Density of States—C.E. Mungan, Spring 2000

According to Stowe Eq. (7.10), the density of states $g(E)$ is given by

$$g(E) \propto E^{n/2} \tag{1}$$

where E is the internal energy of a system and n is its number of degrees of freedom. For a single particle in a 3D box, $n = 3$ due to the three independent translational kinetic energy terms,

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \equiv \frac{p^2}{2m}. \tag{2}$$

Thus, according to Eq. (1), we would expect the density of states to vary with the energy to the 3/2 power.

In fact, however, quantum mechanics gives a different answer. According to the de Broglie relation and the boundary condition that there must be nodes in the wavefunction (of wavelength λ) at the walls of the cubical box (of length L on a side), we have

$$p_x = \frac{h}{\lambda} = \frac{h}{2L} n_x \tag{3}$$

and similarly for p_y and p_z, where the quantum numbers $\{n_x, n_y, n_z\}$ take on positive integral values. Hence each quantum state occupies an equal volume $(h/2L)^3$ in momentum space. For a range of momenta from p to $p+dp$, the number of states is thus equal to the volume of one octant of a spherical shell of radius p in momentum space divided by the volume per state,

$$g(p)\,dp = \frac{8L^3}{h^3}\frac{4\pi}{8}p^2 dp. \tag{4}$$

Using Eq. (2) to rewrite this in terms of energy gives the well-known result,

$$g(E)\,dE = 2\pi\left(\frac{\sqrt{2m}L}{h}\right)^3 E^{1/2} dE \quad \Rightarrow \quad g(E) \propto E^{1/2}, \tag{5}$$

i.e., the density of states varies with the energy to the 1/2 not the 3/2 power. What has Stowe done wrong?

Closer inspection of his Chap. 7 reveals that Eq. (7.10) is only an approximate result. In Appendix 7A he more formally derives the equation,

$$g(E) \propto \left(\sqrt{E}\right)^{n-1} \tag{6}$$

which reduces to Eq. (1) for the usual case in statistical mechanics of $n = \nu N$ being large, since N, the number of particles in the system, is expected to be of the order of Avogadro's number. The number of degrees of freedom per particle is ν where the assumption has been made that each degree of freedom corresponds to a quadratic term in the energy, $\varepsilon_i \propto q_i^2$, with q_i being any

generalized position or momentum coordinate. Examples of such energy terms include $p_x^2/2m$, $L_y^2/2I_y$, and $kz^2/2$. As in Stowe Eq. (7A.2), let us absorb the constants such as the mass, moment of inertia, or spring constant into new variables r_i so that $\varepsilon_i \equiv r_i^2$.

Putting $n = 3$ into Eq. (6) implies that the density of states should vary with the energy to the first power, which is still wrong! Clearly Stowe's derivation in this Appendix needs patching up. The number of states accessible to the ith degree of freedom is proportional to the "volume" $\int dr_i$ over the allowed values of the generalized coordinate r_i. This can be seen either from the argument leading to Eq. (4) above, or from the Heisenberg Uncertainty Principle as discussed in connection with Eq. (2.12') in Stowe; these are equivalent because Eq. (4) just says the number of states is $\Omega = V_r V_p / h^3$ where V_r and V_p are the volumes in real and momentum space, respectively. The total number of accessible states is the product of the number available to each independent degree of freedom, so that

$$g(r)dr \propto \prod_{i=1}^{n} \int dr_i \tag{7}$$

subject to the constraint that the sum of the energies in all modes lies within dE of the total internal energy of the system,

$$\sum_{i=1}^{n} \varepsilon_i \equiv \sum_{i=1}^{n} r_i^2 \equiv r^2 = E\,. \tag{8}$$

This constraint makes the integration a volume integral over an n-dimensional spherical shell, which is equal to its thickness dr times its surface area. But the latter area is proportional to the shell's radius r raised to the power of n–1, so that

$$g(r)dr \propto r^{n-1}dr\,. \tag{9}$$

As before, we now change variables to E to find

$$g(E)dE \propto \left(\sqrt{E}\right)^{n-1} \frac{dE}{\sqrt{E}} \quad \Rightarrow \quad g(E) \propto E^{n/2-1}. \tag{10}$$

Substituting $n = 3$ now correctly gives a dependence on the energy to the 1/2 power in agreement with Eq. (5).

One practical upshot of this new result is that the solution to problem 7-13 must now be modified. If the density of states is linearly proportional to energy, then Eq. (10) implies that $n = 4$, not $n = 2$ from Eq. (1). In fact, for $n = 2$ the density of states is actually independent of energy. This agrees with the fact that for a 1D SHO (which has one kinetic and one potential degree of freedom), the energy levels are uniformly spaced with energy and are nondegenerate, so that we expect $g(E)$ to be constant. (I previously attempted to explain away a linear prediction in terms of phonons. The concept of phonons is not even defined for a single-particle system!) Note that for a 2D ($n = 4$) and a 3D ($n = 6$) SHO, the level spacing is still uniform, but the

degeneracy of level m increases as m and m^2, respectively, as is proven below, so that we correctly expect $g(E)$ to vary as E and E^2, respectively.

Appendix—Degeneracies of a 2D and a 3D Simple Harmonic Oscillator

First consider the 2D case. We have two non-negative quantum numbers n_x and n_y which together add up to the single quantum number m labeling the level. Therefore the degeneracy of level m is the number of different permutations of values for $\{n_x, n_y\}$. For example, if $m = 3$, there are four permutations, namely {3,0}, {2,1}, {1,2}, and {0,3}. Similarly, we can see in general that for level m the possible arrangements of the quantum numbers are $\{m,0\}$, $\{m–1,1\}$, ..., $\{0,m\}$ for a total degeneracy of m+1.

Next consider the 3D case. We now have three non-negative integers which must add up to a given value $m = n_x + n_y + n_z$. The problem reduces to that of putting m coins into 3 boxes. We can put m into the n_x box, leaving 0 to put in the n_y and n_z boxes, which gives 1 permutation. Next, we can put m–1 into the n_x box, leaving 1 to put in the n_y and n_z boxes; there are 2 ways of doing this. Then, we can put m–2 into the n_x box, leaving 2 to distribute between the other two boxes; there are 3 ways to do this distribution. We continue subtracting 1 from what we put into the n_x box until we are putting 0 there and distributing all m among the other two boxes in m+1 possible ways according to the 2D case above. Thus the total degeneracy of level m for a 3D SHO is

$$1 + 2 + 3 + \cdots + (m+1) = \sum_{i=1}^{m+1} i = (m+1)(m+2)/2 . \tag{11}$$