

1	Q. CHEM	MICRO	ENERGY LEVELS
10^{23}	THERMO	MACRO	U, V, H, P, T, μ

MICRO $\xrightarrow{\text{S. M.}}$ MACRO
 (SCHRÖDINGER)
 EQ

1860 - 1900 BOLTZMANN \longrightarrow KINETIC
 MAXWELL THEORY OF GASES
 (CLASSICAL)

1900 - 1905 J. GIBBS \longrightarrow STAT THERMO

ASSUMED CLASSICAL BEHAVIOR OF THE
 PARTICLES.

\Rightarrow SOME INCORRECT RESULTS

⊗ ACCORDING TO Q.M. ALL KIND OF MOTIONS ARE QUANTIZED : TRANSLATIONAL, ROTATIONAL, VIBRATIONAL AND ELECTRONIC

ON THE OTHER HAND MOST CHEMICAL SYSTEMS CONSIST OF A LARGE NUMBER OF PARTICLES. A COMMON MEASURE OF THE AMOUNT OF SUBSTANCE IS THE MOLE (mol) WHICH CONSISTS OF 6.022×10^{23} PARTICLES, e.g. 18 mL OF WATER.

THEREFORE WE HAVE A LARGE NUMBER OF PARTICLES AND A SET OF ENERGY LEVELS. HOW ARE THESE LEVEL POPULATED?

BOLTZMANN DISTRIBUTION

THE RATIO OF THE AVERAGE NUMBER OF PARTICLES WITH ENERGIES E_i AND E_j IS GIVEN BY

$$\frac{N_i}{N_j} = e^{-\frac{E_i - E_j}{k_B T}}$$

WHERE $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ IS THE BOLTZMANN CONSTANT AND T THE ABSOLUTE TEMPERATURE.

IN PRINCIPLE WE COULD SOLVE EITHER NEWTON'S LAW OR SCHRÖDINGER EQ FOR 10^{23} PARTICLES. IN PRACTICE SOLVING AND TRACKING 10^{23} INTERACTING PARTICLES IS IMPOSSIBLE, MODERN SUPER COMPUTERS ARE ABLE TO HANDLE BETWEEN $10^5 - 10^{10}$ MOLECULES AND TRACK THEM FOR TIMES UP TO 10^{-2} SEC. EVEN FOR DILUTE SYSTEMS, 10^{18} PARTICLES, IS QUITE HARD TO DESCRIBE.

IF WE CONSIDER THE CHARACTERISTIC TIMES

TIME BETWEEN COLLISIONS $\tau \sim 10^{-10}$ S

TIME IN THERMODYNAMICS $\tau \sim 10^{-1}$ S

GIVEN THESE TIMES WE COULD CONSIDER TIME AVERAGES OF THE MICROSCOPIC DESCRIPTION

AT FIRST,
WE WANT TO CONSIDER AN AVERAGE
IN TIME OF THE MICROSCOPIC PROPERTIES

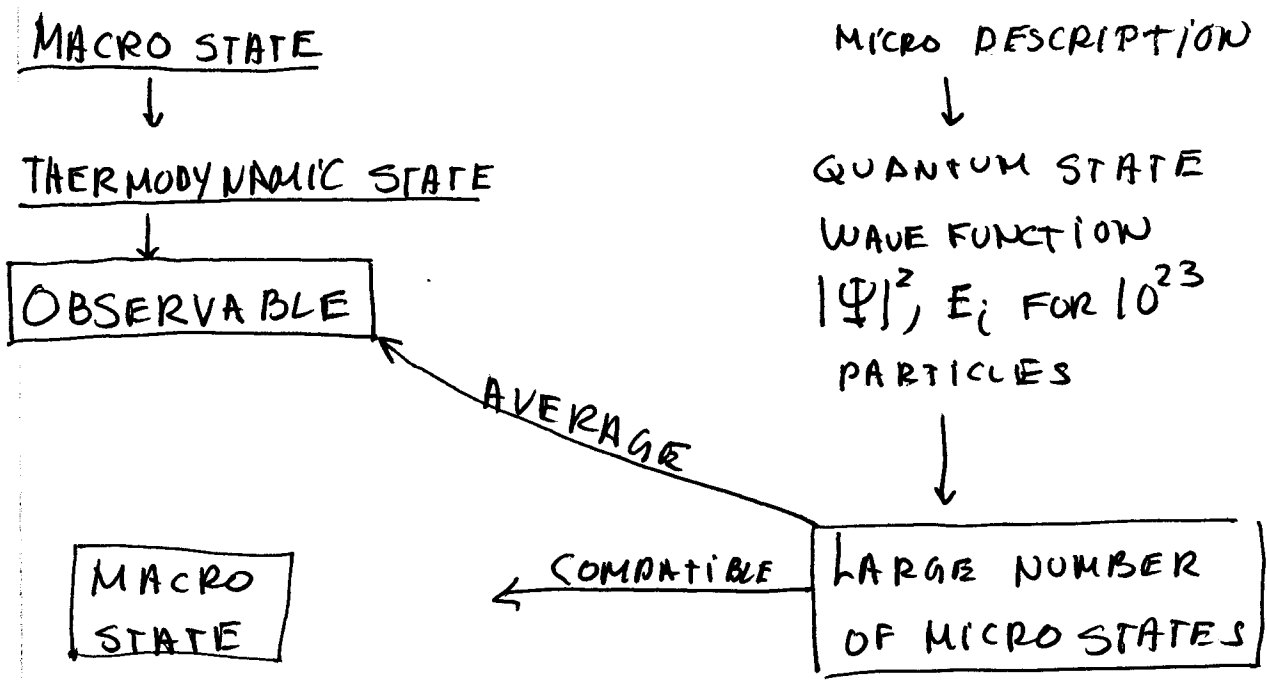
$$\overline{A} \equiv \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(z') dz'$$

↑ MACRO
 ↑ MICRO

A MACROSTATE IS CONSISTENT WITH A
LARGE NUMBER OF MICRO STATES.

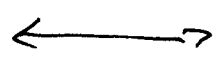
IN PRACTICE THESE TIME AVERAGES
CANNOT BE PERFORMED SINCE WE REALLY
DON'T KNOW THE TIME BEHAVIOR OF
THE MICRO PROPERTY, $A(z')$.

TO SOLVE THIS PROBLEM, WE DEFINE
THE CONCEPT OF ENSEMBLE, WHICH
IS A HYPOTHETICAL (MENTAL) COLLECTION
OF A LARGE NUMBER OF COPIES OF
THE SYSTEM EACH OF WHICH
IS CONSISTENT WITH THE
MACRO STATE, i.e., $N, V, T, E,$



WE HAVE A NUMBER OF DIFFERENT WAYS IN WHICH WE CAN POPULATE THE QUANTUM LEVELS (ENERGY) AND STILL END UP WITH THE SAME TOTAL ENERGY.

DIFFERENT
CONSTRAINTS
N, V, E
N, V, T



DIFFERENT
ENSEMBLE
CANONICAL
CANONICAL
(VARIABLE E_T)

μ, V, T

GRAND CANONICAL
(VARIABLES E AND N)

N, P, T

PRESSURE ENSEMBLE
(VARIABLE V AND E)

BUT EACH OF WHICH IS IN A DIFFERENT MICRO STATE.

ERGODIC (PROPERTY) SYSTEM

THE MACRO SYSTEM IN ITS TIME EVOLUTION CAN, IN PRINCIPLE, VISIT ALL THE DIFFERENT ALLOWED MICRO STATES.

POSTULATE I (ERGODIC HYPOTHESIS)

SYSTEM'S

THE TIME AVERAGE OF A PROPERTY IS

EQUAL TO THE AVERAGE OF THE PROPERTY OVER THE ENSEMBLE AT ONE INSTANT OF TIME



CONSEQUENTLY, IN ORDER TO CALCULATE THE AVERAGES WE NEED TO KNOW

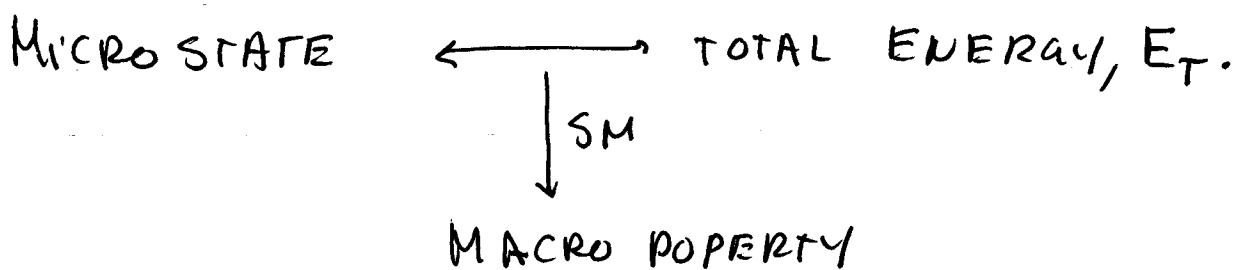
- a) THE MICRO STATES THAT ARE CONSISTENT WITH THE MACRO CONSTRAINTS

b) THE NUMBER OF SYSTEMS IN THE ENSEMBLE IN EACH MICRO STATE

THE MICRO STATE PROBABILITY

CANONICAL ENSEMBLE

WE FIX N , V AND T AND VARY THE TOTAL ENERGY.



WE NEED THE PROBABILITY OF FINDING THE SYSTEM IN THE i^{th} MICRO STATE

$$P(E_i) \sim \frac{n_i}{n_T}$$

$$E_T = \sum_i E_i$$

WHERE

N_i = # OF MICRO STATES IN
THE ENSEMBLE WITH
ENERGY E_i

N_T = TOTAL # OF SYSTEMS
IN THE ENSEMBLE

FOR THE CANONICAL ENSEMBLE,
THE PROBABILITY THAT THE MACRO
SYSTEM IS IN THE i^{th} MICRO STATE
IS GIVEN BY

$$P(E_i) = \frac{g_i \bar{\Omega}^{-\beta E_i}}{\sum \bar{\Omega}^{-\beta E_i}} = \frac{N_i}{N_T}$$

(ALL MICRO STATES).

WHERE g_i IS THE DEGENERACY OF
THE E_i .

THIS EXPRESSION IS RELATED TO THE
BOLTZMANN DISTRIBUTION.

BOLTZMANN DISTRIBUTION

$$\frac{N_i}{N_j} = \mathcal{Q}^{-\frac{E_i - E_j}{k_B T}}$$

WE CONSIDER

$$N_i = A \mathcal{Q}^{-\beta E_i}$$

WHERE $\beta = \frac{1}{k_B T}$.

THE E_i PROBABILITY IS

$$P(E_i) = \frac{N_i}{N_T}$$

WHERE

$$N_T = A \sum_i \mathcal{Q}^{-\beta E_i}$$

$$P(E_i) = \frac{\mathcal{Q}^{-\beta E_i}}{\sum_i \mathcal{Q}^{-\beta E_i}}$$

$$P_i = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}} \equiv \frac{e^{-\beta E_i}}{q}$$

$$\sum P_i = 1$$

$$\boxed{\bar{E} = \frac{\sum E_i e^{-\beta E_i}}{q} = \sum E_i P_i}$$

FROM THERMO

$$dE = -p \cdot dV$$

FROM QM $E_i(V)$

$$dE_i = \left(\frac{\partial E_i}{\partial V} \right)_\beta dV$$

$$d\bar{E} = \sum P_i dE_i = \left[\sum_i \left(\frac{\partial E_i}{\partial V} \right)_\beta P_i \right] dV$$

$$\left(\frac{\partial E_i}{\partial V}\right)_T \equiv -P_i$$

$$d\bar{E} = -\left(\sum_i P_i P_i\right) dV = -\bar{p} dV$$

$$d\bar{E} = d\left(\sum E_i P_i\right)$$

$$= \sum dE_i P_i + \sum E_i dP_i$$

$$dE_i = \left(\frac{\partial E_i}{\partial V}\right)_T dV = -P_i dV$$

$$d\bar{E} = -\bar{p} dV + \sum_i E_i dP_i$$

$$\text{But } E_i = -\frac{1}{\beta} [\ln P_i + \ln q]$$

$$d\bar{E} + \bar{p} dV = -\frac{1}{\beta} \sum \ln P_i dP_i - \frac{1}{\beta} \ln q \sum dP_i$$

BUT

$$\sum P_i = 1$$

THEREFORE

$$\sum dP_i = 0$$

AND

$$d\bar{E} + \bar{p}dV = -\frac{1}{\beta} \sum \ln P_i dP_i$$

NOW

$$d(\sum P_i \ln P_i) = \sum \ln P_i dP_i + \sum dP_i$$

$$\boxed{d\bar{E} + \bar{p}dV = -\frac{1}{\beta} d(\sum P_i \ln P_i)}$$

FROM THERMO

$$dE + p dV = T dS$$

$$\beta \sim \frac{1}{T}$$

$$S \sim -\sum P_i \ln P_i$$

$$\beta = \frac{1}{k_B T}$$

$$S = -k \sum P_i \ln P_i$$