

I) Forms of the Canonical Distn

1) Sec. 3.4 text

replica systems

A) 1) given $n_1, n_2, n_3, \dots, n_m$, w/ $g_1, g_2, \dots$

g_m degenerate states (ass'd w/ the quantum energy states $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_m$), then the number

of ways of distr. buting the

n_j systems in g_j available

(degenerate) energy states [no limit w/

on number of systems in state

$(\epsilon_j, g_j)]$ is: $\boxed{g_j^{n_j}}$

A2) In the case where there are no degenerate states, ($g_j = 1$ for all j) the number of ways of observing a given distribution set, $\{n_1, n_2, \dots, n_m\}$,

$$\text{is } W \{n\} = \frac{\tilde{N}}{n_1! n_2! \dots n_m!}$$

A3) so, for a given distn set,

$\{n\}$, and g_j degenerate energy

states for each quantum energy,

ϵ_j . The total number of ways

of observing this given set is

$$W(\{n_j\}) = \frac{\tilde{N}_j! (\prod_j g_j^{n_j})}{n_1! n_2! n_3! \dots n_m!}$$

$$\boxed{w(\{n_j\}) = \frac{\tilde{N}_j! \prod_j g_j^{n_j}}{\prod_j n_j!}} \quad (2.1)$$

A.4) Given (2.1) AND given the usual constraints on the $\tilde{N}$ systems within the canonical ensemble

$$\tilde{N} = \sum_j n_j$$

$$\tilde{E} = \sum_j n_j E_j$$

(where again n_j = no. of systems in quantum state E_j), THEN apply again the

the same procedure:

$$(i) \quad F(\{n_j\}) \equiv \ln W(\{n_j\}) + \beta' [\tilde{E} - \sum_j n_j E_j] + \alpha' [\tilde{N} - \sum_j n_j]$$

$$\begin{aligned} \text{or} \quad F(\{n_j\}) &= \tilde{N} \ln \tilde{N} - \sum_j n_j \ln \tilde{N} + \sum_j n_j \ln g_j \\ &\quad - \sum_j [n_j \ln n_j - n_j] + \beta' [\tilde{E} - \sum_j n_j E_j] + \alpha' [\tilde{N} - \sum_j n_j] \end{aligned}$$

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$$\therefore F(\epsilon N) = \tilde{N} \ln \tilde{N} + \sum_j \eta_j \ln g_j - \sum_j \eta_j \ln \eta_j + B' [E - \sum_j \epsilon_j \eta_j] + \alpha' [\tilde{N} - \sum_j \eta_j] \quad (3.1)$$

A.5) $[B', \alpha' = \text{Lagrange Multipliers}]$
 AT EQUILIBRIUM, THE MOST PROBABLE DISTRIBUTION set, $\epsilon N^* = \sum \epsilon_j \eta_j^*$, IS THE ONE THAT MAXIMIZES $W(\epsilon N)$;
 SO

$$\left[\frac{\partial F}{\partial \eta_j} = 0 = \ln g_j - \ln \eta_j - 1 - B' \epsilon_j - \alpha' \right] \quad (3.2)$$

A.6) (3.2) $\Rightarrow \frac{\eta_j^*}{g_j} \propto e^{-B' \epsilon_j}$

or $\left[\eta_j^* \propto g_j e^{-B' \epsilon_j} \right] \quad (3.3)$

or $\left[\eta_j^* = A_0 g_j e^{-B' \epsilon_j} \right] \quad (3.3a)$

A.7) GET A_0 :

$$\tilde{N} = \sum_j \eta_j^* = A_0 \sum_j g_j e^{-B' \epsilon_j}$$

$$\therefore A_0 = \tilde{N} / \sum_j g_j e^{-B' \epsilon_j}$$

$$\therefore P(E_r) \equiv \frac{n_r^*}{\tilde{N}} = \frac{g_r e^{-\beta E_r}}{Q}$$

(4.1)

$$\text{where } Q = \sum_r g_r e^{-\beta E_r}$$

⊕ Important take-away from

(4.1): For the typical case of degenerate energy levels, or effectively degenerate

levels, the degree of degeneracy $\equiv$ no. of deg. states

(for energy E_j) $\equiv g_j$. can

be roughly interpreted as a statistical weight factor for level j .

We use this interpretation in writing down the probability, $P(E)$, and partition fn., Q , for the case of effectively continuous energy levels (next section)

⊕ (4.1) assumes that

$g_j \gg 1$ and $n_j \gg 1$ so that

[Describe g, E con'd]

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The simple formula, $f_i^1 = f_{int} - f$,
could be used. See Ch. 6.1

for a derivation that parallels
(at least mathematically)

the above derivation. [Pathria
does not derive (4.1) - merely
states / hand waves it.]

B) ^{EFFECTIVELY} CONTINUOUS ^{DEGENERATE} ENERGY STATES.

- 1) MOTIVATION: QUANTUM ENERGY COVERS
CAN / TYPICALLY DO BECOME
VERY CLOSELY SPACED. FOR
EXAMPLE, THE Q ENERGY STATES
FOR A SINGLE ^{QUANTUM} ptcl. in a
BOX OF VOL. V IS GIVEN BY:

$$E_{x,y,z} = \frac{h^2}{8mV^{2/3}} [n_x^2 + n_y^2 + n_z^2] \quad (1.4.6 \text{ Pathria})$$

SINCE h IS SO SMALL

($h = 6.6256 (10^{-27}) \text{ erg-sec}$; $m_{\text{electron}} = 1.67 (10^{-27}) \text{ kg}$)
THEN FOR V 's $\geq$ A FEW $\text{\AA}$ OR nm 's

(CONTINUOUS ENERGY EX. CONT'D)

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for only slightly different n 's
 E 's become very closely

spaced. Assume a box of $L = 1 \text{ nm}$

$= 10^{-9} \text{ m} \rightarrow V = 10^{-27} \text{ m}^3$. So for a single proton, say:

$$\frac{h^2}{8mV^{2/3}} \approx \frac{(6.6)^2 10^{-54} \text{ erg}^2}{(8)(1.67)(10^{-27})^{2/3} \text{ kg} \cdot 10^{-18} \text{ m}^2/\text{s}^2}$$

$$\approx 3(10^{-23}) \text{ J} \approx 3(10^{-16}) \text{ erg}$$

④ Lots give: the proton a. energy of characteristic

$$\text{say } \frac{3}{2} kT = \frac{3}{2} k(300 \text{ K}) \approx (1.5)(1.38)(10^{-23}) \frac{\text{J}}{\text{K}} (300 \text{ K}) \\ \approx 2.07(10^{-20}) \text{ J} \approx 6(10^{-13}) \text{ erg}$$

$$\therefore E = \frac{3}{2} kT = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

$$\Rightarrow \left[n_x^2 + n_y^2 + n_z^2 \approx \frac{6(10^{-13}) \text{ erg}}{3(10^{-16}) \text{ erg}} = \underline{\underline{2000}} \right] \quad (6.1)$$
$$\equiv E^* \quad (\text{see 1.4.6 text})$$

Effectively
continuous energy states
approx

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⊕ Now, use the formulas we derived in ch. 1 to first get the total number of quantum energy states, $\sum (N=1, \nu, E)$, that satisfy (6.1):

$$\sum (N, \nu, E) \approx \frac{\pi}{6} \epsilon^*{}^{3/2} \quad \left(\begin{array}{l} \text{see} \\ \text{Eq} \\ 1.4.14 \end{array} \right)$$

$$\text{where } \epsilon^* = \frac{E}{\frac{h^2}{8mV^{2/3}}} \approx 2000 \quad \left(\text{see 1.4.6} \right)$$

$$\begin{aligned} \therefore \sum (N=1, \nu, E) &\approx \left(\frac{1}{2} \right) (2000)^{3/2} \\ &\approx 1.5 (10 \cdot 10^2)^{3/2} \\ &\approx \underline{\underline{(45 \times 10^3)}} \end{aligned}$$

(i.e. ~45000 different quantum states lie below and at $E = \frac{3}{2} kT$)

7 LET'S GO BACK TO (E.1) and
 estimate the number of
 states that lie w/in ϵ^*
 FOR TEMPERATURE MEASUREMENT
 uncertainty, ΔT , of say $(3)10^{-3}K$.
 IN THIS CASE

$$\Delta \epsilon^* \equiv \text{uncertainty in } \epsilon^* \text{ ass'd w/ uncertainty } \Delta T$$

$$\approx (\epsilon^*) \left(\frac{\Delta T}{T} \right)$$

$$\approx 2(10^3)(10^{-3})$$

$$\approx 2$$

8 $\therefore$, ROUGHLY SPEAKING, THE
 NUMBER OF QUANTUM
 STATES w/in $\epsilon^* - \Delta \epsilon^* \leq \epsilon \leq \epsilon^* + \Delta \epsilon^*$
 IS ~ 5 or so, SINCE
 WE CANNOT discriminate
 between energy states
 that lie w/in the error band

(EFFECTIVELY CONTINUOUS
ENERGY STATES) CONT'D

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ΔE , (or or) ~~it~~ associated

⑨

w/ our thermometer, then the
effective degeneracy, g , for

the quantum energy state

corresponding to $E^* \approx 2000$

is on the order of 5 (or so).

⑩ If we increase the volume, V ,
occupied by our single
proton, to say 10^3 nm^3 , then

$$\boxed{E^* \approx 2(10^5)}$$

$\therefore$ for a moment uncertainty, ΔT ,
say $3(10^{-3}) \text{ K}$, then

$$\frac{\Delta E^*}{E^*} = \frac{\Delta T}{T} = 10^{-4}$$

$$\Rightarrow \boxed{\Delta E^* \approx 20}$$

$\therefore$ since we cannot resolve (dimensionless)
energy levels / level differences
smaller than $\Delta E^* \approx 20$, then
we can use the same analysis
as in Ch. 1 to estimate

ERE continuous energy states
CONT'D

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the number of quantum states —
in the positive octant of the
 $n_x n_y n_z$ space — w/in a spherical
shell of vol ΔV^* :

$$\Delta V^* = \frac{4\pi R^2 \Delta R}{8}$$

where

$$\text{and } n_x^2 + n_y^2 + n_z^2 = R^2 = \epsilon^* \frac{2(10^9)}{h^2}$$

$$\Delta R = \Delta(\epsilon^* h) = \frac{1}{2\epsilon^* h} d\epsilon^*$$

$$= \frac{d\epsilon^*}{2\epsilon^* h} \approx \frac{20}{2(20(10^9))^{1/2}}$$

$$\approx \sqrt{2(10^{-2})}$$

⊕ Along, say, the n_x -axis, ($n_y = n_z = 0$), the
approx. thickness, $\Delta R = \frac{d\epsilon^*}{\frac{1}{2}\epsilon^{*1/2}}$ of
the nominally constant-energy
shell (of radius R^*) is $\Delta R \approx 2(10^{-2})$.

$$\text{⊕ also, } R \approx 4.5(10^2) = n_x$$

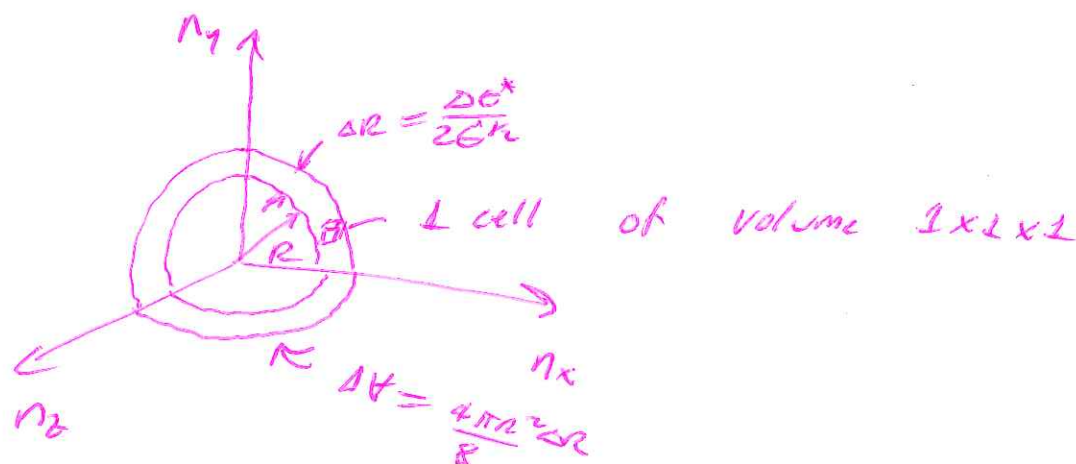
$$\text{⊕ } \boxed{\Delta V = \frac{4\pi}{8} R^2 \Delta R \approx (1.5) 2(10^9) 2(10^{-2}) \approx \underline{\underline{6000}}} \quad (10.1)$$

⊕ ∴ since the spacing in $n_x n_y n_z$
space between adjacent states is 1,
then (10.1) implies that w/in the
shell of volume ΔV , there are N_{cells} , where

$$\Delta\epsilon \approx N_{\text{cells}} * \left(\frac{\text{vol per cell}}{\text{cell}} \right)$$

$$\approx N_{\text{cells}} (1^3)$$

$$\Rightarrow \left[N_{\text{cell}} \approx \frac{\Delta\epsilon}{(1)^3} \approx 6000 \right]$$



⊕ IN ORDER TO ESTIMATE THE NUMBER OF ENERGY STATES, N_s

THAT ARE ASSOCIATED w/ THOSE N_{cell} VOLUMES, STRETCH / DEFORM THE SHELL ABOUT INTO AN EQUIVALENT SHEET (OF AREA $\frac{4\pi R^2}{8}$ AND THICKNESS ΔV) :

$$\Delta V : L \approx \sqrt{\frac{4\pi R^2}{8}} \approx 1.2 R \approx (1.2)(4.5)(10^2) \approx 500 = \left[\begin{array}{l} 500 \\ \text{pts} \\ \text{in} \\ n_x \text{ dir} \end{array} \right]$$

$$\Delta\epsilon \approx \left[\begin{array}{l} L \\ n_z \end{array} \right] \left[\begin{array}{l} L \\ n_x \end{array} \right] \left[\begin{array}{l} L \\ n_y \end{array} \right] \approx \left[\begin{array}{l} 500 \\ \text{pts in } n_z \\ \text{direction} \end{array} \right] * \left[\begin{array}{l} 500 \\ \text{pts in } n_x \\ \text{direction} \end{array} \right] * \left[\begin{array}{l} 500 \\ \text{pts in } n_y \\ \text{direction} \end{array} \right]$$

Diagram of a rectangular sheet with dimensions L (vertical), L (horizontal), and L (depth). The axes are labeled n_x , n_y , and n_z .

$$\Delta L \approx \Delta R = 2(10^2)$$

EFFECTIVE CONF. ENERGY STATES

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$$\begin{aligned}\therefore N_s &\approx L \times L \times \Delta L \approx g \equiv \text{effective degeneracy} \\ &\approx (500)^2 (2) (10^2) \\ &\approx 50 (10^2) \\ &\approx \underline{\underline{5000}}\end{aligned}$$

associated w/
energy ϵ^*

FINAL TAKE-AWAY 1

FOR A SINGLE QUANTUM stat. (proton here) in a ^{cube} box having ^{edge} lengths of 10 nm, AND AN EQUIVALENT TEMP.

OF 300 K, AND FOR A MEASUREMENT UNCERTAINTY OF $\Delta T = 3 (10^{-2})$ K,

THE EFFECTIVE DEGENERACY, [g], WHICH IS EXACTLY THE

NUMBER OF QUANTUM STATES,

[$\Omega(N=1, V, E=\frac{3}{2}kT)$] WITHIN THE

ABOVE ENERGY SHELL (pg 11),

IS LARGE, ON THE ORDER

OF [5000 $\approx$ g],

TAKE-AWAY 2

THE EFFECTIVE DEGENERACY, g_j ,
ASSOCIATED WITH A GIVEN ENERGY
LEVEL, E_j :

- 1) ARISES DUE TO MEASUREMENT
UNCERTAINTY;
- 2) BECOMES VERY LARGE,
FOR EXAMPLE, AS THE NUMBER
OF PTLS, $N \uparrow$, AS $T \uparrow$
AND/OR AS $V \uparrow$, WE CAN
SEE THE LAST TWO EFFECTS
BY TRACKING BACKWARD
THROUGH OUR EXAMPLES:

$$i) N_s \approx \Delta V = \frac{4\pi R^2 \Delta R}{8}$$

ii)

$$= \frac{\pi}{2} E^* \frac{\Delta E^*}{2 E^* k}$$

$$= \frac{\pi}{4} E^{*1/2} \Delta E^* \left(\frac{\Delta E^*}{E^*} = \frac{\Delta T}{T} \right)$$

$$= \frac{\pi}{4} \left(\frac{8mV^{2/3} E}{h^2} \right)^{3/2} \left(\frac{\Delta T}{T} \right) \quad \downarrow \quad \boxed{\Delta E = \frac{\Delta T}{T} E^*}$$

$$\boxed{E = \frac{3}{2} kT}$$

EFFECT. CONTINUOUS EN. STATES CONTIN

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$$N_S \approx \left(\frac{\pi}{4} \right) \left(\frac{8mV^{2/3}K}{h^2} \right)^{3/2} T^{1/2} \Delta T = g_{\text{ptcl}} \quad (14)$$

2) FREQUENTLY CONTINUOUS EN. STATES

a) NOW, LET

$g(E) dE =$ NUMBER OF QUANTUM
ENERGY STATES
W/IN THE RANGE
OF ENERGIES:

$$E - dE \leq E' \leq E + dE$$

b) $g(E)$ IS CALLED THE DENSITY
OF STATES (ABOUT E)

④ $g(E)$ HAS UNITS OF no. states
energy

$$\therefore g(E) \equiv \frac{1}{J} \equiv \frac{1}{\text{erg}} \text{ etc}$$

c) USE THE INTERPRETATION ON

PG. 4 THAT $g_i \equiv g(E_i) \Delta E_i$

IS A weight Factor THAT

MUST BE INTRODUCED WHEN

THE "quantum" energy levels $E_1, E_2, E_3 \dots$

HAVE EFFECTIVE DEGENERACIES

OF $g_1 = g(E_1) \Delta E_1, g_2 = g(E_2) \Delta E_2$

etc.

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* Insert Before 2) on pg 14 *

TAKE-AWAY 3: (where ΔR is determined by experimental uncertainty)
 Since $\Delta R = \frac{\Delta E^*}{2E^{1/2}}$ is much less than 1 (in the present example),

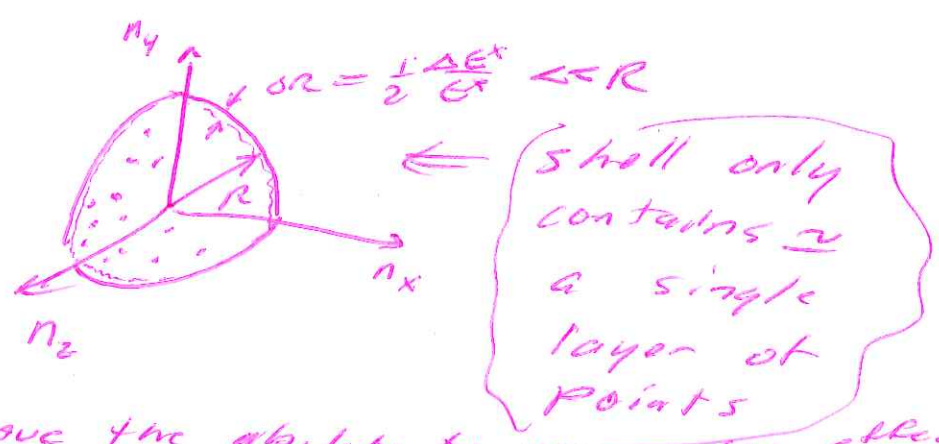
and since the change in unit R associated with a change in n_x, n_y , or n_z is 1 then since the shell thickness, ΔR , is $\ll 1$

Geometrically, the (approximate) actual (quantum) degeneracy,

$$g_{\text{act}} = g(E = \frac{3}{2} kT) \approx \frac{4\pi R^2}{8} \Delta R = \Delta V$$

($\approx 5-6000$ in this example).

GEOMETRIC PICTURE



④ If we have the ability to measure kT effective temp. of a single proton in a $10 \times 10 \times 10$ cm box

an uncertainty $\Delta p/p = 10^{-2}$ then we can't do any better in resolving quantum energy states

$$\therefore Q = \sum_i g(E_i) \Delta E_i e^{-\beta E_i}$$

$$\text{or } \boxed{Q = \int_0^{\infty} g(E) e^{-\beta E} dE} \quad (15.1)$$

$$\text{ALSO } \boxed{P(E) dE = g(E) e^{-\beta E} dE / Q}$$

d)

$$\begin{aligned} \langle f \rangle &= \frac{\sum_i f(E_i) g(E_i) e^{-\beta E_i}}{\sum_i g(E_i) e^{-\beta E_i}} \\ \langle f \rangle &= \frac{\int_0^{\infty} f(E) g(E) e^{-\beta E} dE}{\int_0^{\infty} g(E) e^{-\beta E} dE} \end{aligned}$$

e) (15.1) Leads to a useful/powerful
Formula for calculating
the density of states, $g(E)$.

$$g(E) = \frac{1}{2\pi i} \int_{B' - i\infty}^{B' + i\infty} Q(B) e^{\beta E} dB = \text{Inverse Laplace transform of } Q$$