Energy Level Population Distributions

- Revisit how molecules (diatomic) are distributed among energy levels in equilibrium
- Boltzmann fraction $\frac{N_i}{N} = \mathrm{f_i}(T) = \frac{g_i e^{-\varepsilon_i/kT}}{Q}$
- Assuming energy modes separable

$$\frac{N(n_{el,i}, v, J, n_x, n_y, n_z)}{N} = \frac{g_{el,i} g_v g_J e^{-(\varepsilon_{el,i}+\varepsilon_v+\varepsilon_J+\varepsilon_{tr})/kT}}{Q_{el} Q_{vib} Q_{rot} Q_{tr}}$$

$$= \frac{g_{el,i} e^{-\varepsilon_{el,i}/kT}}{Q_{el}} \frac{g_v e^{-\varepsilon_v/kT}}{Q_v} \frac{g_J e^{-\varepsilon_J/kT}}{Q_{rot}} \frac{e^{-\varepsilon_{tr}/kT}}{Q_{tr}}$$

$$= \mathrm{f}_{el}(n_{el,i}) \mathrm{f}_{vib}(v) \mathrm{f}_{rot}(J) \mathrm{f}_{tr}(n_x, n_y, n_z)$$

Internal Energy Mode Populations

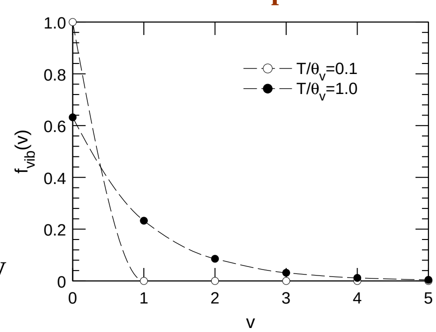
- Electronic
  - already examined
- Vibration

$$\mathrm{f_{vib}}(\mathrm{v}) = \frac{e^{-\theta_v(\mathrm{v}+1/2)/T}}{e^{-\theta_v/2T} \Big/ \left(1 - e^{-\theta_v/T}\right)}$$

$$= e^{-\mathrm{v}\theta_v/T}\left(1 - e^{-\theta_v/T}\right)$$

- v=0 always largest fraction
- $\mathrm{f_{vib}}$ drops monotonically with v

Vibrational Population



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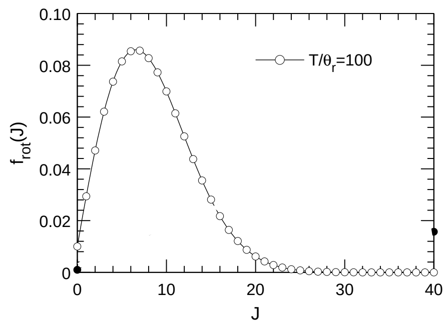
Internal Energy Mode Populations

- Rotation ($T >> \theta_r$)

$$f_{rot}(J) = \frac{(2J+1)e^{-\theta_r J(J+1)/T}}{T/\sigma\theta_r}$$

- Why does f_{rot} have peak, while f_{vib} always maximum for v=0?

Rotational Population



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Translational Energy Mode Population

- Translation

$$f_{tr}(n^2) = \frac{e^{-\theta_{tr} n^2/T}}{\left(2\pi mkT/h^2\right)^{3/2} V}$$

  - with

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

$$\theta_{tr} = h^2/\left(8mV^{2/3}\right)$$

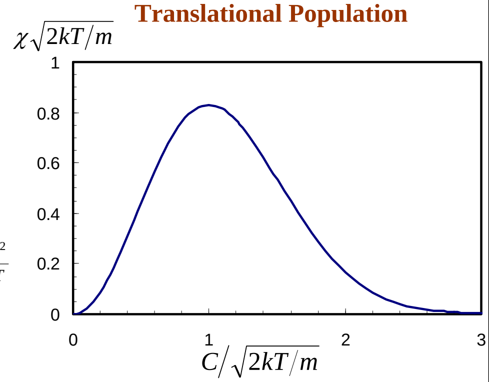
  - or in terms of speed

$$C = \sqrt{2\varepsilon_{tr}/m}$$

$$\chi(C) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} C^2 e^{-\frac{mC^2}{2kT}}$$

Maxwell (-Boltzmann) Speed Distribution

Translational Population



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Probability Distributions

- Given these probability distributions, one can ask questions such as:
  - which energy level is most probable at given T
  - which energy level provides greatest contribution to energy of mode at given T
  - at what temperature does a given level i reach a maximum value

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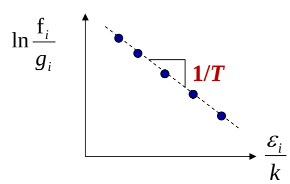
Boltzmann Plots

- Recall what happens if we plot Boltzmann fractions

$$f_i(T) = \frac{g_i e^{-\varepsilon_i/kT}}{Q}$$

$$\Rightarrow \ln\frac{f_i}{g_i} = -\frac{\varepsilon_i}{kT} - \ln Q$$



  - a way to FIND temperature
- Could make such a plot for each energy mode and if each internally in equilibrium
  - get T_{tr}, T_{rot}, T_{vib}, T_{el}
  - if system in equilibrium,
  - if modes not in equilibrium with each other,
- Also possible that distribution not Boltzmann
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