1 3C25: Density of States, Phonons and Electron States

By the *density of states* of a system we normally mean the number of allowed energy levels of that system per unit energy interval. In this note we aim to show why this is a useful concept, and how the density of states may be derived for a few simple systems. We consider these two points in reverse order.

1.1 Why is the density of states useful?

The density of states plays a central role in many physical situations. The reason for this is quite simple: when one considers which states of a system are occupied, the energy of the states is the controlling factor. Thus such properties as total energies may be derived from a knowledge of the density of states, as may changes of energy with temperature. Similarly, in a Fermi system, many properties are determined by the number of electrons which within a small energy (thermal energy) of the Fermi surface[1] – this in turn is determined by the density of states at the Fermi energy. The fundamental difference between an insulator and a conductor, for example, is that in the former the density of states at the Fermi energy is zero, in the latter it is non- zero. Paramagnetism of a free electron gas, too, is determined by the density of states at the Fermi energy.

Some measurements can measure the density of electronic states in a fairly direct way. The photoelectron spectrum is one example. Electrons released from a material by x-rays of energy $h\nu$ are passed through a spectrometer to measure their kinetic energy E_k, and their binding energy E_b is thus obtained from

$$E_b = h\nu - E_k, \tag{1}$$

and the number of electrons released with each energy gives the density of states – or, to be more precise, the product of the density of states with the Fermi function. It is possible to use the inverse process (inverse photoelectron spectroscopy or bremsstrahlung spectroscopy) to look at the density of states in the unoccupied regime. In this technique, electrons of known energy are fired at a solid. Some of them will enter empty states in the energy bands of the solid, emitting a photon in the process. Again, from the numbers of photons emitted at different energies a picture may be built up of the product of the density of states and the complement of the Fermi function. Somewhat similar information may be derived from x-ray spectroscopy, in which electronic transitions are made to and from the core levels of atoms in the solid, which have sharply-defined energies.

Naturally, the density of states cannot tell us everything about every process. In considering transport processes such as thermal and electrical conductivity we need to consider the scattering of the particles or excitations involved in the transport (phonons and/or electrons in the former case, electrons and holes and/or ions in the latter case). In the scattering event both energy and momentum must be preserved, so more than a density of states is necessary.

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[1] If one takes, rather arbitrarily, the important energy range to be that over which the Fermi function takes values between 0.9 and 0.1, the range is $E_F - 2.2kT$ to $E_F + 2.2kT$.

1.2 Evaluating the density of states

In principle, the density of states may be computed exactly, by calculating the energies of all the allowed states in the specimen. This is foolproof, applicable to liquids and crystalline, defective and amorphous solids. Unfortunately, except for perfect crystalline systems, it is impossible – approximations have to be made. The idea of solving the wave equation for the whole system, however, brings into focus the importance of the boundary conditions without which the problem is undetermined. Whether we are dealing with phonons and a classical wave equation or electrons and the Schrödinger equation, the size of the macroscopic system determines the boundary conditions.

Consider, then, a perfect periodic system in one dimension, of length L, with a unit cell dimension a. There are two ways of choosing the boundary conditions, and in each case the eigenfunctions will satisfy Bloch's theorem and be labelled by a wavevector k:

1. rigid boundaries, with the wave function equal to zero at the boundaries[2], leading to wave functions of the form $\phi_k(x)\sin(kx)$;

2. periodic boundaries, in which the system is looped back on itself and the displacements at $x = 0$ are the same as those at $x = L$. The solutions are then running waves, $\phi_k(x)\exp(\pm ikx)$.

The functions $\phi_k(x)$ are periodic with the period of the *lattice* (repeat distance a).

1.2.1 Transition from summation to integral

It is worth justifying the transition from a summation over discrete states to an integral over a continuous energy distribution. Consider a cubic specimen of side length $L = 0.01$ m, treated as an infinitely deep potential well. The eigenstates have energies $E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$, that is, $(n_x^2 + n_y^2 + n_z^2) \times 3 \times 10^{-15}$ eV. In a typical system, the width of a band will be a few electron volts - say 3 eV. Thus if $n_x^2 = n_y^2 = n_z^2$ we have $n_x \approx 1.6 \times 10^7$. To find the energy spacing near the top of the band we may calculate the energy difference between the state (n_x, n_y, n_z) and $(n_x - 1, n_y, n_z)$, which is 1.2×10^{-7}eV. This is very small, and the assumption of a continuum of energies is a good one.

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[2] For elastic waves, it could be argued that a more realistic boundary condition would be to have zero stresses, not zero displacements, at the boundaries. This would merely change the form of the eigenfunction from a sine to a cosine, and would not affect the density of states.

It is instructive to compare the two choices of boundary condition.

Rigid boundaries	**Periodic boundaries**
The eigenfunctions must be zero at $x = 0$ and $x = L = Na$, so that $$\sin(kL) = 0 \qquad (2)$$ or $$k = n\frac{\pi}{L}, \qquad (3)$$ that is, the states are uniformly distributed in k-space with separation π/L. The density of states in k-space is therefore the inverse of the spacing, $$g(k) = L/\pi.$$ In this case states k and $-k$ are equivalent, as $$\sin(-kx) = -\sin(kx), \qquad (4)$$ and the two wavefunctions differ only by a constant multiplier. The allowed values of n are $n = 1, 2, ..N-1$, since if we set $n = 0$ we have a wavefunction which is identically zero. Similarly, if we take the wavefunction to be representative of the displacements of an atom, if $n = N$ the atomic displacements of the atoms at ma are $$\sin(N\pi ma/Na) = \sin(m\pi) = 0, \qquad (5)$$ and larger values of n repeat functions which have been generated by smaller values of n. Thus there are $N-1$ distinct wavefunctions, corresponding to the $N-1$ mobile atoms in the chain of $N+1$ atoms which is Na long. Each degree of freedom is thus accounted for. The density of states will generally appear in the form of an integral $$F(X) = \int_0^\infty f(k\vert X)g(k)dk \qquad (6)$$ where X represents such variables as temperature or field.	The eigenfunctions must be equal at $x = 0$ and L, so that $$\exp(ikL) = 1 \qquad (7)$$ or $$k = n\frac{2\pi}{L}, \qquad (8)$$ that is, the states are uniformly distributed in k-space with separation $2\pi/L$. The density of states in k-space is therefore the inverse of the spacing, $$g(k) = L/2\pi.$$ In this case states k and $-k$ are not equivalent, as $\exp(-ikx)$ and $\exp(ikx)$ are distinct functions. The allowed values of n are $n = -N/2, -(N/2-1), ..., 0, 1, 2, ..\ (N-1)/2$, giving N modes, again accounting for all the degrees of freedom. Note that this enumeration of the allowed values of n ensures that for even N one does not include both $n = -N/2$ and $n = N/2$, as these are equivalent: $$\begin{aligned} \exp(&- 2i(N/2)\pi ma/Na) = (-1)^m \\ &= \exp(2i(N/2)\pi ma/Na). \qquad (9) \end{aligned}$$ The density of states will generally appear in the form of an integral $$F(X) = \int_{-\infty}^\infty f(k\vert X)g(k)dk \qquad (10)$$ where X represents such variables as temperature or field: in many cases this may be written $$F(X) = 2\int_0^\infty f(k\vert X)g(k)dk \qquad (11)$$ thus recovering the result of the fixed boundary case.

1.3 Density of states in energy

Now consider how to relate the density of states in energy to the density of states in wavevector. First, assume that there is a one-to-one mapping from wavevector to energy through the function $E(\mathbf{k})$. Then the number of states in the energy interval E to $E + dE$ is the same as the number of states in the corresponding interval in $\mathbf{k}$ space.

1.3.1 One dimension

Here the number of states in the energy interval E to $E + dE$ is the same as the number of states in the corresponding interval k to $k + dk$,

$$g(E)dE = g(k)dk \tag{12}$$

or

$$g(E) = g(k)dk/dE. \tag{13}$$

That is, the density of states in reciprocal space, derived from the macroscopic boundary conditions on the system, is related through the dispersion relation dE/dk to the density of states in energy.

1.3.2 Two dimensions

Let us suppose that E depends only on the modulus of $\mathbf{k}$, that is, that the energy surface is isotropic (for a more general treatment, see the following section for the three-dimensional case). If we adopt the fixed boundary condition scheme, for a crystal L_x by L_y then in each dimension the allowed values of the corresponding component of $\mathbf{k}$ are spaced by the appropriate L/π. In an area of k space $dk_x dk_y$, then, the number of points will be

$$g(\mathbf{k})dk_x dk_y = \frac{L_x L_y}{\pi^2} dk_x dk_y \tag{14}$$

which may be written in polar coordinates as

$$g(\mathbf{k})kdkd\theta = \frac{L_x L_y}{\pi^2} kdkd\theta \tag{15}$$

and under the assumption that the property to be studied is also symmetrical in k the θ integral may be done at once to give

$$g(\mathbf{k})kdk = 2\frac{L_x L_y}{\pi} kdk. \tag{16}$$

Hence we obtain

$$g(E) = 2\frac{L_x L_y}{\pi} k/(dE/dk). \tag{17}$$

1.3.3 Three dimensions

Let us adopt a somewhat more formal treatment here. There are two approaches, one using a geometrical method and the other using properties of the Dirac delta function: we use the former. For each branch of the dispersion relation, we may write

$$g(\omega)d\omega = \int_{\text{shell}} g(\mathbf{k})d^3k, \tag{18}$$

where the shell represents that volume of k space for which the frequency lies between ω and $\omega + d\omega$. This shell may be represented geometrically by considering a constant energy surface S in k space. The gradient of ω with respect to $\mathbf{k}$ is, of course, perpendicular to the constant frequency surface, so the volume element d^3k may be written as an element dS_ω of the surface of constant frequency ω multiplied by the height $dk_\perp$, where

$$d\omega = |\nabla_k \omega| dk_\perp. \tag{19}$$

Thus, as $g(\mathbf{k}) = (L/2\pi)^3$

$$g(\omega)d\omega = \left(\frac{L}{2\pi}\right)^3 \int dS_\omega dk_\perp = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\omega}{|\nabla_k \omega|} d\omega, \tag{20}$$

the integral being taken over the surface of constant frequency ω. Note that the gradient of the frequency $|\nabla_k \omega|$ is simply the magnitude of the group velocity v_g.

1.3.4 The Debye approximation in three dimensions

In the Debye approximation the phase and group velocities are both taken to be equal to the same constant, v. Then the constant frequency surfaces are spheres, and the surface area of the constant frequency surface corresponding to ω is $4\pi k(\omega)^2 = 4\pi(\omega/v)^2$. Then

$$g(\omega) = \frac{\omega^2 L^3}{2\pi^2 v^3}. \tag{21}$$

Again here it is necessary to introduce the cut-off Debye freqency

$$\omega_D = \frac{v(6\pi^2 N)^{1/3}}{L}. \tag{22}$$

Remember that an expression similar to equation 22 will result from each polarisation and each branch.

1.3.5 Free electrons in three dimensions

For free electrons, the dispersion relation

$$E = \hbar^2 k^2 / 2m \tag{23}$$

gives a group velocity

$$v_g = (1/\hbar)(dE/dk) = \hbar k/m. \tag{24}$$

From equation 21, then,

$$g(\omega) = \left(\frac{L}{2\pi}\right)^3 \int dS_\omega dk_\perp = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi k_\omega^2}{|\hbar k_\omega/m|}, \tag{25}$$

for each spin state, or

$$g(E) = \frac{L^3}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}. \tag{26}$$

Contrast this with the energy-independent density of states in two dimensions, and proportionality to $E^{-1/2}$ in one dimension.

At absolute zero, states will be filled in ascending order of energy, two electrons of antiparallel spin in each energy level, until the total number of electrons N_e have been accommodated. The topmost occupied energy level is the Fermi energy, E_F, which is therefore

$$E_F = \frac{\hbar}{2m}\left(\frac{3\pi^2 N_e}{L^3}\right)^{2/3}. \tag{27}$$

1.4 Simple features of densities of states

In what follows, we shall adopt the fixed boundary condition scheme, so that in each dimension $g(k) = L/\pi$.

1.4.1 The oscillations of a linear chain of atoms

In the Debye approximation, the dispersion relation is taken to be

$$\omega = v|k|, \tag{28}$$

where the velocity of sound v is taken to be a constant, and the density of states in frequency is thus

$$g(\omega) = g(k)/v = L/\pi v. \tag{29}$$

In order to obtain the correct number of degrees of freedom, it is necessary to impose a cut-off frequency, the Debye frequency ω_D, defined by the requirement that

$$N = \int_0^{\omega_D} g(\omega) d\omega \tag{30}$$

that is,

$$\omega_D = v\pi/a. \tag{31}$$

A more accurate treatment of the physics, however, removes the need for the artificial cutoff. From the true dispersion relation for waves on a linear atomic chain of atomic mass M and spring constant λ

$$\begin{aligned} \omega &= \sqrt{4\lambda/M}|\sin ka/2| && (32) \\ &= \omega_m|\sin ka/2| && (33) \end{aligned}$$

we obtain (see problem sheet)

$$\frac{dk}{d\omega} = \frac{2}{a}\frac{1}{\sqrt{(\omega_m^2 - \omega^2)}}. \tag{34}$$

The density of states in energy, then, is

$$g(\omega) = \frac{2L}{\pi a}\frac{1}{\sqrt{(\omega_m^2 - \omega^2)}}, \tag{35}$$

which is singular at $\omega = \omega_m$, but which when integrated over all the allowed values of ω automatically gives N, the correct number of degrees of freedom (strictly for a length $L = Na$ we expect $N - 1$ degrees of freedom, but when N is large the difference is negligible).

1.4.2 Phonons - more than one atom per unit cell

When there is more than one atom per unit cell, there will be more than one solution of the dynamical equation for the system – that is, more than one phonon mode. These branches of the spectrum may be treated independently, and the final expression for the density of states written as the sum over modes s

$$g(\omega) = \frac{L}{\pi}\sum_s \frac{1}{v_s}, \tag{36}$$

with similar expressions in 2 and 3 dimensions. Often the optical branches are much flatter than the acoustic branches, and to a good approximation ω is independent of k. The density of states in such branches may be replaced by a delta function, that is, the branch may be represented as an Einstein oscillator.

1.4.3 Electrons - beyond free electrons

There are similar differences between the density of states curves for electrons when the band structure is considered and the free electron picture to those between the Debye and discrete atomic lattice for phonons. For example, the distortion of the dispersion relation away from the free electron dispersion at the Brillouin zone boundaries will produce zero group velocities at the zone boundary. This, in turn, produces peaks in the density of states.

Even stronger deviations from the free electron model occur in the noble metals and transition metals, in which the broad, quasi-free s electron band overlaps the much narrower d band. The peak in the density of states arising from the d states has profound effects, for example on the colour of the metals and on their magnetic properties (see problem sheets).

1.4.4 Electrons - semiconductors

The densities of states in the valence and conduction bands of semiconductors are normally treated in the effective mass approximation. That is, the carriers in the bands are assumed to behave like particles with $E(k) = \hbar^2 k^2 / 2m^*$. The equations for free electrons derived above then apply.

1.4.5 Electrons - amorphous solids

Although amorphous solids do not possess translational symmetry, so that Bloch's theorem does not hold, it must be possible to write down a Schrödinger equation for the system and extract a density of states from it. The density of states can be very different in an amorphous material from that in the crystalline equivalent: even the character of the states may differ, in that they may be localised rather than delocalised. These localised states occur at the edges of the energy bands, and may profoundly affect the electrical properties by allowing hopping conductivity in an otherwise insulating material.

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