The Density of States

When describing very large systems in which an exact treatment of all particles is impractical or undesirable, we often statistically treat the influence of these many degrees of freedom, and call them a bath. In this limit, an important quantity is the density of states, $g(E)\,dE$, which describes the number of quantum states available in the bath within an energy range from E to $E+dE$. In condensed matter physics, the density of states is commonly described in reciprocal space as a function of the state wavevector, $g(k)$, with the density of states being a count of the number of states in a given range of wavevectors dk and unit volume. For describing molecular dynamics and spectroscopy we will generally be interested in the energy representation. These expressions can be linked through the appropriate dispersion relationship $E(k)$.

For the case that the eigenstates of a Hamiltonian E_n are known, the density of states is a simple count of states at any given frequency, i.e. a histogram

$$g(E) = \sum_{n=1}^{\infty} \delta\left(E - E_n\right) \tag{1.1}$$

Note that the delta function is a probability distribution function so that the units of $g(E)$ are inverse energy. The total number of states in the system can be obtained by integrating g(E) over all energies. Thus we expect for a system of N atoms there are $3N$ degrees of freedom, and therefore

$$\int dE\, g(E) = 3N$$

Densities of state become more important with problems that involve a large number of degrees of freedom whose energy spectrum is continuous rather than discrete, as expected in condensed matter. In this limit the density of states is a continuous function that describes the number of quantum states available within a given range of energies or wavevectors for a given volume. Furthermore, the form of the density of states becomes strongly dependent on the dimensionality of the problem.

Probability distribution functions

The density of states only represents those states that present in the system, and does not deal with whether they are occupied. The thermal occupation of the available states is described by probability distribution functions $f(E)$, which give the probability of finding a microstate of energy E occupied at a temperature T. For our purposes, we are most interested in

$f(E) = e^{-\beta E}$ Boltzmann

$f(E) = (e^{\beta E} \pm 1)$ + Fermi-Dirac; – Bose-Einstein

Where $\beta=(k_B T)^{-1}$. With the density of states and the probability distribution function, the mean value of a macroscopic variable dependent on E or the expectation value of a microscopic variable A can be obtained from

$$\langle A \rangle = \int A(E)\, g(E)\, f(E) dE$$

Discrete States and the Energy Representation

Nominally, the density of states as a function of energy for the discrete states of a bound potential are simply given by eq. (1.1). However, these systems form an excellent place to gain intuition about how the density of states related to the form of the potential –and thereby the splitting of states– and dimensionality as multiple degrees of freedom are added. Whereas the discrete density of states is a histogram, it is possible to investigate the energy dependence of the density of states in the classical limit by treating the quantum number as a continuous variable rather than a discrete one. One can calculate the density of states at a given energy from a derivative of the state count with respect to energy

$$g(E) = \frac{dN}{dE} \tag{1.2}$$

In a one dimensional system, the quantum number n is equivalent to the total state count at energy E, $dN/dn=1$, and $g(E) = dn/dE$.

To begin let's consider the density of states for a particle-in-a-box. For a particle of mass m confined to a box of length L, the quantum states available to the system for a one- and three-dimensional box are

$$\begin{aligned} E_{1D} &= \alpha n^2 = \frac{\hbar^2 k_n^2}{2m} && n = 1,2,3... \\ E_{3D} &= \alpha\left(n_x^2 + n_y^2 + n_z^2\right) && n_x, n_y, n_z = 1,2,3... \end{aligned} \tag{1.3}$$

where $\alpha = \hbar^2\pi^2/2mL^2$. We see here that the energy level spacing grows as n^2. Whereas there is only one state for a given energy in the 1D case, in the 3D case the degeneracy of states grows with energy. From 1.2 we have

$$n = \sqrt{\frac{E_{1D}}{\alpha}} \qquad dn = \frac{1}{2\sqrt{\alpha E}} dE_{1D} \tag{1.4}$$

and using eq. (1.2) the density of states is

$$g_{1D}(E) = \frac{1}{2\alpha^{1/2}} E^{-1/2} = \frac{(2m)^{1/2} L}{2\pi\hbar} E^{-1/2} \tag{1.5}$$

Here the density of states drops as $E^{-1/2}$, which reflects the growing spacing of states with energy. If we normalize to the length of the box, g_{1D}/L, we obtain the density of states as number of states per unit energy per unit length.

In the 3D case, we have a degeneracy of states that grows with increasing quantum numbers. Rather than treating each of the three quantum numbers explicitly, it becomes helpful in the classical limit to define

$$n^2 = n_x^2 + n_y^2 + n_z^2 .$$

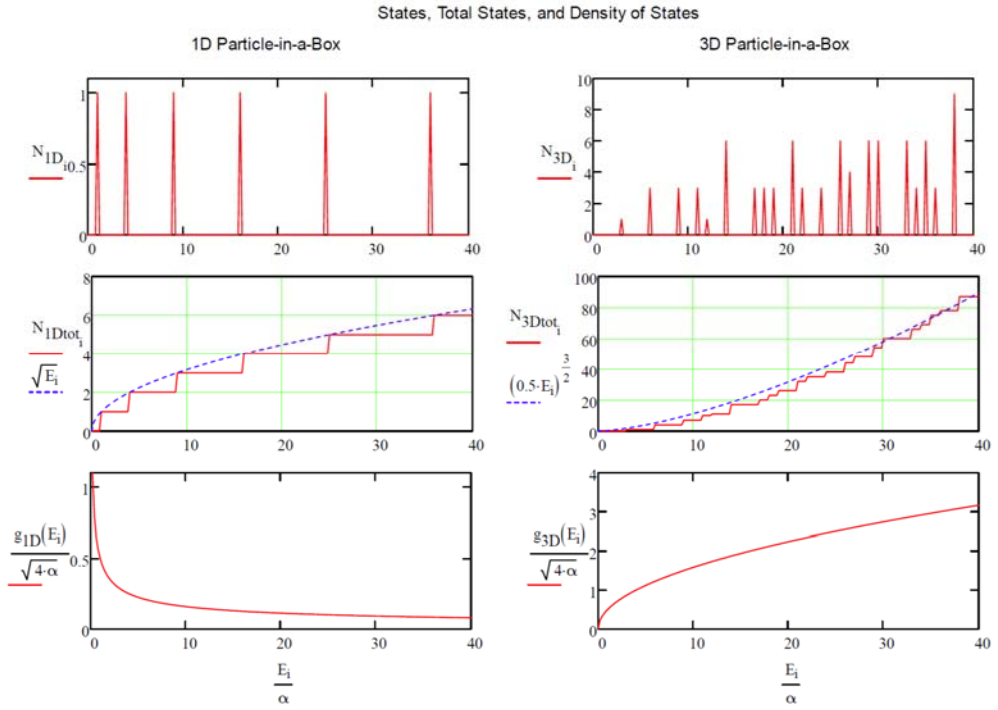
Then treating n as a continuous variable, we see that it represents the radius of a sphere in the n_x, n_y, n_z dimensions. Remembering that we only have positive quantum numbers, we are therefore only concerned with one octant of the sphere. The volume of this octant represents the total number of states with energies below E, $N=\pi n^3/6$. The density of states can be obtained using eq. (1.2). Then

$$g_{3D}(E) = \frac{\pi n^2}{2} \frac{dn}{dE} . \tag{1.6}$$

Equivalently, we can thing of the density of states for a given energy, $g(E)\,dE$, being obtained by finding the number of states within a spherical shell of radius n and thickness dn. The volume of this shell is $\frac{1}{2}\pi n^2 dn$, and we obtain eq. (1.6). Using eq. (1.4) we find

$$g_{3D}(E) = \frac{\pi}{4\alpha^{3/2}} E^{1/2} = \frac{(2m)^{3/2} L^3}{4\pi^2 \hbar^3} E^{1/2} \tag{1.7}$$

In the 3D case we see that the growing degeneracy of states leads to an overall increase with energy that scales as $\sqrt{E}$. We obtain the density of states as number of states per unit energy per unit volume from g_{1D}/L^3. Although derived for a box, these results are not dependent on the shape of the system.



Similar arguments can be used to obtain the density of states for a 1D and 3D Harmonic Oscillator with energies:

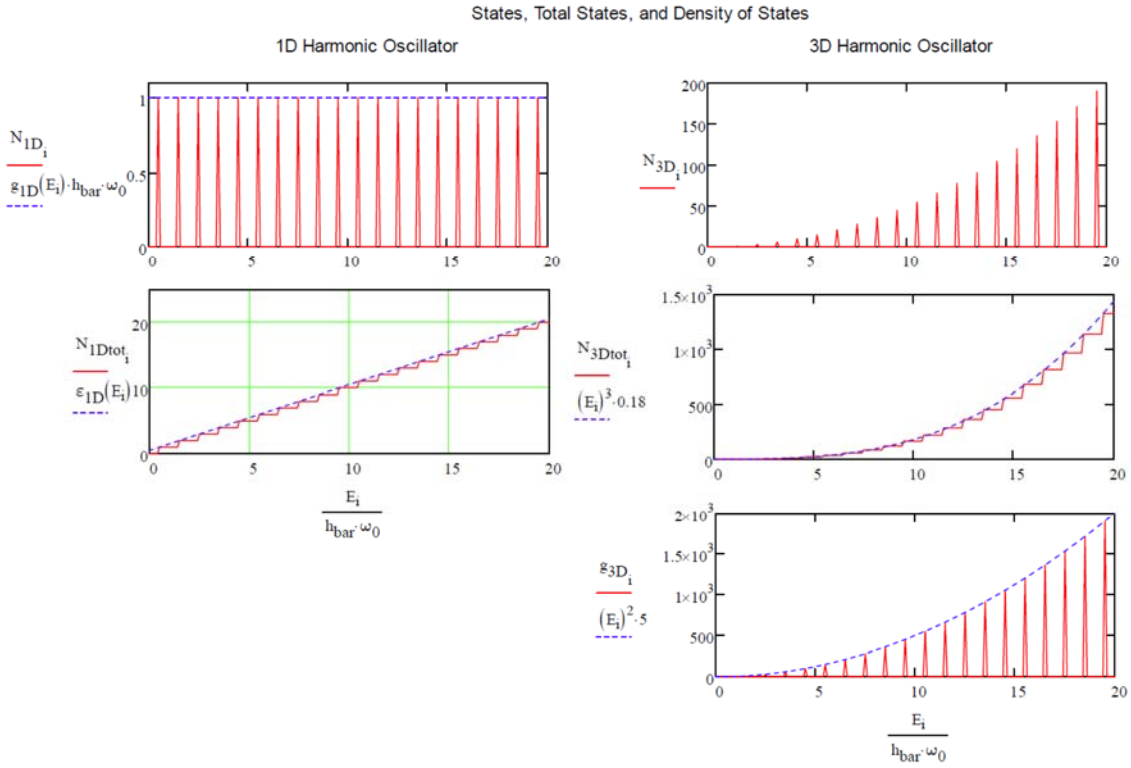
$$\begin{aligned} E_{1D} &= \hbar\omega_0(n+\tfrac{1}{2}) & n &= 0,1,2,\ldots \\ E_{3D} &= \hbar\omega_0(n_x+n_y+n_z+\tfrac{3}{2}) & n_x, n_y, n_z &= 0,1,2,\ldots \end{aligned} \tag{1.8}$$

Since the energy levels of a 1D quantum harmonic oscillator are equally spaced by a value $\hbar\omega_0$, the density of states is constant:

$$g_{1D}(E) = \frac{1}{\hbar\omega_0}.$$

In the case of a 3D oscillators, the degeneracy of states grows as E^2, leading to

$$g_{3D}(E) = \frac{E^2}{2(\hbar\omega_0)^3}.$$



The harmonic oscillator density of states can be generalized to the case of multiple independent harmonic oscillators. For n oscillators with fundamental energies $\varepsilon_n = \hbar\omega_n$, the density of states is given by the convolution for the density of states of the individual oscillators. This leads to

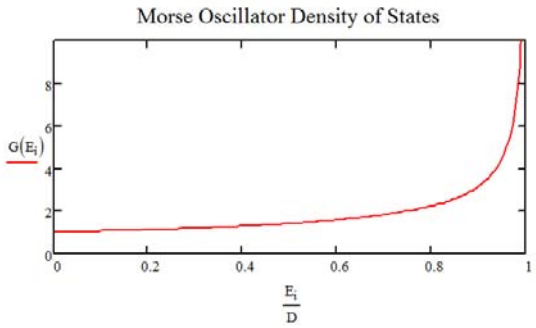
$$g_{harm}(E) = \frac{E^{n-1}}{(n-1)!\prod_{i=1}^{n}\varepsilon_i}$$

Anharmonicity can lead to strong deviations from harmonic behavior. For dissociative potentials, the 1D density of states will rise to a singularity at the dissociation energy, whereas bending potentials can be expected to have densities of state that drop with energy, analogous to the particle- in-a-box example. In the case of a 1D Morse Oscillator with energy levels

$$E(n) = \hbar\omega_0\left(n+\frac{1}{2}\right) - \frac{(\hbar\omega_0)^2}{4D}\left(n+\frac{1}{2}\right)^2$$

The density of states is found to increase with energy as

$$g(E) = \left(\hbar\omega_0\left(1-\frac{E}{D}\right)\right)^{-1/2}.$$



Continuum States and the Wavevector Representation

In the case of condensed matter or particles in free space the quantum states available to the system are continuous. Examples of these states include phonons, photons, and particles in dissociative potentials. Under these circumstances the degrees of freedom and the volume available to the system are treated as infinite. To proceed we need to define a volume over which to quantize the system and evaluate the density of states. In practice it is most useful to perform these calculations in reciprocal or *k*-space, and relate to the energy representation with

$$g(E)\,dE = g(k)\,dk \tag{1.9}$$

Similar to our analysis above, the density of states can be obtained from the derivative of the cumulative state count in *k*-space with respect to *k*

$$g(k) = \frac{dN(k)}{dk} \tag{1.10}$$

To work with a specific example, let's return to the example of the 3-D particle-in-a-box, and write the energies in *k*-space as

$$\begin{aligned} E_{3D} &= \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \\ k_i &= \frac{2\pi}{L_i} m_i \qquad m_i = 0, \pm 1, \pm 2 \cdots \end{aligned} \tag{1.11}$$

Note in the limit $L_i \rightarrow \infty$ we obtain the kinetic energy of a free particle. Analogous to our previous discussion in *n* space, we recognize that we can calculate the density of states by counting states in *k*-space by integrating over a volume. Each state in eq. (1.11) is labeled by three quantum numbers that represent a point on a cubic grid defined by the k_x, k_y, k_z dimensions. Defining $k^2 = k_x^2 + k_y^2 + k_z^2$, we can determine the total number of states below a given *k* by integrating over a sphere with radius *k* to obtain the *k*-space volume, and dividing by the volume of a single state, $k_x k_y k_z = (2\pi)^3 / L_x L_y L_z$. This leads to $N(k) = 4\pi k^3 V/[3(2\pi)^3]$, where *V* is the real-space volume $L_x L_y L_z$. Then, the density of states evaluated using eqs. (1.9) and (1.10) is

$$g_{3D}(E) = \frac{V}{(2\pi)^3} 4\pi k^2 \frac{dk}{dE} \tag{1.12}$$

From our dispersion relationship eq. (1.11) we find

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad dk = \frac{1}{\hbar}\sqrt{\frac{m}{2E}}\,dE \tag{1.13}$$

which is just the dispersion relationship for a free particle. Then, the density of states is in terms of states per unit energy is

$$g_{3D}(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{1.14}$$

A further multiplicative factor of (2*S*+1) can be added to account for the spin multiplicity of the particle. In the case of free-particles we will typically choose a sufficiently large quantization volume *V* over which to quantize the states of interest. The density of states per unit energy per

unit volume is obtained by dividing out the factor V, and is independent of the shape of the volume.

Photons are another case of continuous quantum states. The dispersion relationship in this case is linear

$$E = \hbar\omega = \hbar ck \tag{1.15}$$

and the density of states for a quantum light field in three dimensions is obtained from eq. (1.12)

$$g(E) = \frac{V}{\pi^2}\frac{1}{(\hbar c)^3}E^2 \tag{1.16}$$

This expression includes an additional factor of two for the two degenerate polarization states for each k of the field.

Similarly we can calculate the density of states for the phonons of a 1D periodic lattice of particles with lattice constant a, which have harmonic interactions between neighbors characterized by a force constant $\kappa = m\omega_0^2$. For this system the dispersion relationship is

$$E(k) = 2\hbar\omega_0\left|\sin\left(ka/2\right)\right|.$$

In the small k limit, we can expand the *sine* and approximate the dispersion by the linear relationship

$$E \approx \hbar\omega_0 ka \tag{1.17}$$

Which leads to a density of states in 1D

$$g_{1D}(E) = \frac{L}{\pi}\frac{\partial k}{\partial E} = \frac{L}{\pi a\hbar\omega_0}. \tag{1.18}$$

Note $a\omega_0$ is the group velocity or speed of sound. For phonons in 3D isotropic media, eq. (1.12) can be used to find

$$g_{3D}(E) = \frac{V}{2\pi^2\left(a\hbar\omega_0\right)^3}E^2. \tag{1.19}$$

For acoustic phonons which follow the behavior in eq. (1.19), a common form is the Debye density of states. This model assumes that the linear behavior in (1.17) holds for all k, up to a maximum allowed energy E_D, the Debye Energy. Then recognizing for a system of N atoms, that an integral over the density of states should recover the 3N total states in the system,

$$3N = \int_0^{E_D} dE\, g(E)$$

The Debye density of states takes the form

$$g_D(E) = 9N\frac{E^2}{E_D^3} \qquad E \le E_D. \tag{1.20}$$

Note the energy scaling relationships for the calculated densities of state. The parabolic dispersion relationship for free particles in eqs. (1.3) and (1.11), applicable for instance to electrons in a conduction band, leads to a $E^{1/2}$ scaling of the density of states in 3D and $E^{-1/2}$ in 1D. On the other hand linear dispersion relations such as those applicable to acoustic phonons (1.17), harmonic vibrations, and photons (1.15), scale independently of E in 1D and as E^2 in 3D.