Math Appendix 1: Interpreting the Planck – Einstein formula for average oscillator energy

According to Planck-Einstein, the thermal radiation data and low temperature heat capacity data could be fit by assuming that, at temperature, T, the average energy of a harmonic oscillator with frequency, f, had the form,

$$\langle E\rangle_f = hf\,p/(1-p)\,, \qquad (A.1)$$

where, $p = \exp[-hf/kT]$ (we will not use this last equation until the very end).

Generally, in probability theory, the average value of an energy would be the sum of the products of the possible energies, E_n, and their corresponding probabilities, P(n). So if the possible energies were, $E_n = nhf$, for integer n, then the average energy would be,

$$\langle E\rangle = E_1P(1) + E_2P(2) + E_3P(3) + \cdots + E_nP(n) + \cdots$$

$$= hf\,\{P(1) + 2P(2) + 3P(3) + \cdots + nP(n) + \cdots\}. \qquad (A.2)$$

Now suppose, $$P(n) = (1-p)p^n. \qquad (A.3)$$

Notice that these probabilities add up to 1 as they should;

$$P(0) + P(1) + P(2) + \cdots + P(n) + \cdots = (1-p)(1 + p + p^2 + \cdots + p^n + \cdots)$$

$$= (1 + p + p^2 + \cdots + p^n + \cdots) - (p + p^2 + \cdots + p^n + \cdots) = 1. \qquad (A.4)$$

Furthermore,

$$\langle E\rangle = hf\,\{p(1-p) + 2p^2(1-p) + 3p^3(1-p) + \cdots + np^n(1-p) + \cdots\}$$

$$= hf\,\{(p + 2p^2 + 3p^3 + \cdots + np^n + \cdots) - (p^2 + 2p^3 + \cdots + (n-1)p^n + \cdots)\}$$

$$= hf\,\{p + p^2 + p^3 + \cdots + p^n + \cdots\} = hf\,p\,\{1 + p + p^2 + \cdots + p^n + \cdots\}$$

$$= hf\,p/(1-p)\,, \qquad (A.5)$$

where the last step follows from the middle of (A.4).

Finally, from $p = \exp[-hf/kT]$, if $hf \ll kT$, then, $p \simeq 1 - hf/kT$ and $\langle E\rangle = hf\,p/(1-p) \simeq (kT - hf) \simeq kT$, the high T, classical limit! At low T we have $\langle E\rangle \simeq hf\exp[-hf/kT] \rightarrow 0$ as $T \rightarrow 0$.