Number of microstates function for Einstein solids

First we want to find the number of accessible states $\Omega(E)$ for an Einstein solid with $M$ phonons and $N$ atoms. A crystal with $N$ atoms has $3N$ vibrational modes, and in the Einstein model each mode has the same fundamental frequency $\nu$. The energy of $3N$ independent harmonic oscillators is

$$E = h\nu \sum_{i=1}^{3N} (n_i + 1/2) = h\nu (M + 3N/2),$$

where $n_i$ is the number of phonons (quanta of vibrational energy) in the $i^{th}$ vibrational mode and $M = \sum_{i=1}^{3N} n_i$. By generalizing the argument given in the problem statement, it should be easy to see that $\Omega(E)$ equals the total number of random walks with $M + 3N - 1$ steps of which $M$ are of one type and $3N - 1$ are of the other. Thus, we obtain

$$\Omega(E) = \frac{(M + 3N - 1)!}{M!(3N - 1)!}. \quad (2)$$

We should multiply this expression by the number of vibrational levels in the interval $\delta E$, to be consistent with the interpretation of $\Omega(E)$ as the number of microstates lying within the energy interval $\delta E$. Then we obtain

$$\Omega(E) = \frac{(M + 3N - 1)! \delta E}{M!(3N - 1)! \ h\nu}. \quad (3)$$

This extra factor turns out to have no effect on any thermodynamic properties of the crystal.

Unless the crystal is in its ground state ($M = 0$) at the absolute zero of temperature, $M$ will generally be much greater than $3N$, and $M >> N >> 1$. Even if 99.99% of the vibrational modes were in the ground state ($n_i = 0$), and we consider a relatively small bulk sample of $10^{20}$ atoms ($1 \text{ mm}^3$ of copper contains roughly this number of atoms), we still have $M = 3 \times 10^{16}$ phonons. So you can see how hard it is to make $M$ small.

Next we use the simple form of Stirling’s approximation $\ln(n!) = n \ln n - n$ to simplify $\ln \Omega$. After neglecting the completely inconsequential 1, the result is

$$\ln \Omega(E) = (M + 3N) \ln(M + 3N) - M \ln M - 3N \ln 3N + \ln (\delta E/h\nu). \quad (4)$$

The energy dependence is contained in $M$,

$$M = \frac{E}{h\nu} - \frac{3N}{2}. \quad (5)$$

In the limit $M \to 0$, we find

$$\ln \Omega(E) \to -M \ln M + \ln (\delta E/h\nu) \to \ln (\delta E/h\nu),$$
since, by l’Hopital’s rule, the limit of \( x \ln x \) as \( x \) goes to zero is zero. Note that in this limit, it really doesn’t make sense for \( \delta E \) to be much wider than the level spacing \( h\nu \), since there is only one state occupied (the ground state, which is nondegenerate). That implies that as \( M \to 0 \), we should also put \( \delta E/h\nu = 1 \), so that \( \ln \Omega(E) = 0 \) in this limit.