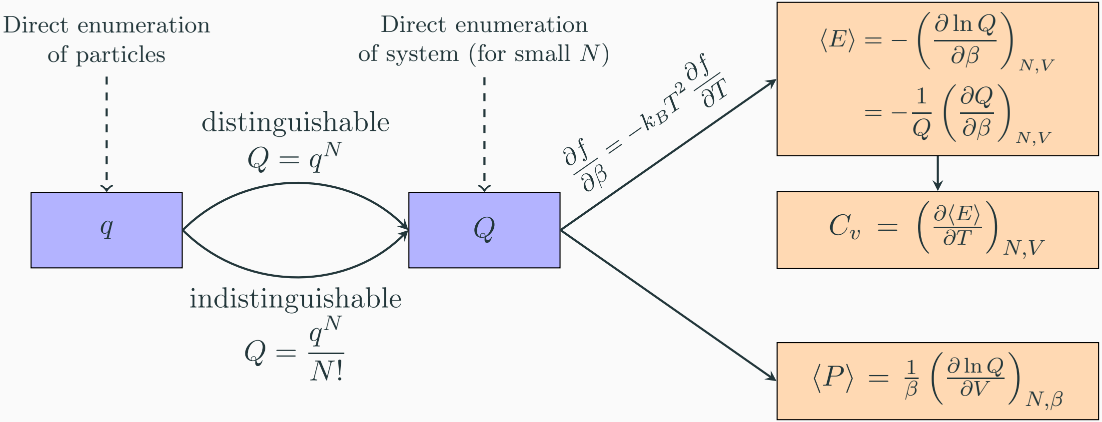
Lecture 6: Molecular Partition Functions

Molecular Partition Functions, Degeneracy

Flow Chart



Direct enumeration of particles
Direct enumeration of system (for small N)
distinguishable
$Q = q^N$
indistinguishable
$Q = \frac{q^N}{N!}$
q
Q
$\frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$
$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$
$C_v = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V}$
$\langle P \rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$

Q vs. q

System

- Q: canonical partition function
- Partition function for the *entire system*
- Microstate energies: E_i

Molecule

- q: molecular partition function
- Partition function for a *single molecule*
- Molecular energies: ε_i

Relating Q to q (for large N)

$$\text{Distinguishable: } Q = q^N$$

$$\text{Indistinguishable: } Q = \frac{q^N}{N!}$$

Relating System to Molecule

Consider N independent, distinguishable molecules

Total energy of the system:

$$\underbrace{E_\ell}_{\text{system microstate}} = \underbrace{\varepsilon_i^a}_{\substack{\text{molecule } a \\ \text{energy level } i}} + \underbrace{\varepsilon_j^b}_{\substack{\text{molecule } b \\ \text{energy level } j}} + \underbrace{\varepsilon_k^c}_{\substack{\text{molecule } c \\ \text{energy level } k}} \cdots$$

(Total energy is a sum of molecular energies)

$$l = (i, j, k \cdots)$$

(Each microstate is a tuple of molecular energies)

System Partition Function

Canonical partition function:

$$Q = \sum_{\ell} e^{-\beta E_\ell}$$

Substitute total energy:

$$Q = \sum_{i,j,k\cdots} e^{-\beta(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c \cdots)}$$

Using $e^{a+b+c} = e^a e^b e^c$

$$Q = \left(\sum_i e^{-\beta \varepsilon_i^a}\right) \left(\sum_j e^{-\beta \varepsilon_j^b}\right) \left(\sum_k e^{-\beta \varepsilon_k^c}\right) \cdots$$

Relating System to Molecule

Each summation is a molecular partition function:

$$Q = q_a \cdot q_b \cdot q_c \cdots$$

For N independent, distinguishable molecules:

$$\boxed{Q = q^N}$$

But in reality, atoms and molecules are indistinguishable, not distinguishaable:

Correcting for overcounting:

$$\boxed{Q = \frac{q^N}{N!}}$$

Molecular Partition Function

Now focus on a single molecule. Total molecular energy can be written as the sum of energies from our degrees of freedom:

$$\varepsilon_{\text{tot}} = \varepsilon_i^{\text{trans}} + \varepsilon_j^{\text{rot}} + \varepsilon_k^{\text{vib}} + \varepsilon_\ell^{\text{elec}}$$

Molecular partition function:

$$\begin{aligned} q &= \sum_i e^{-\beta\varepsilon_i} \\ &= \sum_{i,j,k} e^{-\beta(\varepsilon_i^{\text{trans}} + \varepsilon_j^{\text{rot}} + \varepsilon_k^{\text{vib}})} \end{aligned}$$

Factorizing:

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}}$$

Degeneracy

Instead of summing over energy states, we can sum over energy levels and account for the degeneracy of each level

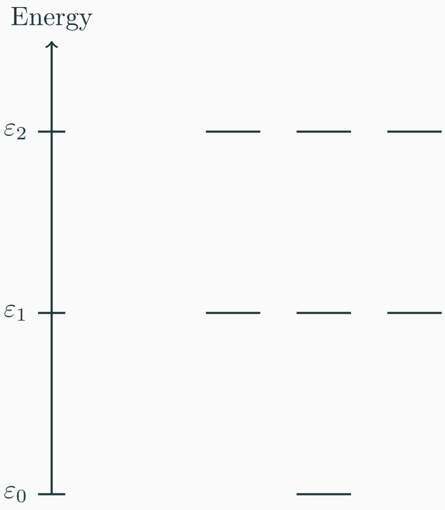
States vs Levels

$$q = \sum_{states} e^{-\beta\varepsilon_i} = \sum_{levels} g_i e^{-\beta\varepsilon_i}$$

g_i is the degeneracy of ε_i

$$q = \sum_{states} e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_0} + 3e^{-\beta\varepsilon_1} + 3e^{-\beta\varepsilon_2}$$

$$q = \sum_{levels} e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_0} + 3e^{-\beta\varepsilon_1} + 3e^{-\beta\varepsilon_2}$$



Example: Writing Q with degeneracy

Consider a system of 3 distinguishable particles that can occupy one of two energy levels, $\varepsilon_0 = 0$ and $\varepsilon_1 = 1$. What are the molecular and canonical partition functions?

Molecular Partition Function

$$q = \sum_{states} e^{-\beta \varepsilon_i} = e^{-\beta \cdot 0} + e^{-\beta \cdot 1} = \boxed{1 + e^{-\beta}}$$

Energy	**Microstates**
3	$(1,1,1)$
2	$(1,1,0), (1,0,1), (0,1,1)$
1	$(1,0,0), (0,1,0), (0,0,1)$
0	$(0,0,0)$

Canonical Partition Function

$$Q = \sum_{levels} \Omega(E) e^{-\beta E_i} = \boxed{1 + 3e^{-\beta \cdot 1} + 3e^{-\beta \cdot 2} + 1e^{-\beta \cdot 3}}$$

Example: Writing Q with degeneracy

Consider a system of N distinguishable particles that can occupy one of two energy levels, $\varepsilon_0 = 0$ and $\varepsilon_1 = 1$ with degeneracy 2. What are the molecular and canonical partition functions?

Molecular Partition Function

$$q = \sum_{levels} g_i e^{-\beta\varepsilon_i} = e^{-\beta\cdot 0} + 2e^{-\beta\cdot 1} = \boxed{1 + 2e^{-\beta}}$$

Canonical Partition Function

$$Q = q^N = \boxed{\left(1 + 2e^{-\beta}\right)^N}$$