta(p) = \sum_{n=1}^\infty n^{-p}$, where here we are concerned with the value of $\zeta(4)$. Since the zeta function is one of the most important functions in all of mathematics (see margin note 24 of this chapter), one can just look up its value on a table to find that $\zeta(4) = \pi^4/90$, thus giving us the stated result that the nasty integral is $\pi^4/15$. However, in the unlikely event that you were stranded on a desert island and did not have access to a table, you could even evaluate this sum explicitly, which we do in the appendix to this chapter.

Notice the similarity to Planck's derivation of the T^4 energy of photons. As a result, the heat capacity is

$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(k_B T)^3}{(\hbar \omega_d)^3} \frac{12\pi^4}{5} \sim T^3.$$

This correctly obtains the desired T^3 specific heat. Furthermore, the prefactor of T^3 can be calculated in terms of known quantities such as the sound velocity. Note that the Debye frequency in this equation is sometimes replaced by a temperature.

$$k_B T_{Debye} = \hbar \omega_d$$

known as the *Debye temperature* (see Table 2.2), so that this equation reads

$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(T)^3}{(T_{Debye})^3} \frac{12\pi^4}{5}.$$

2.2.3 Debye's "Interpolation"

Unfortunately, now Debye has a problem. In the expression just derived, the heat capacity is proportional to T^3 up to arbitrarily high temperature. We know however, that the heat capacity should level off to $3k_B N$ at high T . Debye understood that the problem with his approximation is that it allowed an infinite number of sound wave modes—up to arbitrarily large $\mathbf{k}$. This would imply more sound wave modes than there are atoms in the entire system. Debye guessed (correctly) that really there should be only as many modes as there are degrees of freedom in the system. We will see in Chapters 9–13 that this is an important general principle. To fix this problem, Debye decided to not consider sound waves above some maximum frequency ω_{cutoff} , with this frequency chosen such that there are exactly $3N$ sound wave modes in the system (three dimensions of motion times N particles). We thus define ω_{cutoff} via

$$3N = \int_0^{\omega_{cutoff}} d\omega g(\omega). \quad (2.7)$$

We correspondingly rewrite Eq. 2.4 for the energy (dropping the zero-point contribution) as²¹

$$\langle E \rangle = \int_0^{\omega_{cutoff}} d\omega g(\omega) \hbar \omega n_B(\beta \hbar \omega). \quad (2.8)$$

Note that at very low temperature, this cutoff does not matter at all, since for large β the Bose factor n_B will very rapidly go to zero at frequencies well below the cutoff frequency anyway.

Let us now check that this cutoff gives us the correct high-temperature limit. For high temperature

$$n_B(\beta \hbar \omega) = \frac{1}{e^{\beta \hbar \omega} - 1} \rightarrow \frac{k_B T}{\hbar \omega}.$$

Table 2.2 Some Debye temperatures.

Material	T_{Debye} (K)
Diamond (C)	1850
Beryllium (Be)	1000
Silicon (Si)	625
Copper (Cu)	315
Silver (Ag)	215
Lead (Pb)	88

Note that hard materials like diamond have high Debye temperatures, whereas soft materials like lead have low Debye temperatures. These data are measured at standard temperature and pressure (meaning the speed of sound and density are measured at this temperature and pressure). Since real materials change depending on the environment (expand with temperature, etc.) the Debye temperature is actually a very weak function of ambient conditions.

²¹Here, since the integral is now cut off, had we kept the zero-point energy, its contribution would now be finite (and temperature independent still).

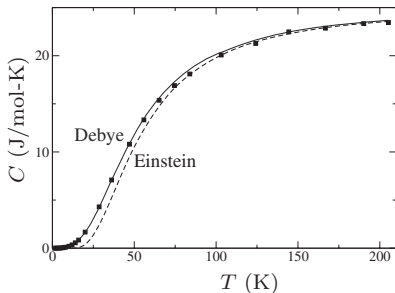


Fig. 2.4 Heat capacity of silver compared to the Debye and Einstein models. The high-temperature asymptote is given by $C = 3R = 24.945 \text{ J/(mol-K)}$. Over the entire experimental range, the fit to the Debye theory is excellent. At low T it correctly recovers the T^3 dependence, and at high T it converges to the law of Dulong–Petit. The Einstein theory clearly is incorrect at very low temperatures. The Debye temperature is roughly 215 K, whereas the Einstein temperature roughly 151 K. Data is taken from C. Kittel, *Solid State Physics*, 2ed Wiley (1956).

²²In magnetic materials there may be still other contributions to the heat capacity reflecting the energy stored in magnetic degrees of freedom. See Part VII, and in particular Exercise 20.3, below.

Thus in the high-temperature limit, invoking Eqs. 2.7 and 2.8 we obtain

$$\langle E \rangle = k_B T \int_0^{\omega_{cutoff}} d\omega g(\omega) = 3k_B T N$$

yielding the Dulong–Petit high-temperature heat capacity $C = \partial \langle E \rangle / \partial T = 3k_B N = 3k_B$ per atom. For completeness, let us now evaluate our cutoff frequency,

$$3N = \int_0^{\omega_{cutoff}} d\omega g(\omega) = 9N \int_0^{\omega_{cutoff}} d\omega \frac{\omega^2}{\omega_d^3} = 3N \frac{\omega_{cutoff}^3}{\omega_d^3}.$$

We thus see that the correct cutoff frequency is exactly the Debye frequency ω_d . Note that $k = \omega_d/v = (6\pi^2 n)^{1/3}$ (from Eq. 2.6) is on the order of the inverse interatomic spacing of the solid.

More generally (in the neither high- nor low-temperature limit) one has to evaluate the integral (Eq. 2.8), which cannot be done analytically. Nonetheless it can be done numerically and then can be compared to actual experimental data as shown in Fig. 2.4. It should be emphasized that the Debye theory makes predictions without any free parameters, as compared to the Einstein theory which had the unknown Einstein frequency ω as a free fitting parameter.

2.2.4 Some Shortcomings of the Debye Theory

While Debye’s theory is remarkably successful, it does have a few shortcomings.

- The introduction of the cutoff seems very *ad hoc*. This seems like a successful cheat rather than real physics.
- We have assumed sound waves follow the law $\omega = vk$ even for very large values of k (on the order of the inverse lattice spacing), whereas the entire idea of sound is a long-wavelength idea, which doesn’t seem to make sense for high enough frequency and short enough wavelength. At any rate, it is known that at high enough frequency the law $\omega = vk$ no longer holds.
- Experimentally, the Debye theory is very accurate, but it is not exact at intermediate temperatures.
- Metals also have a term in the heat capacity that is proportional to T , so the overall heat capacity is $C = \gamma T + \alpha T^3$ and at low enough T the linear term will dominate.²² You can’t see this contribution on the plot Fig. 2.4, but at very low T it becomes evident, as shown in Fig. 2.5.

Of these shortcomings, the first three can be handled more properly by treating the details of the crystal structure of materials accurately (which we will do starting in Chapter 9). The final issue requires us to carefully study the behavior of electrons in metals to discover the origin of this linear T term (see Section 4.2).

Nonetheless, despite these problems, Debye’s theory was a substantial improvement over Einstein’s.²³

²³Debye was pretty smart too... even though he was a chemist.