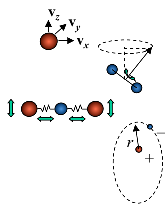
TD Properties and Energy Levels

- To get TD properties, we need (assuming Boltzmann limit) to know the partition function (Q) of the substance
  - based on molecular energy levels
- We have seen that molecular motion (and therefore energies) can be organized into different modes
  - translation of center-of-mass (CM)
  - rotation of nuclei about CM
  - vibration of nuclei about CM
  - orbit (and spin) of electrons about nuclei
    - nucleus also has structure (protons and neutrons, which also have spin)
      - but 1st excited energy level ~10^{10} K, so can typically neglect



Energy Mode
translational
rotational (internal)
vibrational (internal)
electronic (internal)
nuclear

Independent Energy Modes

- What happens if some energy modes are **independent**, meaning we can write the energy of some level as $\varepsilon_{jk} = \varepsilon_j + \varepsilon_k$
- Then we can write the partition function as
  - *the partition function becomes factorable into Q's for each mode*

$$Q = \sum_j \sum_k g_{jk} e^{-\varepsilon_{jk}/kT}$$
$$= \sum_j \sum_k g_j g_k e^{-(\varepsilon_j + \varepsilon_k)/kT}$$
$$= \sum_j g_j e^{-\varepsilon_j/kT} \sum_k g_k e^{-\varepsilon_k/kT} = Q_j Q_k$$

- When are energy modes independent?
  - motions are separable (classical interpretation)
    - motions in one mode do not depend on the motions of the other modes
  - wave functions are separable (QM interpretation)
    - $\psi = \psi_j \psi_k$, wave function can be divided into different sets of orthogonal wave functions that contain no interaction terms

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Independent Energy Modes: Gases

- For gases that are reasonably approximated as TPG, we can generally write with very good accuracy

  $\varepsilon = \varepsilon_{tr} + \varepsilon_{int}$ *translational + internal energy*

  - and also with good accuracy

    $\varepsilon_{int} = \varepsilon_{elec} + (\varepsilon_{rot,vib})$ ← *does not exist for monatomic gases*

  - and with moderate accuracy

    $\varepsilon_{rot,vib} = \varepsilon_{vib} + \varepsilon_{rot}$

    - rotation (centrifugal effects) can influence vibrational motions/energy
    - vibrational motion (nuclei spacing) can change moment of inertia and rotational motions/energies

- So for gases (TPG or near TPG), can start with simple model

$$\boxed{Q = Q_{tr}Q_{elec}\underbrace{(Q_{vib}Q_{rot})}_{}}$$

Q_{int}

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Independent Modes and TD Properties

- Independence of energy modes extends to macroscopic properties through dependence on partition function
- Example: macroscopic energy, E

$$E = NkT^2 \left.\frac{\partial \ln Q}{\partial T}\right|_V = NkT^2 \left.\frac{\partial \ln\left(Q_{tr}Q_{elec}Q_{vib}Q_{rot}\right)}{\partial T}\right|_V$$

$$= NkT^2\left[\left.\frac{\partial \ln Q_{tr}}{\partial T}\right|_V + \left.\frac{\partial \ln Q_{elec}}{\partial T}\right|_V + \left.\frac{\partial \ln Q_{vib}}{\partial T}\right|_V + \left.\frac{\partial \ln Q_{rot}}{\partial T}\right|_V\right]$$

$$E = E_{tr} + E_{elec} + E_{vib} + E_{rot}$$

macroscopic energy is separable in same way as microscopic energy

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Independent Modes and TD Properties

- Now examine entropy, S

$$S = kN\left[\ln\frac{Q}{N} + 1 + T\left.\frac{\partial \ln Q}{\partial T}\right|_V\right]$$

$$= kN\left[\ln\frac{Q_{tr}Q_{\text{int}}}{N} + 1 + T\left.\frac{\partial \ln Q_{tr}Q_{\text{int}}}{\partial T}\right|_V\right]$$

for clarity, lump all internal energy modes together for now

$$= kN\left[\ln\frac{Q_{tr}}{N} + \ln Q_{\text{int}} + 1 + T\left.\frac{\partial \ln Q_{tr}}{\partial T}\right|_V + T\left.\frac{\partial \ln Q_{\text{int}}}{\partial T}\right|_V\right]$$

$$= \underbrace{kN\left[\ln\frac{Q_{tr}}{N} + 1 + T\left.\frac{\partial \ln Q_{tr}}{\partial T}\right|_V\right]}_{S_{tr}} + \underbrace{kN\left[\ln Q_{\text{int}} + T\left.\frac{\partial \ln Q_{\text{int}}}{\partial T}\right|_V\right]}_{S_{int}}$$

choose to put N and 1 terms into translational S

S also separable, but translational mode has different form for S than internal modes, because CM motion gives rise to pressure (and diffusion)