Boltzmann Limit

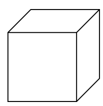
- When can we assume that Boltzmann limit is "accurate", i.e., when $g_i >> N_i$ or **number of quantum states that can have particles >> number of particles**?
- **Number of particles**
  - TPG@SATP ~10^{19} molecules/cm^3 (from $pV=NkT$)
- **Degeneracies**
  - simple case: atom, only electronic and translational quantum states, defined by (n,l,m ; n_x,n_y,n_z)

    $\varepsilon_i = \varepsilon_{el,i} + \varepsilon_{tr,i}$

    $g_i = g_{el,i}\, g_{tr,i}$
  - also assume atoms at STP can only be in 3 elec. energy levels
    - 3 n values, with complete degeneracy for all l, m
  1) **electronic degeneracy**
     - magnetic quantum number ($g_m=2l+1$), typically $l \leq 2$
     - electron spin ($g=2s+1$), typically $s \leq 3/2$
       - so $g_{el,i} <$ O(20)
     - therefore $g_{el,i}$ ~~>>~~ $N_{el,i}$ (at least one n contains $\geq 10^{19}/3$ atoms)
  - What about translations, how many quantum states there?

Translational Energy QM States

- Consider the particle in a "box" for a cube
  - recall QM solution of Schrödinger's equation for 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 STP for N_2 in a "small" box (L=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)

$$\Rightarrow n_{x,KE_{avg,x}} \approx 2\sqrt{mkT}\,\frac{L}{h} \approx 4.2 \times 10^8$$

$k = 1.38 \times 10^{-23}\, J/K$

$h = 6.626 \times 10^{-34}\, J s$

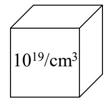
$T_{STP} = 298K,\ m_{N_2} \cong 4.7 \times 10^{-26}\, kg$

- But this was just 1-D of cube

  number of transl. states with $KE<KE_{avg} \approx (n_{i,\,KE_{avg,i}})^3 \approx 7 \times 10^{25}$

Boltzmann Limit Validity

- So in our 1 cm box, if all our molecules were to be found in just these states ***are "accessible" at STP***
  at least 10^{26} quantum states could be populated
  – number actually greater since some molecules must be in even higher energy states for the average *KE* to be correct



L=1 cm

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

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

$\Rightarrow$**quantum states 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 approx. same energy $\Rightarrow$ degeneracy $g_{tr,i} >> N_i$

Extended Degeneracies