2.3 $N_A = N_B = 3$ and $q_{\mathrm{total}} = 6$

The multiplicity of an Einstein solid:

$$\Omega(N, q) = \binom{q + N - 1}{q}.$$

Determine the multiplicity function (using $q_B = q_{\mathrm{total}} - q_A$)

$$\Omega(q_A) = \Omega_A(q_A)\Omega_B(q_B).$$

Together with the fundamental assumption of statistical mechanics

> *In an isolated system in thermal equilibrium, all accessible microstates are equally probable.*

this gives

$$P(q_A) = \frac{\Omega(q_A)}{\Omega(\mathrm{all})}.$$

With $N_A = 300$, $N_B = 200$, and $q_{\text{total}} = 100$

- Macrostate with $q_A = 60$ gets the largest multiplicity = the highest probability
- New feature: an enormous ratio. The most likely macrostate is about 10^{33} times more probable than the least likely macrostate.
- Irreversibility — starting out away from the peak (i.e. away from $q_A = 60$) random rearrangements of the energy will take us towards the peak; we will never move in the opposite direction.
- This spontaneous flow of energy will stop when we are at (or very close to) the most likely macrostate.
- ⇒Law of increase of multiplicity — only a strong statement about probabilities, not a *fundamental law*.

With $N = 10^{20}$, $q_A, q_B \gg N$

Multiplicity of a large Einstein solid:

$$\Omega(N, q) = \binom{q + N - 1}{q} = \left(\frac{eq}{N}\right)^N, \quad q \gg N.$$

Two solids in contact, each of size N:

$$\Omega_{\text{total}}(q_A) = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N.$$

With $q_A = q/2 + x$ and $q_B = q/2 - x$:

$$\Omega(x) = \Omega_{\max} \exp\left(-\frac{x^2}{q^2/4N}\right).$$

- The peak is extremely narrow: Width $= q/\sqrt{N} \ll q$.
- This implies that the random fluctuations in the energy away from the most likely macrostate are utterly unmeasurable.
- This is *the thermodynamic limit*.

Summary

- Starting assumption: *All microstates are equally probable*.
- Still, the probability for the *macrostates* are very different.
  The system will only be found in a small fraction of all the possible *macrostates*.
- The spontaneous flow of energy will stop when we are at (or very close to) the most likely macrostate $\Rightarrow$ law of increase of multiplicity.
- The fluctuations are extremely small for big systems.