

Solid State Physics

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What is Condensed Matter Physics?

1.1 Length, time, energy scales

We will be concerned with:

- $\omega, T \ll 1eV$
- $|x_i - x_j|, \frac{1}{q} \gg 1\text{\AA}$

as compared to energies in the MeV for nuclear matter, and GeV or even TeV , in particle physics.

The properties of matter at these scales is determined by the behavior of collections of many ($\sim 10^{23}$) atoms.

In general, we will be concerned with scales much smaller than those at which gravity becomes very important, which is the domain of astrophysics and cosmology.

1.2 Microscopic Equations vs. States of Matter, Phase Transitions, Critical Points

Systems containing many particles exhibit properties which are special to such systems. Many of these properties are fairly insensitive to the details at length scales shorter than 1\AA and energy scales higher than $1eV$ – which are quite adequately described by the equations of non-relativistic quantum mechanics. Such properties are *emergent*. For example, precisely the same microscopic equations of motion – Newton’s equations – can describe two different systems of 10^{23} H_2O molecules.

$$m \frac{d^2 \vec{x}_i}{dt^2} = - \sum_{j \neq i} \vec{\nabla}_i V(\vec{x}_i - \vec{x}_j) \quad (1.1)$$

Or, perhaps, the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i,j} V(\vec{x}_i - \vec{x}_j) \right) \psi(\vec{x}_1, \dots, \vec{x}_N) = E \psi(\vec{x}_1, \dots, \vec{x}_N) \quad (1.2)$$

However, one of these systems might be water and the other ice, in which case the properties of the two systems are completely different, and the similarity between their microscopic descriptions is of no practical consequence. As this example shows, many-particle systems exhibit various *phases* – such as ice and water – which are not, for the most part, usefully described by the microscopic equations. Instead, new low-energy, long-wavelength physics *emerges* as a result of the interactions among large numbers of particles. Different phases are separated by *phase transitions*, at which the low-energy, long-wavelength description becomes *non-analytic* and exhibits singularities. In the above example, this occurs at the freezing point of water, where its *entropy* jumps discontinuously.

1.3 Broken Symmetries

As we will see, different phases of matter are distinguished on the basis of symmetry. The microscopic equations are often highly symmetrical – for instance, Newton’s laws are translationally and rotationally invariant – but a given phase may exhibit much less symmetry. Water exhibits the full translational and rotational symmetry of Newton’s laws; ice, however, is only invariant under the discrete translational and rotational group of its crystalline lattice. We say that the translational and rotational symmetries of the microscopic equations have been *spontaneously* broken.

1.4 Experimental probes: X-ray scattering, neutron scattering, NMR, thermodynamic, transport

There are various experimental probes which can allow an experimentalist to determine in what phase a system is and to determine its quantitative properties:

- Scattering: send neutrons or X-rays into the system with prescribed energy, momentum and measure the energy, momentum of the outgoing neutrons or X-rays.
- NMR: apply a static magnetic field, B , and measure the absorption and emission by the system of magnetic radiation at frequencies of the order of $\omega_c = geB/m$. Essentially the scattering of magnetic radiation at low frequency by a system in a uniform B field.
- Thermodynamics: measure the response of macroscopic variables such as the energy and volume to variations of the temperature, pressure, etc.

- Transport: set up a potential or thermal gradient, $\nabla\varphi$, ∇T and measure the electrical or heat current \vec{j} , \vec{j}_Q . The gradients $\nabla\varphi$, ∇T can be held constant or made to oscillate at finite frequency.

1.5 The Solid State: metals, insulators, magnets, superconductors

In the solid state, translational and rotational symmetries are broken by the arrangement of the positive ions. It is precisely as a result of these broken symmetries that solids are *solid*, i.e. that they are rigid. It is energetically favorable to break the symmetry in the same way in different parts of the system. Hence, the system resists attempts to create regions where the residual translational and rotational symmetry groups are different from those in the bulk of the system. The broken symmetry can be detected using X-ray or neutron scattering: the X-rays or neutrons are scattered by the ions; if the ions form a lattice, the X-rays or neutrons are scattered coherently, forming a diffraction pattern with peaks. In a crystalline solid, discrete subgroups of the translational and rotational groups are preserved. For instance, in a cubic lattice, rotations by $\pi/2$ about any of the crystal axes are symmetries of the lattice (as well as all rotations generated by products of these). Translations by one lattice spacing along a crystal axis generate the discrete group of translations.

In this course, we will be focussing on crystalline solids. Some examples of non-crystalline solids, such as plastics and glasses will be discussed below. Crystalline solids fall into three general categories: *metals*, *insulators*, and *superconductors*. In addition, all three of these phases can be further subdivided into various magnetic phases. Metals are characterized by a non-zero conductivity at $T = 0$. Insulators have vanishing conductivity at $T = 0$. Superconductors have infinite conductivity for

$T < T_c$ and, furthermore, exhibit the Meissner effect: they expel magnetic fields.

In a magnetic material, the electron spins can order, thereby breaking the spin-rotational invariance. In a ferromagnet, all of the spins line up in the same direction, thereby breaking the spin-rotational invariance to the subgroup of rotations about this direction while preserving the discrete translational symmetry of the lattice. (This can occur in a metal, an insulator, or a superconductor.) In an antiferromagnet, neighboring spins are oppositely directed, thereby breaking spin-rotational invariance to the subgroup of rotations about the preferred direction *and* breaking the lattice translational symmetry to the subgroup of translations by an even number of lattice sites.

Recently, new states of matter – the fractional quantum Hall states – have been discovered in effectively two-dimensional systems in a strong magnetic field at very low T . Tomorrow's experiments will undoubtedly uncover new phases of matter.

1.6 Other phases: liquid crystals, quasicrystals, polymers, glasses

The liquid – with full translational and rotational symmetry – and the solid – which only preserves a discrete subgroup – are but two examples of possible realizations of translational symmetry. In a *liquid crystalline phase*, translational and rotational symmetry is broken to a combination of discrete and continuous subgroups. For instance, a *nematic* liquid crystal is made up of elementary units which are line segments. In the nematic phase, these line segments point, on average, in the same direction, but their positional distribution is as in a liquid. Hence, a nematic phase breaks rotational invariance to the subgroup of rotations about the preferred direction and preserves the full translational invariance. Nematics are used in LCD displays.

In a *smectic* phase, on the other hand, the line segments arrange themselves into layers, thereby partially breaking the translational symmetry so that discrete translations perpendicular to the layers and continuous translations along the layers remain unbroken. In the *smectic-A* phase, the preferred orientational direction is the same as the direction perpendicular to the layers; in the *smectic-C* phase, these directions are different. In a hexatic phase, a two-dimensional system has broken orientational order, but unbroken translational order; locally, it looks like a triangular lattice. A *quasicrystal* has rotational symmetry which is broken to a 5-fold discrete subgroup. Translational order is completely broken (locally, it has discrete translational order). *Polymers* are extremely long molecules. They can exist in solution or a chemical reaction can take place which cross-links them, thereby forming a gel. A *glass* is a rigid, ‘random’ arrangement of atoms. Glasses are somewhat like ‘snapshots’ of liquids, and are probably non-equilibrium phases, in a sense.

Review of Quantum Mechanics

2.1 States and Operators

A quantum mechanical system is defined by a Hilbert space, \mathcal{H} , whose vectors, $|\psi\rangle$ are associated with the states of the system. A state of the system is represented by the set of vectors $e^{i\alpha}|\psi\rangle$. There are linear operators, \mathcal{O}_i which act on this Hilbert space. These operators correspond to physical observables. Finally, there is an inner product, which assigns a complex number, $\langle\chi|\psi\rangle$, to any pair of states, $|\psi\rangle, |\chi\rangle$. A state vector, $|\psi\rangle$ gives a complete description of a system through the expectation values, $\langle\psi|\mathcal{O}_i|\psi\rangle$ (assuming that $|\psi\rangle$ is normalized so that $\langle\psi|\psi\rangle = 1$), which would be the average values of the corresponding physical observables if we could measure them on an infinite collection of identical systems each in the state $|\psi\rangle$.

The adjoint, \mathcal{O}^\dagger , of an operator is defined according to

$$\langle\chi|(\mathcal{O}|\psi\rangle) = (\langle\chi|\mathcal{O}^\dagger)|\psi\rangle \quad (2.1)$$

In other words, the inner product between $|\chi\rangle$ and $\mathcal{O}|\psi\rangle$ is the same as that between $\mathcal{O}^\dagger|\chi\rangle$ and $|\psi\rangle$. An Hermitian operator satisfies

$$\mathcal{O} = \mathcal{O}^\dagger \quad (2.2)$$

while a unitary operator satisfies

$$\mathcal{O}\mathcal{O}^\dagger = \mathcal{O}^\dagger\mathcal{O} = 1 \quad (2.3)$$

If \mathcal{O} is Hermitian, then

$$e^{i\mathcal{O}} \quad (2.4)$$

is unitary. Given an Hermitian operator, \mathcal{O} , its eigenstates are orthogonal,

$$\langle \lambda' | \mathcal{O} | \lambda \rangle = \lambda \langle \lambda' | \lambda \rangle = \lambda' \langle \lambda' | \lambda \rangle \quad (2.5)$$

For $\lambda \neq \lambda'$,

$$\langle \lambda' | \lambda \rangle = 0 \quad (2.6)$$

If there are n states with the same eigenvalue, then, within the subspace spanned by these states, we can pick a set of n mutually orthogonal states. Hence, we can use the eigenstates $|\lambda\rangle$ as a basis for Hilbert space. Any state $|\psi\rangle$ can be expanded in the basis given by the eigenstates of \mathcal{O} :

$$|\psi\rangle = \sum_{\lambda} c_{\lambda} |\lambda\rangle \quad (2.7)$$

with

$$c_{\lambda} = \langle \lambda | \psi \rangle \quad (2.8)$$

A particularly important operator is the Hamiltonian, or the total energy, which we will denote by H . Schrödinger's equation tells us that H determines how a state of the system will evolve in time.

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \quad (2.9)$$

If the Hamiltonian is independent of time, then we can define energy eigenstates,

$$H |E\rangle = E |E\rangle \quad (2.10)$$

which evolve in time according to:

$$|E(t)\rangle = e^{-i\frac{Et}{\hbar}} |E(0)\rangle \quad (2.11)$$

An arbitrary state can be expanded in the basis of energy eigenstates:

$$|\psi\rangle = \sum_i c_i |E_i\rangle \quad (2.12)$$

It will evolve according to:

$$|\psi(t)\rangle = \sum_j c_j e^{-i\frac{E_j t}{\hbar}} |E_j\rangle \quad (2.13)$$

For example, consider a particle in $1D$. The Hilbert space consists of all continuous complex-valued functions, $\psi(x)$. The position operator, \hat{x} , and momentum operator, \hat{p} are defined by:

$$\begin{aligned} \hat{x} \cdot \psi(x) &\equiv x \psi(x) \\ \hat{p} \cdot \psi(x) &\equiv -i\hbar \frac{\partial}{\partial x} \psi(x) \end{aligned} \quad (2.14)$$

The position eigenfunctions,

$$x \delta(x - a) = a \delta(x - a) \quad (2.15)$$

are Dirac delta functions, which are not continuous functions, but can be defined as the limit of continuous functions:

$$\delta(x) = \lim_{a \rightarrow 0} \frac{1}{a\sqrt{\pi}} e^{-\frac{x^2}{a^2}} \quad (2.16)$$

The momentum eigenfunctions are plane waves:

$$-i\hbar \frac{\partial}{\partial x} e^{ikx} = \hbar k e^{ikx} \quad (2.17)$$

Expanding a state in the basis of momentum eigenstates is the same as taking its Fourier transform:

$$\psi(x) = \int_{-\infty}^{\infty} dk \tilde{\psi}(k) \frac{1}{\sqrt{2\pi}} e^{ikx} \quad (2.18)$$

where the Fourier coefficients are given by:

$$\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \psi(x) e^{-ikx} \quad (2.19)$$

If the particle is free,

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (2.20)$$

then momentum eigenstates are also energy eigenstates:

$$\hat{H} e^{ikx} = \frac{\hbar^2 k^2}{2m} e^{ikx} \quad (2.21)$$

If a particle is in a Gaussian wavepacket at the origin at time $t = 0$,

$$\psi(x, 0) = \frac{1}{a\sqrt{\pi}} e^{-\frac{x^2}{a^2}} \quad (2.22)$$

Then, at time t , it will be in the state:

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \frac{a}{\sqrt{\pi}} e^{-i\frac{\hbar k^2 t}{2m}} e^{-\frac{1}{2}k^2 a^2} e^{ikx} \quad (2.23)$$

2.2 Density and Current

Multiplying the free-particle Schrödinger equation by ψ^* ,

$$\psi^* i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \psi^* \frac{\partial^2}{\partial x^2} \psi \quad (2.24)$$

and subtracting the complex conjugate of this equation, we find

$$\frac{\partial}{\partial t} (\psi^* \psi) = \frac{i\hbar}{2m} \vec{\nabla} \cdot (\psi^* \vec{\nabla} \psi - (\vec{\nabla} \psi^*) \psi) \quad (2.25)$$

This is in the form of a continuity equation,

$$\frac{\partial \rho}{\partial t} = \vec{\nabla} \cdot \vec{j} \quad (2.26)$$

The density and current are given by:

$$\rho = \psi^* \psi$$

$$\vec{j} = \frac{i\hbar}{2m} \left(\psi^* \vec{\nabla} \psi - (\vec{\nabla} \psi^*) \psi \right) \quad (2.27)$$

The current carried by a plane-wave state is:

$$\vec{j} = \frac{\hbar}{2m} \vec{k} \frac{1}{(2\pi)^3} \quad (2.28)$$

2.3 δ -function scatterer

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \delta(x) \quad (2.29)$$

$$\psi(x) = \begin{cases} e^{ikx} + R e^{-ikx} & \text{if } x < 0 \\ T e^{ikx} & \text{if } x > 0 \end{cases} \quad (2.30)$$

$$\begin{aligned} T &= \frac{1}{1 - \frac{mV}{\hbar^2 k} i} \\ R &= \frac{\frac{mV}{\hbar^2 k} i}{1 - \frac{mV}{\hbar^2 k} i} \end{aligned} \quad (2.31)$$

There is a *bound state* at:

$$ik = \frac{mV}{\hbar^2} \quad (2.32)$$

2.4 Particle in a Box

Particle in a 1D region of length L :

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (2.33)$$

$$\psi(x) = A e^{ikx} + B e^{-ikx} \quad (2.34)$$

has energy $E = \hbar^2 k^2 / 2m$. $\psi(0) = \psi(L) = 0$. Therefore,

$$\psi(x) = A \sin\left(\frac{n\pi}{L} x\right) \quad (2.35)$$

for integer n . Allowed energies

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad (2.36)$$

In a 3D box of side L , the energy eigenfunctions are:

$$\psi(x) = A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \quad (2.37)$$

and the allowed energies are:

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (2.38)$$

2.5 Harmonic Oscillator

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k x^2 \quad (2.39)$$

Writing $\omega = \sqrt{k/m}$, $\tilde{p} = p/(km)^{1/4}$, $\tilde{x} = x(km)^{1/4}$,

$$H = \frac{1}{2} \omega (\tilde{p}^2 + \tilde{x}^2) \quad (2.40)$$

$$[\tilde{p}, \tilde{x}] = -i\hbar \quad (2.41)$$

Raising and lowering operators:

$$\begin{aligned} a &= (\tilde{x} + i\tilde{p}) / \sqrt{2\hbar} \\ a^\dagger &= (\tilde{x} - i\tilde{p}) / \sqrt{2\hbar} \end{aligned} \quad (2.42)$$

Hamiltonian and commutation relations:

$$\begin{aligned} H &= \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \\ [a, a^\dagger] &= 1 \end{aligned} \quad (2.43)$$

The commutation relations,

$$[H, a^\dagger] = \hbar\omega a^\dagger$$

$$[H, a] = -\hbar\omega a \quad (2.44)$$

imply that there is a ladder of states,

$$\begin{aligned} Ha^\dagger|E\rangle &= (E + \hbar\omega) a^\dagger|E\rangle \\ Ha|E\rangle &= (E - \hbar\omega) a|E\rangle \end{aligned} \quad (2.45)$$

This ladder will continue down to negative energies (which it can't since the Hamiltonian is manifestly positive definite) unless there is an $E_0 \geq 0$ such that

$$a|E_0\rangle = 0 \quad (2.46)$$

Such a state has $E_0 = \hbar\omega/2$.

We label the states by their $a^\dagger a$ eigenvalues. We have a complete set of H eigenstates, $|n\rangle$, such that

$$H|n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle \quad (2.47)$$

and $(a^\dagger)^n|0\rangle \propto |n\rangle$. To get the normalization, we write $a^\dagger|n\rangle = c_n|n+1\rangle$. Then,

$$\begin{aligned} |c_n|^2 &= \langle n|aa^\dagger|n\rangle \\ &= n + 1 \end{aligned} \quad (2.48)$$

Hence,

$$\begin{aligned} a^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\ a|n\rangle &= \sqrt{n}|n-1\rangle \end{aligned} \quad (2.49)$$

2.6 Double Well

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (2.50)$$

where

$$V(x) = \begin{cases} \infty & \text{if } |x| > 2a + 2b \\ 0 & \text{if } b < |x| < a + b \\ V_0 & \text{if } |x| < b \end{cases}$$

Symmetrical solutions:

$$\psi(x) = \begin{cases} A \cos k'x & \text{if } |x| < b \\ \cos(k|x| - \phi) & \text{if } b < |x| < a + b \end{cases} \quad (2.51)$$

with

$$k' = \sqrt{k^2 - \frac{2mV_0}{\hbar^2}} \quad (2.52)$$

The allowed k 's are determined by the condition that $\psi(a + b) = 0$:

$$\phi = \left(n + \frac{1}{2}\right) \pi - k(a + b) \quad (2.53)$$

the continuity of $\psi(x)$ at $|x| = b$:

$$A = \frac{\cos(kb - \phi)}{\cos k'b} \quad (2.54)$$

and the continuity of $\psi'(x)$ at $|x| = b$:

$$k \tan \left(\left(n + \frac{1}{2}\right) \pi - ka \right) = k' \tan k'b \quad (2.55)$$

If k' is imaginary, $\cos \rightarrow \cosh$ and $\tan \rightarrow i \tanh$ in the above equations.

Antisymmetrical solutions:

$$\psi(x) = \begin{cases} A \sin k'x & \text{if } |x| < b \\ \text{sgn}(x) \cos(k|x| - \phi) & \text{if } b < |x| < a + b \end{cases} \quad (2.56)$$

The allowed k 's are now determined by

$$\phi = \left(n + \frac{1}{2}\right) \pi - k(a + b) \quad (2.57)$$

$$A = \frac{\cos(kb - \phi)}{\sin k'b} \quad (2.58)$$

$$k \tan \left(\left(n + \frac{1}{2} \right) \pi - ka \right) = -k' \cot k'b \quad (2.59)$$

Suppose we have n wells? Sequences of eigenstates, classified according to their eigenvalues under translations between the wells.

2.7 Spin

The electron carries spin-1/2. The spin is described by a state in the Hilbert space:

$$\alpha|+\rangle + \beta|-\rangle \quad (2.60)$$

spanned by the basis vectors $|\pm\rangle$. Spin operators:

$$\begin{aligned} s_x &= \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ s_y &= \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ s_z &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \quad (2.61)$$

Coupling to an external magnetic field:

$$H_{\text{int}} = -g\mu_B \vec{s} \cdot \vec{B} \quad (2.62)$$

States of a spin in a magnetic field in the \hat{z} direction:

$$\begin{aligned} H|+\rangle &= -\frac{g}{2}\mu_B |+\rangle \\ H|-\rangle &= \frac{g}{2}\mu_B |-\rangle \end{aligned} \quad (2.63)$$

2.8 Many-Particle Hilbert Spaces: Bosons, Fermions

When we have a system with many particles, we must now specify the states of all of the particles. If we have two distinguishable particles whose Hilbert spaces are

spanned by the bases

$$|i, 1\rangle \quad (2.64)$$

and

$$|\alpha, 2\rangle \quad (2.65)$$

Then the two-particle Hilbert space is spanned by the set:

$$|i, 1; \alpha, 2\rangle \equiv |i, 1\rangle \otimes |\alpha, 2\rangle \quad (2.66)$$

Suppose that the two single-particle Hilbert spaces are identical, e.g. the two particles are in the same box. Then the two-particle Hilbert space is:

$$|i, j\rangle \equiv |i, 1\rangle \otimes |j, 2\rangle \quad (2.67)$$

If the particles are identical, however, we must be more careful. $|i, j\rangle$ and $|j, i\rangle$ must be physically the same state, i.e.

$$|i, j\rangle = e^{i\alpha} |j, i\rangle \quad (2.68)$$

Applying this relation twice implies that

$$|i, j\rangle = e^{2i\alpha} |i, j\rangle \quad (2.69)$$

so $e^{i\alpha} = \pm 1$. The former corresponds to bosons, while the latter corresponds to fermions. The two-particle Hilbert spaces of bosons and fermions are respectively spanned by:

$$|i, j\rangle + |j, i\rangle \quad (2.70)$$

and

$$|i, j\rangle - |j, i\rangle \quad (2.71)$$

The n -particle Hilbert spaces of bosons and fermions are respectively spanned by:

$$\sum_{\pi} |i_{\pi(1)}, \dots, i_{\pi(n)}\rangle \quad (2.72)$$

and

$$\sum_{\pi} (-1)^{\pi} |i_{\pi(1)}, \dots, i_{\pi(n)}\rangle \quad (2.73)$$

In position space, this means that a bosonic wavefunction must be completely symmetric:

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_n) = \psi(x_1, \dots, x_j, \dots, x_i, \dots, x_n) \quad (2.74)$$

while a fermionic wavefunction must be completely antisymmetric:

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_n) = -\psi(x_1, \dots, x_j, \dots, x_i, \dots, x_n) \quad (2.75)$$

Review of Statistical Mechanics

3.1 Microcanonical, Canonical, Grand Canonical Ensembles

In statistical mechanics, we deal with a situation in which even the quantum state of the system is unknown. The expectation value of an observable must be averaged over:

$$\langle \mathcal{O} \rangle = \sum_i w_i \langle i | \mathcal{O} | i \rangle \quad (3.1)$$

where the states $|i\rangle$ form an orthonormal basis of \mathcal{H} and w_i is the probability of being in state $|i\rangle$. The w_i 's must satisfy $\sum w_i = 1$. The expectation value can be written in a basis-independent form:

$$\langle \mathcal{O} \rangle = Tr \{ \rho \mathcal{O} \} \quad (3.2)$$

where ρ is the density matrix. In the above example, $\rho = \sum_i w_i |i\rangle \langle i|$. The condition, $\sum w_i = 1$, i.e. that the probabilities add to 1, is:

$$Tr \{ \rho \} = 1 \quad (3.3)$$

We usually deal with one of three ensembles: the microcanonical ensemble, the canonical ensemble, or the grand canonical ensemble. In the microcanonical ensemble,

we assume that our system is isolated, so the energy is fixed to be E , but all states with energy E are taken with equal probability:

$$\rho = C \delta(H - E) \quad (3.4)$$

C is a normalization constant which is determined by (3.3). The entropy is given by,

$$S = -\ln C \quad (3.5)$$

In other words,

$$S(E) = \ln(\# \text{ of states with energy } E) \quad (3.6)$$

Inverse temperature, $\beta = 1/(k_B T)$:

$$\beta \equiv \left(\frac{\partial S}{\partial E} \right)_V \quad (3.7)$$

Pressure, P :

$$\frac{P}{k_B T} \equiv \left(\frac{\partial S}{\partial V} \right)_E \quad (3.8)$$

where V is the volume.

First law of thermodynamics:

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \quad (3.9)$$

$$dE = k_B T dS - P dV \quad (3.10)$$

Free energy:

$$F = E - k_B T S \quad (3.11)$$

Differential relation:

$$dF = -k_B S dT - P dV \quad (3.12)$$

or,

$$S = -\frac{1}{k_B} \left(\frac{\partial F}{\partial T} \right)_V \quad (3.13)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (3.14)$$

while

$$\begin{aligned} E &= F + k_B T S \\ &= F - T \left(\frac{\partial F}{\partial T} \right)_V \\ &= -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \end{aligned} \quad (3.15)$$

In the canonical ensemble, we assume that our system is in contact with a heat reservoir so that the *temperature is constant*. Then,

$$\rho = C e^{-\beta H} \quad (3.16)$$

It is useful to drop the normalization constant, C , and work with an unnormalized density matrix so that we can define the partition function:

$$Z = \text{Tr} \{ \rho \} \quad (3.17)$$

or,

$$Z = \sum_a e^{-\beta E_a} \quad (3.18)$$

The average energy is:

$$\begin{aligned} E &= \frac{1}{Z} \sum_a E_a e^{-\beta E_a} \\ &= - \frac{\partial}{\partial \beta} \ln Z \\ &= -k_B T^2 \frac{\partial}{\partial T} \ln Z \end{aligned} \quad (3.19)$$

Hence,

$$F = -k_B T \ln Z \quad (3.20)$$

The chemical potential, μ , is defined by

$$\mu = \frac{\partial F}{\partial N} \quad (3.21)$$

where N is the particle number.

In the grand canonical ensemble, the system is in contact with a reservoir of heat *and* particles. Thus, the temperature and chemical potential are held fixed and

$$\rho = C e^{-\beta(H-\mu N)} \quad (3.22)$$

We can again work with an unnormalized density matrix and construct the grand canonical partition function:

$$\mathcal{Z} = \sum_{N,a} e^{-\beta(E_a - \mu N)} \quad (3.23)$$

The average number is:

$$N = -k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \quad (3.24)$$

while the average energy is:

$$E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} + \mu k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \quad (3.25)$$

3.2 Bose-Einstein and Planck Distributions

3.2.1 Bose-Einstein Statistics

For a system of free bosons, the partition function

$$Z = \sum_{E_a, N} e^{-\beta(E_a - \mu N)} \quad (3.26)$$

can be rewritten in terms of the *single-particle eigenstates* and the single-particle energies ϵ_i :

$$E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \dots \quad (3.27)$$

$$\begin{aligned} Z &= \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i - \mu \sum_i n_i)} \\ &= \prod_i \left(\sum_{n_i} e^{-\beta(n_i \epsilon_i - \mu n_i)} \right) \end{aligned}$$

$$= \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \quad (3.28)$$

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (3.29)$$

The chemical potential is chosen so that

$$\begin{aligned} N &= \sum_i \langle n_i \rangle \\ &= \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned} \quad (3.30)$$

The energy is given by

$$\begin{aligned} E &= \sum_i \langle n_i \rangle \epsilon_i \\ &= \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned} \quad (3.31)$$

N is increased by increasing μ ($\mu \leq 0$ always). Bose-Einstein condensation occurs when

$$N > \sum_{i \neq 0} \langle n_i \rangle \quad (3.32)$$

In such a case, $\langle n_0 \rangle$ must become large. This occurs when $\mu = 0$.

3.2.2 The Planck Distribution

Suppose N is not fixed, but is arbitrary, e.g. the numbers of photons and neutrinos are not fixed. Then there is no Lagrange multiplier μ and

$$\langle n_i \rangle = \frac{1}{e^{\beta\epsilon_i} - 1} \quad (3.33)$$

Consider photons (two polarizations) in a cavity of side L with $\epsilon_k = \hbar\omega_k = \hbar ck$ and

$$k = \frac{2\pi}{L} (m_x, m_y, m_z) \quad (3.34)$$

$$E = 2 \sum_{m_x, m_y, m_z} \omega_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle \quad (3.35)$$

We can take the thermodynamic limit, $L \rightarrow \infty$, and convert the sum into an integral. Since the allowed \vec{k} 's are $\frac{2\pi}{L}(m_x, m_y, m_z)$, the \vec{k} -space volume per allowed \vec{k} is $(2\pi)^3/L^3$. Hence, we can take the infinite-volume limit by making the replacement:

$$\begin{aligned}\sum_{\vec{k}} f(\vec{k}) &= \frac{1}{(\Delta\vec{k})^3} \sum_{\vec{k}} f(\vec{k}) (\Delta\vec{k})^3 \\ &= \frac{L^3}{(2\pi)^3} \int d^3\vec{k} f(\vec{k})\end{aligned}\quad (3.36)$$

Hence,

$$\begin{aligned}E &= 2V \int_0^{k_{\max}} \frac{d^3k}{(2\pi)^3} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \\ &= 2V \int_0^{k_{\max}} \frac{d^3k}{(2\pi)^3} \frac{\hbar ck}{e^{\beta\hbar ck} - 1} \\ &= \frac{Vk_B^4}{\pi^2(\hbar c)^3} T^4 \int_0^{\beta\hbar ck_{\max}} \frac{x^3 dx}{e^x - 1}\end{aligned}\quad (3.37)$$

For $\beta\hbar ck_{\max} \gg 1$,

$$E = \frac{Vk_B^4}{\pi^2(\hbar c)^3} T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}\quad (3.38)$$

and

$$C_V = \frac{4Vk_B^4}{\pi^2(\hbar c)^3} T^3 \int_0^\infty \frac{x^3 dx}{e^x - 1}\quad (3.39)$$

For $\beta\hbar ck_{\max} \ll 1$,

$$E = \frac{Vk_{\max}^3}{3\pi^2} k_B T\quad (3.40)$$

and

$$C_V = \frac{Vk_{\max}^3 k_B}{3\pi^2}\quad (3.41)$$

3.3 Fermi-Dirac Distribution

For a system of free fermions, the partition function

$$Z = \sum_{E_a, N} e^{-\beta(E_a - \mu N)}\quad (3.42)$$

can again be rewritten in terms of the *single-particle eigenstates* and the single-particle energies ϵ_i :

$$E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \dots \quad (3.43)$$

but now

$$n_i = 0, 1 \quad (3.44)$$

so that

$$\begin{aligned} Z &= \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i - \mu \sum_i n_i)} \\ &= \prod_i \left(\sum_{n_i=0}^1 e^{-\beta(n_i \epsilon_i - \mu n_i)} \right) \\ &= \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \end{aligned} \quad (3.45)$$

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \quad (3.46)$$

The chemical potential is chosen so that

$$N = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \quad (3.47)$$

The energy is given by

$$E = \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} + 1} \quad (3.48)$$

3.4 Thermodynamics of the Free Fermion Gas

Free electron gas in a box of side L :

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \quad (3.49)$$

with

$$k = \frac{2\pi}{L} (m_x, m_y, m_z) \quad (3.50)$$

Then, taking into account the 2 spin states,

$$\begin{aligned}
 E &= 2 \sum_{m_x, m_y, m_z} \epsilon_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle \\
 &= 2V \int_0^{k_{\max}} \frac{d^3 k}{(2\pi)^3} \frac{\frac{\hbar^2 k^2}{2m}}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} \\
 (3.51)
 \end{aligned}$$

$$N = 2V \int_0^{k_{\max}} \frac{d^3 k}{(2\pi)^3} \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} \quad (3.52)$$

At $T = 0$,

$$\frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} = \theta\left(\mu - \frac{\hbar^2 k^2}{2m}\right) \quad (3.53)$$

All states with energies less than μ are filled; all states with higher energies are empty.

We write

$$k_F = \frac{\sqrt{2m\mu_{T=0}}}{\hbar}, \quad \epsilon_F = \mu_{T=0} \quad (3.54)$$

$$\frac{N}{V} = 2 \int_0^{k_F} \frac{d^3 k}{(2\pi)^3} = \frac{k_F^3}{3\pi^2} \quad (3.55)$$

$$\begin{aligned}
 \frac{E}{V} &= 2 \int_0^{k_F} \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \\
 &= \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \\
 &= \frac{3}{5} \frac{N}{V} \epsilon_F \quad (3.56)
 \end{aligned}$$

$$2 \int \frac{d^3 k}{(2\pi)^3} = \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int d\epsilon \epsilon^{\frac{1}{2}} \quad (3.57)$$

For $k_B T \ll \epsilon_F$,

$$\begin{aligned}
 \frac{N}{V} &= \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \\
 &= \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} + \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} \left(\frac{1}{e^{\beta(\epsilon - \mu)} + 1} - 1 \right) + \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon - \mu)} + 1}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} - \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{-\beta(\epsilon-\mu)} + 1} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty \frac{k_B T dx}{e^x + 1} \left((\mu + k_B T x)^{\frac{1}{2}} - (\mu - k_B T x)^{\frac{1}{2}} \right) + O(e^{-\beta\mu}) \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} + \frac{(2m)^{\frac{3}{2}}}{\pi^2\hbar^3} \sum_{n=1}^{\infty} (k_B T)^{2n} \left[\mu^{\frac{3}{2}-2n} \frac{1}{(2n-1)!} \frac{\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{5}{2}-2n\right)} \int_0^\infty dx \frac{x^{2n-1}}{e^x + 1} \right] \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} \left[1 + \frac{3}{2} \left(\frac{k_B T}{\mu} \right)^2 I_1 + O(T^4) \right] \tag{3.58}
\end{aligned}$$

with

$$I_k = \int_0^\infty dx \frac{x^k}{e^x + 1} \tag{3.59}$$

We will only need

$$I_1 = \frac{\pi^2}{12} \tag{3.60}$$

Hence,

$$(\epsilon_F)^{\frac{3}{2}} = \mu^{\frac{3}{2}} \left[1 + \frac{3}{2} \left(\frac{k_B T}{\mu} \right)^2 I_1 + O(T^4) \right] \tag{3.61}$$

To lowest order in T , this gives:

$$\begin{aligned}
\mu &= \epsilon_F \left(1 - \left(\frac{k_B T}{\epsilon_F} \right)^2 I_1 + O(T^4) \right) \\
&= \epsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + O(T^4) \right) \tag{3.62}
\end{aligned}$$

$$\begin{aligned}
\frac{E}{V} &= \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} \left(\frac{1}{e^{\beta(\epsilon-\mu)} + 1} - 1 \right) + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} - \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{-\beta(\epsilon-\mu)} + 1} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty \frac{k_B T dx}{e^x + 1} \left((\mu + k_B T x)^{\frac{3}{2}} - (\mu - k_B T x)^{\frac{3}{2}} \right) + O(e^{-\beta\mu}) \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} + \frac{(2m)^{\frac{3}{2}}}{\pi^2\hbar^3} \sum_{n=1}^{\infty} (k_B T)^{2n} \left[\mu^{\frac{5}{2}-2n} \frac{1}{(2n-1)!} \frac{\Gamma\left(\frac{5}{2}\right)}{\Gamma\left(\frac{7}{2}-2n\right)} \int_0^\infty dx \frac{x^{2n-1}}{e^x + 1} \right]
\end{aligned}$$

$$\begin{aligned}
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} \left[1 + \frac{15}{2} \left(\frac{k_B T}{\mu} \right)^2 I_1 + O(T^4) \right] \\
&= \frac{3}{5} \frac{N}{V} \epsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + O(T^4) \right)
\end{aligned} \tag{3.63}$$

Hence, the specific heat of a gas of free fermions is:

$$C_V = \frac{\pi^2}{2} N k_B \frac{k_B T}{\epsilon_F} \tag{3.64}$$

Note that this can be written in the more general form:

$$C_V = (\text{const.}) \cdot k_B \cdot g(\epsilon_F) k_B T \tag{3.65}$$

The number of electrons which are thermally excited above the ground state is $\sim g(\epsilon_F) k_B T$; each such electron contributes energy $\sim k_B T$ and, hence, gives a specific heat contribution of k_B . Electrons give such a contribution to the specific heat of a metal.

3.5 Ising Model, Mean Field Theory, Phases

Consider a model of spins on a lattice in a magnetic field:

$$H = -g\mu_B B \sum_i S_i^z \equiv 2h \sum_i S_i^z \tag{3.66}$$

with $S_i^z = \pm 1/2$. The partition function for such a system is:

$$Z = \left(2 \cosh \frac{h}{k_B T} \right)^N \tag{3.67}$$

The average magnetization is:

$$S_i^z = \frac{1}{2} \tanh \frac{h}{k_B T} \tag{3.68}$$

The susceptibility, χ , is defined by

$$\chi = \left(\frac{\partial}{\partial h} \sum_i S_i^z \right)_{h=0} \tag{3.69}$$

For free spins on a lattice,

$$\chi = \frac{1}{2} N \frac{1}{k_B T} \quad (3.70)$$

A susceptibility which is inversely proportional to temperature is called a *Curie* susceptibility. In problem set 3, you will show that the susceptibility is much smaller for a system of electrons.

Now consider a model of spins on a lattice such that each spin interacts with its neighbors according to:

$$H = -\frac{1}{2} \sum_{\langle i,j \rangle} J S_i^z S_j^z \quad (3.71)$$

This Hamiltonian has a symmetry

$$S_i^z \rightarrow -S_i^z \quad (3.72)$$

For $k_B T \gg J$, the interaction between the spins will not be important and the susceptibility will be of the Curie form. For $k_B T < J$, however, the behavior will be much different. We can understand this qualitatively using *mean field theory*.

Let us approximate the interaction of each spin with its neighbors by an interaction with a mean-field, h :

$$H = -\sum_i h S_i^z \quad (3.73)$$

with h given by

$$h = \sum_i J \langle S_i^z \rangle = Jz \langle S_i^z \rangle \quad (3.74)$$

where z is the coordination number. In this field, the partition function is just $2 \cosh \frac{h}{k_B T}$ and

$$\langle S^z \rangle = \tanh \frac{h}{k_B T} \quad (3.75)$$

Using the self-consistency condition, this is:

$$\langle S^z \rangle = \tanh \frac{Jz \langle S^z \rangle}{k_B T} \quad (3.76)$$

For $k_B T < Jz$, this has non-zero solutions, $S^z \neq 0$ which break the symmetry $S_i^z \rightarrow -S_i^z$. In this *phase*, there is a spontaneous magnetization. For $k_B T > Jz$, there is only the solution $S^z = 0$. In this phase the symmetry is unbroken and there is no spontaneous magnetization. At $k_B T = Jz$, there is a critical point at which a phase transition occurs.

Broken Translational Invariance in the Solid State

4.1 Simple Energetics of Solids

Why do solids form? The Hamiltonian of the electrons and ions is:

$$H = \sum_i \frac{p_i^2}{2m_e} + \sum_a \frac{P_a^2}{2M} + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_{a>b} \frac{Z^2 e^2}{|R_a - R_b|} - \sum_{i,a} \frac{Z e^2}{|r_i - R_b|} \quad (4.1)$$

It is invariant under the symmetry, $\vec{r}_i \rightarrow \vec{r}_i + \vec{a}$, $\vec{R}_a \rightarrow \vec{R}_a + \vec{a}$. However, the energy can usually be minimized by forming a crystal. At low enough temperature, this will win out over any possible entropy gain in a competing state, so crystallization will occur. Why is the crystalline state energetically favorable? This depends on the type of crystal. Different types of crystals minimize different terms in the Hamiltonian. In *molecular and ionic crystals*, the potential energy is minimized. In a molecular crystal, such as solid nitrogen, there is a van der Waals attraction between molecules caused by polarization of one by the other. The van der Waals attraction is balanced by short-range repulsion, thereby leading to a crystalline ground state. In an ionic crystal, such as NaCl, the electrostatic energy of the ions is minimized (one must be careful to take into account charge neutrality, without which the electrostatic

energy diverges). In *covalent and metallic crystals*, crystallization is driven by the minimization of the electronic kinetic energy. In a metal, such as sodium, the kinetic energy of the electrons is lowered by their ability to move throughout the metal. In a covalent solid, such as diamond, the same is true. The kinetic energy gain is high enough that such a bond can even occur between just two molecules (as in organic chemistry). The energetic gain of a solid is called the *cohesive energy*.

4.2 Phonons: Linear Chain

4.3 Quantum Mechanics of a Linear Chain

As a toy model of a solid, let us consider a linear chain of masses m connected by springs with spring constant B . Suppose that the equilibrium spacing between the masses is a . The equilibrium positions define a $1D$ lattice. The lattice ‘vectors’, \vec{R}_j , are defined by:

$$\vec{R}_j = ja \quad (4.2)$$

They connect the origin to all points of the lattice. If \vec{R} and \vec{R}' are lattice vectors, then $\vec{R} + \vec{R}'$ are also lattice vectors. A set of basis vectors is a minimal set of vectors which generate the full set of lattice vectors by taking linear combinations of the basis vectors. In our $1D$ lattice, a is the basis vector.

Let u_i be the displacement of the i^{th} mass from its equilibrium position and let p_i be the corresponding momentum. Let us assume that there are N masses, and let’s impose a periodic boundary condition, $u_i = u_{i+N}$. The Hamiltonian for such a system is:

$$H = \frac{1}{2m} \sum_i p_i^2 + \frac{1}{2} B \sum_i (u_i - u_{i+1})^2 \quad (4.3)$$

Let us use the Fourier transform representation:

$$\begin{aligned} u_j &= \frac{1}{\sqrt{N}} \sum_k u_k e^{ikja} \\ p_j &= \frac{1}{\sqrt{N}} \sum_k p_k e^{ikja} \end{aligned} \quad (4.4)$$

As a result of the periodic boundary condition, the allowed k 's are:

$$k = \frac{2\pi n}{Na} \quad (4.5)$$

We can invert (4.4):

$$\begin{aligned} \frac{1}{\sqrt{N}} \sum_j u_j e^{ik'ja} &= \frac{1}{N} \sum_k \sum_j u_k e^{i(k-k')ja} \\ \frac{1}{\sqrt{N}} \sum_j u_j e^{ik'ja} &= u_{k'} \end{aligned} \quad (4.6)$$

Note that $u_k^\dagger = u_{-k}$, $p_k^\dagger = p_{-k}$ since $u_j^\dagger = u_j$, $p_j^\dagger = p_j$. They satisfy the commutation relations:

$$\begin{aligned} [p_k, u_{k'}] &= \frac{1}{N} \sum_{j,j'} e^{ikja} e^{ik'j'a} [p_j, u_{j'}] \\ &= \frac{1}{N} \sum_{j,j'} e^{ikja} e^{ik'j'a} - i\hbar \delta_{jj'} \\ &= -i\hbar \frac{1}{N} \sum_j e^{i(k-k')ja} \\ &= -i\hbar \delta_{kk'} \end{aligned} \quad (4.7)$$

Hence, p_k and $u_{k'}$ commute unless $k = k'$.

The displacements described by u_k are the same as those described by $u_{k+\frac{2\pi m}{a}}$ for any integer n :

$$\begin{aligned} u_{k+\frac{2\pi m}{a}} &= \frac{1}{\sqrt{N}} \sum_j u_j e^{-i(k+\frac{2\pi m}{a})ja} \\ &= \frac{1}{\sqrt{N}} \sum_j u_j e^{-ikja} \\ &= u_k \end{aligned} \quad (4.8)$$

Hence,

$$k \equiv k + \frac{2\pi m}{a} \quad (4.9)$$

Hence, we can restrict attention to $n = 0, 1, \dots, N-1$ in (4.5). The Hamiltonian can be rewritten:

$$H = \sum_k \frac{1}{2m} p_k p_{-k} + 2B \left(\sin \frac{ka}{2} \right)^2 u_k u_{-k} \quad (4.10)$$

Recalling the solution of the harmonic oscillator problem, we define:

$$\begin{aligned} a_k &= \frac{1}{\sqrt{2\hbar}} \left[\left(4mB \left(\sin \frac{ka}{2} \right)^2 \right)^{\frac{1}{4}} u_k + \frac{i}{\left(4mB \left(\sin \frac{ka}{2} \right)^2 \right)^{\frac{1}{4}}} p_k \right] \\ a_k^\dagger &= \frac{1}{\sqrt{2\hbar}} \left[\left(4mB \left(\sin \frac{ka}{2} \right)^2 \right)^{\frac{1}{4}} u_{-k} - \frac{i}{\left(4mB \left(\sin \frac{ka}{2} \right)^2 \right)^{\frac{1}{4}}} p_{-k} \right] \end{aligned} \quad (4.11)$$

(Recall that $u_k^\dagger = u_{-k}$, $p_k^\dagger = p_{-k}$.) which satisfy:

$$[a_k, a_k^\dagger] = 1 \quad (4.12)$$

Then:

$$H = \sum_k \hbar \omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right) \quad (4.13)$$

with

$$\omega_k = 2 \left(\frac{B}{m} \right)^{\frac{1}{2}} \left| \sin \frac{ka}{2} \right| \quad (4.14)$$

Hence, the linear chain is equivalent to a system of N independent harmonic oscillators. Its thermodynamics can be described by the Planck distribution.

The operators a_k^\dagger, a_k are said to create and annihilate *phonons*. We say that a state $|\psi\rangle$ with

$$a_k^\dagger a_k |\psi\rangle = N_k |\psi\rangle \quad (4.15)$$

has N_k phonons of momentum k . Phonons are the quanta of lattice vibrations, analogous to photons, which are the quanta of oscillations of the electromagnetic field.

Observe that, as $k \rightarrow 0$, $\omega_k \rightarrow 0$:

$$\begin{aligned}\omega_{k \rightarrow 0} &= \left(\frac{Ba}{m/a} \right)^{\frac{1}{2}} k \\ &= \left(\frac{Ba}{\rho} \right)^{\frac{1}{2}} k\end{aligned}\quad (4.16)$$

The physical reason for this is simple: an oscillation with $k = 0$ is a uniform translation of the linear chain, which costs no energy.

Note that the reason for this is that the Hamiltonian is invariant under translations $u_i \rightarrow u_i + \lambda$. However, the ground state is not: the masses are located at the points $x_j = ja$. Translational invariance has been spontaneously broken. Of course, it could just as well be broken with $x_j = ja + \lambda$ and, for this reason, $\omega_k \rightarrow 0$ as $k \rightarrow 0$. An oscillatory mode of this type is called a *Goldstone mode*.

Consider now the case in which the masses are not equivalent. Let the masses alternate between m and M . As we will see, the *phonon spectra* will be more complicated. Let a be the distance between one m and the next m . The Hamiltonian is:

$$H = \sum_i \left(\frac{1}{2m} p_{1,i}^2 + \frac{1}{2M} p_{2,i}^2 + \frac{1}{2} B (u_{1,i} - u_{2,i})^2 + \frac{1}{2} B (u_{2,i} - u_{1,i+1})^2 \right) \quad (4.17)$$

The equations of motion are:

$$\begin{aligned}m \frac{d^2}{dt^2} u_{1,i} &= -B [(u_{1,i} - u_{2,i}) - (u_{2,i-1} - u_{1,i})] \\ M \frac{d^2}{dt^2} u_{2,i} &= -B [(u_{2,i} - u_{1,i}) + (u_{2,i} - u_{1,i+1})]\end{aligned}\quad (4.18)$$

Going again to the Fourier representation, $\alpha = 1, 2$

$$u_{\alpha,j} = \frac{1}{\sqrt{N}} \sum_k u_{\alpha,k} e^{ikja} \quad (4.19)$$

Where the allowed k 's are:

$$k = \frac{2\pi}{N} n \quad (4.20)$$

if there are $2N$ masses. As before,

$$u_{\alpha,k} = u_{\alpha,k+\frac{2\pi n}{a}} \quad (4.21)$$

$$\begin{pmatrix} m \frac{d^2}{dt^2} & 0 \\ 0 & M \frac{d^2}{dt^2} \end{pmatrix} \begin{pmatrix} u_{1,k} \\ u_{2,k} \end{pmatrix} = \begin{pmatrix} 2B & -B(1+e^{ika}) \\ -B(1+e^{-ika}) & 2B \end{pmatrix} \begin{pmatrix} u_{1,k} \\ u_{2,k} \end{pmatrix} \quad (4.22)$$

Fourier transforming in time:

$$\begin{pmatrix} -m\omega_k^2 & 0 \\ 0 & -M\omega_k^2 \end{pmatrix} \begin{pmatrix} u_{1,k} \\ u_{2,k} \end{pmatrix} = \begin{pmatrix} 2B & -B(1+e^{ika}) \\ -B(1+e^{-ika}) & 2B \end{pmatrix} \begin{pmatrix} u_{1,k} \\ u_{2,k} \end{pmatrix} \quad (4.23)$$

This eigenvalue equation has the solutions:

$$\omega_{\pm}^2 = B \left[\frac{1}{M} + \frac{1}{m} \pm \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{nM} \left(\sin \frac{ka}{2}\right)^2} \right] \quad (4.24)$$

Observe that

$$\omega_{k \rightarrow 0}^- = \left(\frac{Ba}{2(m+M)/a} \right)^{\frac{1}{2}} k \quad (4.25)$$

This is the *acoustic* branch of the phonon spectrum in which m and M move in phase. As $k \rightarrow 0$, this is a translation, so $\omega_k^- \rightarrow 0$. Acoustic phonons are responsible for sound. Also note that

$$\omega_{k=\pi/a}^- = \left(\frac{2B}{M} \right)^{\frac{1}{2}} \quad (4.26)$$

Meanwhile, ω^+ is the *optical* branch of the spectrum (these phonons scatter light), in which m and M move in opposite directions.

$$\omega_{k \rightarrow 0}^+ = \sqrt{2B \left(\frac{1}{m} + \frac{1}{M} \right)} \quad (4.27)$$

$$\omega_{k=\pi/a}^+ = \left(\frac{2B}{m} \right)^{\frac{1}{2}} \quad (4.28)$$

so there is a gap in the spectrum of width

$$\omega_{\text{gap}} = \left(\frac{2B}{m} \right)^{\frac{1}{2}} - \left(\frac{2B}{M} \right)^{\frac{1}{2}} \quad (4.29)$$

Note that if we take $m = M$, we recover the previous results, with $a \rightarrow a/2$.

This is an example of what is called a *lattice with a basis*. Not every site on the chain is equivalent. We can think of the chain of $2N$ masses as a lattice with N sites. Each lattice site has a two-site basis: one of these sites has a mass m and the other has a mass M . Sodium Chloride is a simple subic lattice with a two-site basis: the sodium ions are at the vertices of an FCC lattice and the chlorine ions are displaced from them.

4.3.1 Statistical Mechanics of a Linear Chain

Let us return to the case of a linear chain of masses m separated by springs of force constant B , at equilibrium distance a . The excitations of this system are phonons which can have momenta $k \in [-\pi/a, \pi/a]$ (since $k \equiv k + \frac{2\pi m}{a}$), corresponding to energies

$$\hbar\omega_k = 2\left(\frac{B}{m}\right)^{\frac{1}{2}} \left| \sin \frac{ka}{2} \right| \quad (4.30)$$

Phonons are bosons whose number is not conserved, so they obey the Planck distribution. Hence, the energy of a linear chain at finite temperature is given by:

$$\begin{aligned} E &= \sum_k \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \\ &= L \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \end{aligned} \quad (4.31)$$

Changing variables from k to ω ,

$$\begin{aligned} E &= 2 \cdot \frac{L}{2\pi} \int_0^{\sqrt{4B/m}} \frac{2}{a} \frac{d\omega}{\sqrt{\frac{4B}{m} - \omega^2}} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= \frac{2N}{\pi} \int_0^{\sqrt{4B/m}} \frac{d\omega}{\sqrt{\frac{4B}{m} - \omega^2}} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= \frac{2N}{\pi} \frac{(k_B T)^2}{\hbar} \int_0^{\beta\hbar\sqrt{4B/m}} \frac{1}{\sqrt{\frac{4B}{m} - \left(\frac{x}{\beta\hbar}\right)^2}} \frac{x dx}{e^x - 1} \end{aligned} \quad (4.32)$$

In the limit $k_B T \ll \hbar\sqrt{4B/m}$, we can take the upper limit of integration to ∞ and drop the x -dependent term in the square root in the denominator of the integrand:

$$E = \frac{N}{\pi} \sqrt{\frac{m}{4B}} \frac{(k_B T)^2}{\hbar} \int_0^\infty \frac{x dx}{e^x - 1} \quad (4.33)$$

Hence, $C_v \sim T$ at low temperatures.

In the limit $k_B T \gg \hbar\sqrt{4B/m}$, we can approximate $e^x \approx 1 + x$:

$$\begin{aligned} E &= \frac{2N}{\pi} \frac{(k_B T)^2}{\hbar} \int_0^{\beta\hbar\sqrt{4B/m}} \frac{dx}{\sqrt{\frac{4B}{m} - \left(\frac{x}{\beta\hbar}\right)^2}} \\ &= Nk_B \end{aligned} \quad (4.34)$$

In the intermediate temperature regime, a more careful analysis is necessary. In particular, note that the density of states, $1/\sqrt{\frac{4B}{m} - \omega^2}$ diverges at $\omega = \sqrt{4B/m}$; this is an example of a *van Hove singularity*. If we had alternating masses on springs, then the expression for the energy would have two integrals, one over the acoustic modes and one over the optical modes.

4.4 Lessons from the 1D chain

In the course of our analysis of the 1D chain, we developed the following strategy, which we will apply to crystals more generally in subsequent sections.

- Expand the Hamiltonian to Quadratic Order
- Fourier transform the Hamiltonian into momentum space
- Identify the Brillouin zone (range of distinct \vec{k} s)
- Rewrite the Hamiltonian in terms of creation and annihilation operators

- Obtain the Spectrum
- Compute the Density of States
- Use the Planck distribution to obtain the thermodynamics of the vibrational modes of the crystal.

4.5 Discrete Translational Invariance: the Reciprocal Lattice, Brillouin Zones, Crystal Momentum

Note that, in the above, momenta were only defined up to $\frac{2\pi n}{a}$. The momenta $\frac{2\pi n}{a}$ form a lattice in k -space, called the reciprocal lattice. This is true of any function which, like the ionic displacements, is a function defined at the lattice sites. For such a function, $f(\vec{R})$, defined on an arbitrary lattice, the Fourier transform

$$\tilde{f}(\vec{k}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} f(\vec{R}) \quad (4.35)$$

satisfies

$$\tilde{f}(\vec{k}) = \tilde{f}(\vec{k} + \vec{G}) \quad (4.36)$$

if \vec{G} is in the set of reciprocal lattice vectors, defined by:

$$e^{i\vec{G}\cdot\vec{R}} = 1, \text{ for all } \vec{R} \quad (4.37)$$

The reciprocal lattice vectors also form a lattice since the sum of two reciprocal lattice vectors is also a reciprocal lattice vector. This lattice is called the *reciprocal lattice* or *dual lattice*.

In the analysis of the linear chain, we restricted momenta to $|k| < \pi/a$ to avoid double-counting of degrees of freedom. This restricted region in k -space is an example

of a *Brillouin zone* (or a first Brillouin zone). All of k -space can be obtained by translating the Brillouin zone through all possible reciprocal lattice vectors. We could have chosen our Brillouin zone differently by taking $0 < k < 2\pi/a$. Physically, there is no difference; the choice is a matter of convenience. What we need is a set of points in k space such that no two of these points are connected by a reciprocal lattice vector *and* such that all of k space can be obtained by translating the Brillouin zone through all possible reciprocal lattice vectors. We could even choose a Brillouin zone which is not connected, e.g. $0 < k < \pi/a$. or $3\pi/a < k < 4\pi/a$.

Later, we will consider solids with a more complicated lattice structure than our linear chain. Once again, phonon spectra will be defined in the Brillouin zone. Since $\tilde{f}(\vec{k}) = \tilde{f}(\vec{k} + \vec{G})$, the phonon modes outside of the Brillouin zone are not physically distinct from those inside. One way of defining the Brillouin zone for an arbitrary lattice is to take all points in k space which are closer to the origin than to any other point of the reciprocal lattice. Such a choice of Brillouin zone is also called the Wigner-Seitz cell of the reciprocal lattice. We will discuss this in some detail later but, for now, let us consider the case of a cubic lattice. The lattice vectors of a cubic lattice of side a are:

$$\vec{R}_{n_1, n_2, n_3} = a(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}) \quad (4.38)$$

The reciprocal lattice vectors are:

$$\vec{G}_{m_1, m_2, m_3} = \frac{2\pi}{a}(m_1\hat{x} + m_2\hat{y} + m_3\hat{z}) \quad (4.39)$$

The reciprocal lattice vectors also form a cubic lattice. The first Brillouin zone (Wigner-Seitz cell of the reciprocal lattice) is given by the cube of side $\frac{2\pi}{a}$ centered at the origin. The volume of this cube is related to the density according to:

$$\int_{\text{B.Z.}} \frac{d^3k}{(2\pi)^3} = \frac{1}{a^3} = \frac{N_{\text{ions}}}{V} \quad (4.40)$$

As we have noted before, the ground state (and the Hamiltonian) of a crystal is invariant under the discrete group of translations through all lattice vectors. Whereas

full translational invariance leads to momentum conservation, lattice translational symmetry leads to the conservation of *crystal momentum* – momentum up to a reciprocal lattice vector. (See Ashcroft and Mermin, appendix M.) For instance, in a collision between phonons, the difference between the incoming and outgoing phonon momenta can be any reciprocal lattice vector, G . Physically, one may think of the missing momentum as being taken by the lattice as a whole. This concept will also be important when we consider the problem of electrons moving in the background of a lattice of ions.

4.6 Phonons: Continuum Elastic Theory

Consider the lattice of ions in a solid. Suppose the equilibrium positions of the ions are the sites \vec{R}_i . Let us describe small displacements from these sites by a displacement field $\vec{u}(\vec{R}_i)$. We will imagine that the crystal is just a system of masses connected by springs of equilibrium length a .

Before considering the details of the possible lattice structures of $2D$ and $3D$ crystals, let us consider the properties of a crystal at length scales which are much larger than the lattice spacing; this regime should be insensitive to many details of the lattice. At length scales much longer than its lattice spacing, a crystalline solid can be modelled as an elastic medium. We replace $\vec{u}(\vec{R}_i)$ by $\vec{u}(\vec{r})$ (i.e. we replace the lattice vectors, \vec{R}_i , by a continuous variable, \vec{r}). Such an approximation is valid at length scales much larger than the lattice spacing, a , or, equivalently, at wavevectors $q \ll 2\pi/a$.

In $1D$, we can take the continuum limit of our model of masses and springs:

$$\begin{aligned} H &= \frac{1}{2} m \sum_i \left(\frac{du_i}{dt} \right)^2 + \frac{1}{2} B \sum_i (u_i - u_{i+1})^2 \\ &= \frac{1}{2} \frac{m}{a} \sum_i a \left(\frac{du_i}{dt} \right)^2 + \frac{1}{2} Ba \sum_i a \left(\frac{u_i - u_{i+1}}{a} \right)^2 \end{aligned}$$

$$\rightarrow \int dx \left(\frac{1}{2}\rho \left(\frac{du}{dt} \right)^2 + \frac{1}{2}\overline{B} \left(\frac{du}{dx} \right)^2 \right) \quad (4.41)$$

where ρ is the mass density and \overline{B} is the bulk modulus. The equation of motion,

$$\frac{d^2u}{dt^2} = \overline{B} \frac{d^2u}{dx^2} \quad (4.42)$$

has solutions

$$u(x, t) = \sum_k u_k e^{i(kx - \omega t)} \quad (4.43)$$

with

$$\omega = \sqrt{\frac{\overline{B}}{\rho}} k \quad (4.44)$$

The generalization to a 3D continuum elastic medium is:

$$\rho \partial_t^2 \vec{u} = (\mu + \lambda) \vec{\nabla} (\vec{\nabla} \cdot \vec{u}) + \mu \nabla^2 \vec{u} \quad (4.45)$$

where ρ is the mass density of the solid and μ and λ are the Lamé coefficients. Under a dilatation, $\vec{u}(\vec{r}) = \alpha \vec{r}$, the change in the energy density of the elastic medium is $\alpha^2(\lambda + 2\mu/3)/2$; under a shear stress, $u_x = \alpha y, u_y = u_z = 0$, it is $\alpha^2\mu/2$. In a crystal – which has only a discrete rotational symmetry – there may be more parameters than just μ and λ , depending on the symmetry of the lattice. In a crystal with cubic symmetry, for instance, there are, in general, three independent parameters. We will make life simple, however, and make the approximation of full rotational invariance.

The solutions are,

$$\vec{u}(\vec{r}, t) = \vec{\epsilon} e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (4.46)$$

where $\vec{\epsilon}$ a unit polarization vector, satisfy

$$-\rho\omega^2\vec{\epsilon} = -(\mu + \lambda)\vec{k}(\vec{k} \cdot \vec{\epsilon}) - \mu k^2\vec{\epsilon} \quad (4.47)$$

For longitudinally polarized waves, $\vec{k} = k\vec{\epsilon}$,

$$\omega_k^l = \pm \sqrt{\frac{2\mu + \lambda}{\rho}} k \equiv \pm v_l k \quad (4.48)$$

while transverse waves, $\vec{k} \cdot \vec{\epsilon} = 0$ have

$$\omega_k^t = \pm \sqrt{\frac{\mu}{\rho}} k \equiv \pm v_s k \quad (4.49)$$

Above, we introduced the concept of the polarization of a phonon. In 3D, the displacements of the ions can be in any direction. The two directions perpendicular to \vec{k} are called *transverse*. Displacements along \vec{k} are called *longitudinal*.

The Hamiltonian of this system,

$$H = \int d^3r \left(\frac{1}{2} \rho (\dot{\vec{u}})^2 + \frac{1}{2} (\mu + \lambda) (\vec{\nabla} \cdot \vec{u})^2 - \frac{1}{2} \mu \vec{u} \cdot \nabla^2 \vec{u} \right) \quad (4.50)$$

can be rewritten in terms of creation and annihilation operators,

$$\begin{aligned} a_{k,s} &= \frac{1}{\sqrt{2\hbar}} \left[\sqrt{\rho\omega_{k,s}} \vec{\epsilon}_s \cdot \vec{u}_k + i \sqrt{\frac{\rho}{\omega_{k,s}}} \vec{\epsilon}_s \cdot \dot{\vec{u}}_k \right] \\ a_{k,s}^\dagger &= \frac{1}{\sqrt{2\hbar}} \left[\sqrt{\rho\omega_{k,s}} \vec{\epsilon}_s \cdot \vec{u}_{-k} - i \sqrt{\frac{\rho}{\omega_{k,s}}} \vec{\epsilon}_s \cdot \dot{\vec{u}}_{-k} \right] \end{aligned} \quad (4.51)$$

as

$$H = \sum_{k,s} \hbar\omega_{k,s} \left(a_{k,s}^\dagger a_{k,s} + \frac{1}{2} \right) \quad (4.52)$$

Inverting the above definitions, we can express the displacement $\vec{u}(\vec{r})$ in terms of the creation and annihilation operators:

$$\vec{u}(\vec{r}) = \sum_{k,s} \sqrt{\frac{\hbar}{2\rho V \omega_k^s}} \vec{\epsilon}_s \left(a_{\vec{k},s} + a_{-\vec{k},s}^\dagger \right) e^{i\vec{k} \cdot \vec{r}} \quad (4.53)$$

$s = 1, 2, 3$ corresponds to the longitudinal and two transverse polarizations. Acting with \vec{u}_k either annihilates a phonon of momentum k or creates a phonon of momentum $-k$.

The allowed \vec{k} values are determined by the boundary conditions in a finite system. For periodic boundary conditions in a cubic system of size $V = L^3$, the allowed \vec{k} 's are $\frac{2\pi}{L} (n_1, n_2, n_3)$. Hence, the \vec{k} -space volume per allowed \vec{k} is $(2\pi)^3/V$. Hence, we can take the infinite-volume limit by making the replacement:

$$\sum_k f(\vec{k}) = \frac{1}{(\Delta\vec{k})^3} \sum_k f(\vec{k}) (\Delta\vec{k})^3$$

$$= \frac{V}{(2\pi)^3} \int d^3\vec{k} f(\vec{k}) \quad (4.54)$$

4.7 Debye theory

Since a solid can be modelled as a collection of independent oscillators, we can obtain the energy in thermal equilibrium using the Planck distribution function:

$$E = V \sum_s \int_{\text{B.Z.}} \frac{d^3k}{(2\pi)^3} \frac{\hbar\omega_s(k)}{e^{\beta\hbar\omega_s(k)} - 1} \quad (4.55)$$

where $s = 1, 2, 3$ are the three polarizations of the phonons and the integral is over the Brillouin zone.

This can be rewritten in terms of the phonon density of states, $g(\omega)$ as:

$$E = V \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad (4.56)$$

where

$$g(\omega) = \sum_s \int_{\text{B.Z.}} \frac{d^3k}{(2\pi)^3} \delta(\omega - \omega_s(k)) \quad (4.57)$$

The total number of states is given by:

$$\begin{aligned} \int_0^\infty d\omega g(\omega) &= \int_0^\infty d\omega \sum_s \int_{\text{B.Z.}} \frac{d^3k}{(2\pi)^3} \delta(\omega - \omega_s(k)) \\ &= 3 \int_{\text{B.Z.}} \frac{d^3k}{(2\pi)^3} \\ &= 3 \frac{N_{\text{ions}}}{V} \end{aligned} \quad (4.58)$$

The total number of normal modes is equal to the total number of ion degrees of freedom.

For a continuum elastic medium, there are two transverse modes with velocity v_t and one longitudinal mode with velocity v_l . In the limit that the lattice spacing is

very small, $a \rightarrow 0$, we expect this theory to be valid. In this limit, the Brillouin zone is all of momentum space, so

$$\begin{aligned} g_{\text{CEM}}(\omega) &= \int \frac{d^3k}{(2\pi)^3} (2\delta(\omega - v_t k) + \delta(\omega - v_l k)) \\ &= \frac{1}{2\pi^2} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \omega^2 \end{aligned} \quad (4.59)$$

In a crystalline solid, this will be a reasonable approximation to $g(\omega)$ for $k_B T \ll \hbar v_t/a$ where the only phonons present will be at low energies, far from the Brillouin zone boundary. At high temperatures, there will be thermally excited phonons near the Brillouin zone boundary, where the spectrum is definitely not linear, so we cannot use the continuum approximation. In particular, this $g(\omega)$ does not have a finite integral, which violates the condition that the integral should be the total number of degrees of freedom.

A simple approximation, due to Debye, is to replace the Brillouin zone by a sphere of radius k_D and assume that the spectrum is linear up to k_D . In other words, Debye assumed that:

$$g_D(\omega) = \begin{cases} \frac{3}{2\pi^2 v^3} \omega^2 & \text{if } \omega < \omega_D \\ 0 & \text{if } \omega > \omega_D \end{cases}$$

Here, we have assumed, for simplicity, that $v_l = v_t$ and we have written $\omega_D = v k_D$. ω_D is chosen so that

$$\begin{aligned} 3 \frac{N_{\text{ions}}}{V} &= \int_0^\infty d\omega g(\omega) \\ &= \int_0^{\omega_D} d\omega \frac{3}{2\pi^2 v^3} \omega^2 \\ &= \frac{\omega_D^3}{2\pi^2 v^3} \end{aligned} \quad (4.60)$$

i.e.

$$\omega_D = \left(6\pi^2 v^3 N_{\text{ions}}/V \right)^{\frac{1}{3}} \quad (4.61)$$

With this choice,

$$E = V \int_0^{\omega_D} d\omega \frac{3}{2\pi^2 v^3} \omega^2 \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$