Lecture 33

Statistical Thermodynamics
Microstate, Macrostate and Entropy

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Topics to Discuss

● Classical Thermodynamics vs. Statistical Thermodynamics

● Microstate, Macrostate and Entropy
   ☐ The concept of probability

Classical Thermodynamics

◆ **The branch of thermodynamics dealing with macroscopic description of the behaviour of matter is called classical thermodynamics or phenomenological thermodynamics.**

  ❑ consider a thermodynamic system as continuous.

  ❑ ignore the fact that the substance is actually composed of atoms or molecules

  ❑ ignore the fact that the behaviour of the system is somehow related to the properties of the particles that compose it.

◆ **The connection between the thermodynamics behaviour of macroscopic system and that of atoms on their sub-microscopic scale is useful for a variety of reasons.**

  ❑ a new level of understanding of how matter behaves emerges from this connection.

  ❑ In the macroscopic level of description, for example, it is sufficient only to know that the heat capacity of A is different from that of B.

  ❑ At the atomistic level of description, it is possible not only to predict this difference in heat capacities of A and B, but also the expected magnitude of those differences.

◆ **Atomistic models provide a level of explanation for the behaviour of a substance; phenomenological information merely provides a consistent description of how it behaves.**

Statistical Thermodynamics

◆ **An atomistic description of the behaviour of matter begins with the idea that each atom in the system can be assigned values of properties that describe its condition.**

- ❑ if it were possible to know the **masses**, **velocities**, **positions**, and all modes of **motion** of all the constituent particles in a system, then this mass of knowledge would serve to describe the **microscopic state** of the system, which, in turn, would determine all of the properties of the system.

- ❑ however, such a description of the state of system by specifying the property (i.e, the energy level) of all the atoms is impossible !!

◆ **To analyse very large collection of numbers, the concept of the distribution function of statistics can be used.**

- ❑ atoms that have similar values of properties are lumped together into classes (in this case, energy levels); the distribution function simply reports the number of particles in each class.

- ❑ in this way the quantity of information required to specify the condition of the system is greatly reduced.

◆ **Description of the behaviour of matter in terms of the distribution of particles over their allowable states is called statistical thermodynamic.**

- ❑ specification of the thermodynamic state of a system in terms of such a distribution function is called the **macrostate** for the system.

- ❑ so statistical thermodynamics is not concerned with the behaviour of individual particles of a system – only the statistical average behaviour of the system.

Microstate, Macrostate and Entropy

● All particles are **DIFFERENT**.

● If any entry in this list is altered, that is, if any particle changes its condition, the system is considered to be in a different microstate.

Particles: a, b, c, d

States: ε_1, ε_2

List of microstates :   (Number of microstates = 2^4 = 16)

Microstate	ε_1	ε_2	Microstate	ε_1	ε_2
A	abcd	-	I	bc	ad
B	abc	d	J	bd	ac
C	abd	c	K	cd	ab
D	acd	b	L	a	bcd
E	bcd	a	M	b	acd
F	ab	cd	N	c	abd
G	ac	bd	O	d	abc
H	ad	bc	P	-	abcd

● All particles are physically **IDENTICAL**.

● Macroscopically observable behaviour of the system is not dependent on **which** particles exists in a given state, but merely on **how many** particles are in that state.

Particles: a, b, c, d

States: ε_1, ε_2

List of macrostates (Number of macrostates = 5)

Macrostate	No. of particles		Corresponding microstates	Number	Probability
	ε_1	ε_2			
I	4	0	A	1	1/16
II	3	1	B, C, D, E	4	4/16
III	2	2	F, G, H, I, J, K	6	6/16
IV	1	3	L, M, N, O	4	4/16
V	0	4	P	1	1/16

◆ Specification of a macrostate requires two numbers: the number of particles in state ε_1 and the number of particles in state ε_2.

◆ For example, the specification of the macrostate labelled II is (3, 1), which means that 3 particles in state ε_1 and 1 in state ε_2.

In general,

◆ If a system composed of N_0 number of particles distributed over r number of available atomic states, a macrostate is specified by assigning a number of particles n_1, n_2, ..., n_r to each of the r state (defined by their energy levels) ε_1, ε_2, ..., ε_r respectively.

◆ Then set of numbers (n_1, n_2, ..., n_r) is a distribution function specifying how the atoms are distributed over the energy levels.

◆ This distribution describes the macrostate for the system.
  ☐ for example, for a twenty-particle system with seven energy states, this list of microstates might read for a particular macrostate as (1, 3, 4, 6, 2, 3, 1).

Number of Microstates in a Macrostate

"How many microstates correspond to the macrostate (n_1, n_2, ... , n_r)?"

Alternately,

"How many different ways can N_0 balls be arranged in r boxes such that there are n_1 balls in the first box, n_2 in the second box and so on to n_r balls in the rth box?"

$$\Omega \;=\; \frac{N_0!}{n_1! \; n_2! \; .... \; n_r!}$$

Ω = number of microstates that correspond to the macrostate

Macrostate I: Ω_I = 4! / (4! . 0!) = 1
Macrostate II: Ω_{II} = 4! / (3! . 1!) = 4
Macrostate III: Ω_{III} = 4! / (2! . 2!) = 6
Macrostate IV: Ω_{IV} = 4! / (1! . 3!) = 4
Macrostate V: Ω_V = 4! / (0! . 4!) = 1

Concept of Probability

◆ **When a thermodynamic process is carried out, the atoms redistribute themselves over their allowable microstates and experience a change in their condition.**

    ❒ this results an overall change in the macrostate of the system.

◆ **Now, since the particles are identical, the average time a particle spends in a given energy level or a microstate is expected to be the same for all particles.**

    ❒ the time spends by a system in a given microstate is the same for all microstate.

    ❒ the time spends by a system in a macrostate is then the sum of the time spends in all the microstates correspond to the given macrostate.

◆ **The fraction of time the system spends in any given macrostate is thus the ratio of the number of microstates that corresponding to that macrostate to the total number of microstates that the system is capable of exhibiting.**

    ❒ This fraction of time is considered to be the **probability** of the system of existing in the given macrostate in any given period of time.

◆ **Thus, the probability that the system exists in the Jth macrostate, will be the ratio of the number of microstates Ω_J corresponds to the Jth macrostate to the total number of microstates the system may exhibit.**

$$P_J = \frac{\Omega_J}{r^{N_0}} = \left(\frac{N_0!}{n_1!\ n_2!\ ....\ n_r!} \right) \frac{1}{r^{N_0}}$$

Macrostate I: $\Omega_I = 1$
Macrostate II: $\Omega_{II} = 4$
Macrostate III: $\Omega_{III} = 6$
Macrostate IV: $\Omega_{IV} = 4$
Macrostate V: $\Omega_V = 1$

FIGURE 10.1
The probability distribution for macrostates has an extremely sharp peak for systems with large numbers of particles and macrostates. Here the most probable macrostate contains the most number of microstates, Ω_{max}.

Ω
(log scale)

Ω_{max}

Most probable macrostate
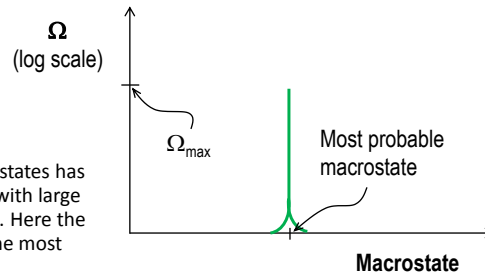
Macrostate

◆ **For systems with large number of particles, this function has an extremely sharp peak at the macrostate containing the maximum number of microstates, Fig.10.1.**

  ☐ macrostates that are only slightly different from the maximum probability state have a much smaller probability of being observed.

◆ **The maximum probability state will be observed almost all of the time, and can be interpreted as the macrostate that corresponds to the equilibrium state for the system.**

◆ In phenomenological thermodynamics, the equilibrium state is also characterised by an extremum; the entropy of an isolated system is a maximum at equilibrium.

◆ So it appears that there might be a connection between the entropy and Ω, the number of microstates corresponding to a given macrostate.

◆ Appropriately so, Boltzmann suggests in his hypothesis that:

$$ S = k \ln \Omega \qquad (10.3) $$

S = entropy of the system
k = Boltzmann's constant = R/N_0
R = the universal gas constant
N_0 = Avogrado's number.

Next Class

Lecture 34

Statistical Thermodynamics
Conditions for Equilibrium