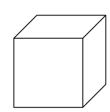
Boltzmann Limit

- When can we assume that the Boltzmann limit is "accurate" (i.e., $g_i >> N_i$ or **many more available quantum states then particles**)?
- **Number of particles**
  - P.G. @ SATP ~ 10^{19} molecules/cm^3 (from $pV=NkT$)
- **Degeneracies of different energy modes (motions)**
  1) **electronic**: magnetic quantum number (g=2l+1) and spin (g=2s+1)
     - $g_{el} < O(10)$
  2) **vibration**: harmonic oscillator has no degeneracy
     - $g_{vib} = 1$
  3) **rotation**: rigid rotor (2J+1)
     - $g_{rot} < O(100)$
- So how can $g_i >> N_i$?
  - translational energy?

Translational Energy QM States

- Consider particle in a "box" (cube)
  - recall Q.M. solution of Sch. eq'n. for (kinetic) energy of single translating particle



L=1 cm

$$\varepsilon_{x,n_x} = n_x^2 \frac{h^2}{8m}\frac{1}{L^2} \quad \text{or} \quad n_x = \sqrt{8m\varepsilon_{x,n_x}}\frac{L}{h}$$

- At SATP for air in a "small" box (1cm), how many QM states have energy less than the average KE of a molecule in x-direction (=1/2 k T… will show this later)

$$\Rightarrow n_{x,KE_{avg,x}} \approx 2\sqrt{mkT}\frac{L}{h}$$

$$n_{x,avgKE} \approx 4.2\times10^8$$

$$k = 1.38\times10^{-23}\frac{J}{K} \text{ Boltzmann's Constant}$$

$$h = 6.626\times10^{-34}\,J\,s$$

$$T_{SATP} = 298K,\, m_{N_2} \cong 4.7\times10^{-26}\,kg$$

- But this was just 1-D of cube

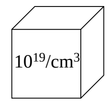
$$\#\text{States with } KE < KE_{avg} = n_{x,KE_{avg}}\, n_{y,KE_{avg}}\, n_{z,KE_{avg}} = n_{x,KE_{avg}}^3 \approx 7\times10^{25}$$

Boltzmann Limit Validity

- So in our 1 cm box, if all our molecules were to be found in just these states

$$\#\,\text{States "accessible"} \approx 10^{26}$$

  - actual number must be greater since some molecules must be in even higher energy states for the average to be correct



$L = 1$ cm

- Number of particles in 1 cm box is ~10^{19}

$$\frac{\#\,\text{QM States that could be populated}}{\#\,\text{Particles}} > \frac{10^{26}}{10^{19}} = 10^{7}$$

⇒**each state is sparsely populated** ☑

Boltzmann limit usually reasonable assumption unless densities are very high (or T's very low)

- For translations, we could "lump" energy states having energies between ε_i and $\Delta\varepsilon_i$ into one energy level (large box) with approximately same ε_i and degeneracy g_i

Extended Degeneracies