

1) IMPORTANCE OF DISTRIBUTION FUNCS

2/10/23

2) Recipe for calc'g Dist'n
only can in any state

1 en state ϵ_1 , 2 systems in ϵ_1

3) Down. of canonical dist'n

- | | | |
|-----|--------------------------|--------------------------|
| | <input type="checkbox"/> | <input type="checkbox"/> |
| (1) | A | B |
| (2) | A | C |
| (3) | A | D |
| (1) | B | A |
| (4) | B | C |
| (5) | B | D |
| (2) | C | A |
| (4) | C | B |
| (6) | C | D |
| (3) | D | A |
| (5) | D | B |
| (6) | D | C |

a) N poss for Box 1
x b) (N-1) " " " " Box 2

c) \therefore Add since systems dist'n then

$$N \cdot (N-1) \cdot (N-2) \dots (N-n_1+1) (N-n_1) \dots$$

$$= \frac{N!}{(N-n_1)!}$$

\approx permutations of N systems within n_1 boxes

\Rightarrow only 6 distinct ways of dist'ng 4 systems in $n_1=2$ boxes
Where order doesn't matter

d) \therefore no. of ways of placing n_1 systems in n_1 boxes in state ϵ_1

- | | |
|--|--|
| <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> | <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> |
| A B C | (1) A B C |
| A B D | (1) A C B |
| A C B | (2) A B D |
| A C D | (2) A D B |
| B A C | (1) B A C |
| B A D | (1) B C A |
| B | (2) B A D |
| | (2) B D A |
| | (1) C A B |
| | (1) C B A |
| | (2) C B D |
| | (2) C D B |

$$P_{N, n_1} = \frac{N!}{n_1! (N-n_1)!}$$

check $P_{4,2} = \frac{4!}{2!2!} = \frac{24}{4} = 6$

check 2: $P_{N, n_1=3} = \frac{24}{(1)6} = 4$

(2) D A B
(2) D B A
(4) D B C
(4) D C B

$$1) W = \frac{N!}{n_1! n_2! \dots}$$

(2)

2) constraint 1: $\sum n_i = N_{\text{sys}}$

constraint 2: $\sum \epsilon_i n_i = E_{\text{TOT}}$

3) Let $F = \ln(W) - \alpha (\sum n_i - N_{\text{sys}}) - \beta (\sum \epsilon_i n_i - E_{\text{TOT}})$

4) population of most likely distribution set
 $\sum n_i = \sum n_i^*$ \Leftrightarrow equil. distribution
 of systems over ensemble
 (subject to constraints)

5)

part 2:

$\sum n_i^* \Leftrightarrow$ the $\sum n_i$ that max's W
 (subject to constraints)

5) $\therefore \delta F|_{\text{max}} \Leftrightarrow \delta F @ \sum n_i^* = 0$

a) $\delta F = \delta \ln N! - \delta \ln [n_1! n_2! \dots]$
 $- \delta [\alpha (\sum n_i - N_{\text{sys}})]$
 $- \delta [\beta (\sum \epsilon_i n_i - E_{\text{TOT}})] = 0$

b) Stirling approx $\ln N! = N \ln N - N$
 $n_i! = n_i \ln n_i - n_i$

(3)

c) ∴ a) $\delta F = 0 = \delta [N \ln N - N]$

$$- \delta [n_1 \ln n_1 - n_1 + (n_2 \ln n_2 - n_2) + \dots]$$

$$\delta [\sum (n_i \ln n_i - n_i)] = \sum [\ln n_i + 1 - 1] \delta n_i$$

$$- \alpha \sum \delta n_i - \beta \sum \epsilon_i \delta n_i$$

d) $\Rightarrow -\sum \ln n_i^* \delta n_i - \alpha \sum \delta n_i - \beta \sum \epsilon_i \delta n_i = 0$

e) (of d) $\Rightarrow -\ln n_i - \alpha - \beta \epsilon_i = 0$

or $n_i^* = e^{-\alpha} e^{-\beta \epsilon_i}$

f) $\sum n_i^* = N \Rightarrow e^{-\alpha} \sum e^{-\beta \epsilon_i} = N$

$\therefore e^{-\alpha} = N/Q$

g)

e) + f) $\Rightarrow \left(\frac{n_i^*}{N} = \frac{e^{-\beta \epsilon_i}}{Q} \right)$

prob. of
obs. n_i given
system
in a
given
state

II) ON Systems ^{OF DYNAMICAL INTERACTING} (IN ^{particles} a canonical ensemble)

A) ROF, Hill, An Intro to Statistical Thermodynamics, Ch. 3

B) Due to separations in dynamical length, ~~and~~ time-scales and/or mass-scales, ^{THE HAMILTONIAN FOR} a Many Quantum dynamic systems can be approximated as a sum of individual Hamiltonians, each describing the (lossless) energetics of subsystems within the system of interest, H_{sys}

C) ~~THE~~ AN important example: multi-atom gas-state molecule:
H for a molecule

$$H_{molecule} = H_{translation} + H_{rotation} + H_{vibr} + H_{electron} \quad (4.1)$$

D) ~~max~~ (4.1) Assumes that the 4 dynamical features of the right; (5) and statistically independent.

dy Better if we can reasonably guess that these dynamicals are essentially independent of another, then a decomposition like (4.1) is valid.

E) Assuming dynamically and statistically independent dynamical modes then the Hamiltonian for a system of N gas molecules is given by:

$$(5.1) \quad \left. \begin{aligned} H_{\text{sys}} \\ \text{N gas} \\ \text{molecules} \end{aligned} \right\} &= \sum_{i=1}^N H_{\text{ptcl } i} \\ &= \sum_{i=1}^N [H_{\text{trans},i} + H_{\text{rot},i} + H_{\text{vib},i} \\ &\quad + H_{\text{electron},i}] \end{aligned}$$

F) Given (5.1), then the system Schrodinger eqn ~~is~~ can be decomposed in N separate S. eqns. (1 for each ptcl.)

6) $\hat{H}_{sys}(\psi_{sys}) = \left[\sum_i \hat{H}_i \right] \psi_{sys} = E_{sys} \psi_{sys}$ (6)

or $\hat{H}_{ptcl i} \psi_i$

(6.1)
$$\left[\hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \dots \right] |\psi_1\rangle |\psi_2\rangle \dots$$
(wave fun ptcl 1 etc)
(eigen energy for ptcl i, etc)

$$= (E_1 + E_2 + \dots) |\psi_1\rangle |\psi_2\rangle \dots$$

where $|\psi_{sys}\rangle = |\psi_1\rangle \cdot |\psi_2\rangle \dots$

12)

14) since $\hat{H}_j = f_n$ of positions, momenta etc for ptcl j alone

then (6.1) ~~is~~ is separable.

(6.2)
$$\hat{H}_1 \psi_1 \psi_2 \psi_3 \dots + \hat{H}_2 \psi_2 \psi_1 \psi_3 \dots + \dots = E_1 \psi_1 \psi_2 \psi_3 \dots + E_2 \psi_1 \psi_2 \psi_3 \dots + \dots$$

I) $\frac{(6.2)}{|\psi_1\rangle |\psi_2\rangle |\psi_3\rangle \dots} \Rightarrow$

(6.3)
$$\left[\frac{\hat{H}_1 \psi_1}{\psi_1} - E_1 \right] + \left[\frac{\hat{H}_2 \psi_2}{\psi_2} - E_2 \right] + \dots = 0$$

J) Finally, since (6.3) must hold for any/all compos of single particle quantum states, $\epsilon_1, \epsilon_2, \dots$

$$\# \left[\hat{H}_j |\psi_j\rangle = \epsilon_j |\psi_j\rangle \right] \quad (7.1)$$

$\forall j = 1, 2, \dots, N$

K) IMPORTANT TAKE-AWAYS:

i) system $\boxed{H} = \boxed{H_{\text{sys}}}$ for any collection of system dynamically and statistically indep. ptcls can be decomposed into N identical in form single particle Schrodinger eqns

ii) under these conditions,

$$E_{\text{sys}} = \underline{\text{SUM of QUANTUM}}$$

eigen-energies, $\{E_1 + E_2 + \dots + E_N\}$

iii) Due to ~~their~~ their dynamical independence for each ptcl in the system each N-ptcl multi-atom molecule in the system can be viewed as its own system (subsystem) but in gas.

c) By same analysis as on pp. 5-7, (7.1) leads to separate S eqns governing each dynamical mode for any given molecule:

$$\begin{aligned}
 \hat{H}_{\text{trans},j} |\psi_{\text{trans},j}\rangle &= E_{\text{trans},j} |\psi_{\text{trans},j}\rangle \\
 \hat{H}_{\text{rot},j} |\psi_{\text{rot},j}\rangle &= E_{\text{rot},j} |\psi_{\text{rot},j}\rangle \\
 \hat{H}_{\text{vib},j} |\psi_{\text{vib},j}\rangle &= E_{\text{vib},j} |\psi_{\text{vib},j}\rangle \\
 \hat{H}_{\text{elec},j} |\psi_{\text{elec},j}\rangle &= E_{\text{elec},j} |\psi_{\text{elec},j}\rangle
 \end{aligned}
 \tag{8.1}$$

where

$$E_j = E_{\text{trans},j} + E_{\text{rot},j} + E_{\text{vib},j} + E_{\text{elec},j}
 \tag{8.2}$$

⊕ $\hat{H}_{i,j}$'s. may can be built for indiv. molecules

⊕ each eqn in (8.1) is an eigenvalue problem having an $[\infty]$ set of eigen-energies, $E_{\text{trans},j,1}, E_{\text{trans},j,2}, \dots$

M) Using (8.2) in (3.1) leads to (9)

$$P(E_i) = \frac{n_i^*}{N} = \frac{e^{-\beta[\epsilon_{tia} + \epsilon_{rib} + \epsilon_{vic} + \epsilon_{eid}]}}{\sum_{a,b,c,d} e^{-\beta[\epsilon_{tia} + \epsilon_{rib} + \epsilon_{vic} + \epsilon_{eid}]}}$$

$$= \frac{u}{\sum_{a,b,c} e^{-\beta[u]} \cdot \left(\sum_d e^{-\beta \epsilon_{eid}} \right)}$$

$$= \frac{u}{\left[\sum_a (e^{-\beta \epsilon_{tia}}) \right] \left[\sum_b e^{-\beta \epsilon_{rib}} \right] \left[\sum_c e^{-\beta \epsilon_{vic}} \right] \cdot \left[\sum_d e^{-\beta \epsilon_{eid}} \right]}$$

(9.1)

$$P(E_i) = \left(\frac{e^{-\beta \epsilon_{tia}}}{\sum_a e^{-\beta \epsilon_{tia}}} \right) \cdot \left(\frac{e^{-\beta \epsilon_{rib}}}{\sum_b e^{-\beta \epsilon_{rib}}} \right) \cdot \left(\frac{e^{-\beta \epsilon_{vic}}}{\sum_c e^{-\beta \epsilon_{vic}}} \right) \cdot \left[\sum_d e^{-\beta \epsilon_{eid}} \right]$$

~~Final~~

(similar for ϵ_{eid})

Importantly, we've shown that (10)
 the partition fun. for an
 individual molecule, Q_1 ,
 is given by ~~the~~ product
 of partition funs ~~that~~
 for each dynamical
mode in the problem

$$(10.1) \quad Q_i = Q_{\text{trans}} \cdot Q_{\text{rot}} \cdot Q_{\text{vib}} \cdot Q_{\text{elec}}$$

where eq.

$$Q_{\text{trans}} = \sum_a e^{-\beta \epsilon_{\text{trans},a}} \quad (10.2)$$

IMP NOTES re (10.1):

- 1) macroscopic thermo props
 det'd by $Q_{\text{sys}} = (Q_1)^N$
 see eq. ch. 3 pathway
- 2) (10.1) tells us that for an
 a system of non-interacting
ptcls, here molecules, we can
 explicitly construct Q_1 by:

a) solving single ptcl. Schrodinger eqn
for a single translating ptcl.

$$\frac{\hat{p}^2}{2m} |\psi_{trans}\rangle = E_{trans} |\psi_{trans}\rangle$$

b) " " " " Schrodinger eqn.
for rotating molecule (about
center of mass) - see, e.g.,
Dunroeder

c) " " " " Schrodinger eqn
for vibrating molecule (about
center of mass) - see Dunroeder

d) " " " " Schrodinger eqn
for a electron cloud of our
M molecule - see Dunroeder