

## STATISTICAL APPROACH TO THERMODYNAMICS

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### Summary

A review of the approach followed to interpret and predict thermodynamic properties of matter in terms of the ones of atoms and molecules is offered. The treatment is mainly focused on the evaluation of the most important thermodynamic state functions, such as internal energy, entropy and free energy. Then their relevance on the state behaviour of ideal and real gases, of solids and charged systems is evidenced and discussed.

At last the contribution of the statistical thermodynamics to the interpretation of the universal behavior of thermodynamic systems in proximity of a second order phase transition is also taken into consideration.

## 1. Introduction

*Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Perhaps it will be wise to approach the subject cautiously.*

*David. L. Goodstein (1975).*

The following section concerns the interpretation and, as far as possible, the prediction of the behaviour of macroscopic chemical systems, in terms of the properties of atoms and molecules. It will be mainly focused on the equilibrium properties at which they have time independent values, and not with the description of the evolution towards the equilibrium itself (see Irreversible Processes: Phenomenological and Statistical Approach). The treatment of these aspect is the main subject of other chapters that could be considered complementary to the present one.

Then we will just be involved in the evaluation of such diverse macroscopic properties of matter as the thermodynamics state functions, the equation of state of gases and liquids, the heat capacities and so on, in terms of molecular structures and intermolecular forces. The approach has both scientific and practical issues as far as the behaviour of the different states of matter is deepened by taking into account its fall-out in the achievements of technological developments. Of relevance in this respect are the studies on phase equilibria, including their role in the separation processes on the characterization of multiphase solid materials and on the distribution of the components present in the atmosphere between different phases (gas, liquid drops, solid particles). The determination of equilibrium conditions in a multiphase and multicomponent reactive system is pursued through the application of the recipes of thermodynamics, that involves the familiarity with state functions such as internal energy  $U$ , entropy  $S$  and free energy  $F$ .

For example the description of a vapour-liquid phase diagram, can be pursued by means of an equation of state that yields a relationship between the state variables: temperature  $T$ , volume  $V$ , pressure  $P$  and composition in the case of multicomponent systems. In practice the determination of the equation of state proceeds from the Helmholtz free energy  $F = U - TS = F(T, V)$  as follows (see Thermodynamics Systems and State Functions):

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = f(T, V) \quad (1)$$

that yields the desired equation of state. The detailed procedures for evaluating the free energy from molecular properties and interactions will be the subject of the present chapter. A comprehensive description of matter in its different states, by evidencing the relationship between the macroscopic scale parameters and microscopic behaviour, is

given in fig. 1. In it a general form of the  $P - T - \tilde{V}$  ( $\tilde{V}$  is the molar volume) surface of a substance is reported, by identifying the region of existence of the phases themselves. In the squares the distribution of the molecules and their possible movements in the various phases are also illustrated.

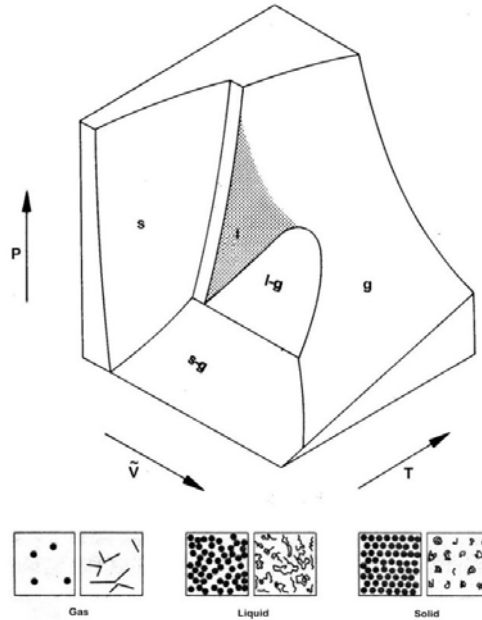
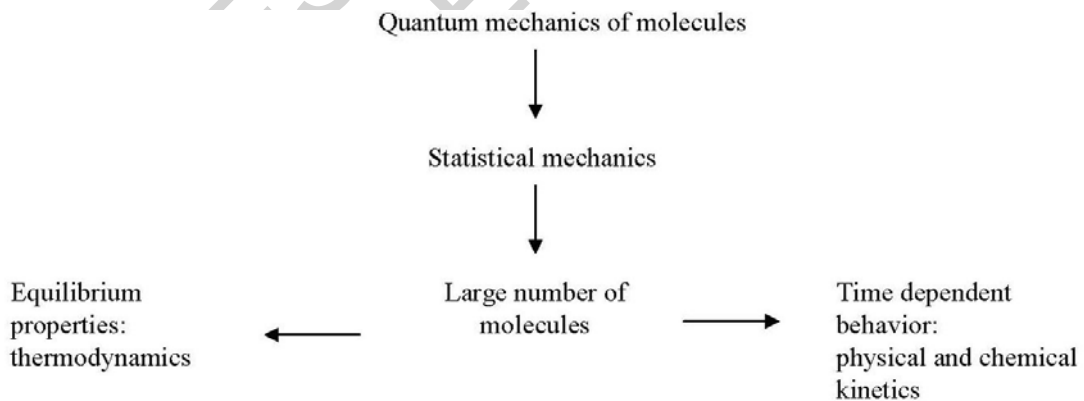


Figure 1: The general form of the  $P - \tilde{V} - T$  surface of a substance, including the gas ( $g$ ) liquid ( $l$ ) and solid ( $s$ ) phase.

Generally speaking the approach to the study of matter starting from molecular information can be outlined as follows:



Scheme 1

As mentioned the subject could be divided in two parts. The first, more fundamental, attempts to understand how the ordered collective behaviour of macroscopic systems can arise from the apparent chaos of the microscopic behaviour or how the time asymmetry observed in macroscopic world can arise from the time symmetric microscopic laws.

The second part is mainly concerned with the equilibrium behaviour of specific systems, particularly trying to grasp how we can take advantage from the knowledge on the microscopic behaviour of molecules, predicted from Quantum Mechanics or experimentally obtained, to calculate their macroscopic thermodynamic properties.

The approach must be of course statistical since we are considering macroscopic systems in which a number in the order of  $10^{23}$  particles are present. Of course it is impossible to follow a detailed history of each of them, while we expect that the average macroscopic behaviour of a thermodynamic system does not depend on all microscopic details. For instance if we want to evaluate the pressure of a gas we should, in principle, follow each molecule as it hits the walls of the container, sum up the forces on the walls and then calculate the pressure. But this approach is quite impractical, unless some conceptual aims are pursued, and then we really need a long term averaged approach.

Let us start by defining the state of a thermodynamic system as the condition at which all his properties are well defined. The essential requirement of the underlying treatment is that such states are totally defined by their quantum mechanical wave function. If the state does not depend on time there is a well defined energy associated to the wave function itself.

Actually, since each thermodynamic system consists of a very high number of particles it is advisable to approach the analysis by means of some models accordingly to some specific properties attributed to the characteristic behaviours of particles themselves. Our analysis will than be focused on the following models:

- **Ideal or perfect monoatomic** (or monoatomic-like) **gases**, in which the particles can be assimilated to non interacting structureless objects.
- **Ideal or perfect polyatomic gases**, in which the internal vibrational and rotational motions of molecules are accounted for.
- **Ideal solids**, in which the crystal is assimilated to a collection of oscillators.
- **Real gases and liquids**, made by a collection of particles interacting through a force defined by a central potential function depending only on the distance between their mass centres.

In the case of the mentioned ideal systems the approach is of course simpler since each particle behaves independently from the others.

As to the real systems, the description can be pursued if the role of intermolecular forces is taken into account. Our treatment will be limited to the cases in which the interacting potential  $\varphi(r)$  is expressed by means of the so called Lennard-Jones potential, given by:

$$\varphi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2)$$

being  $r$  the distance between the center-of-mass of the two considered molecules.  $\varepsilon$  and  $\sigma$  are two characteristic parameters whose meaning is illustrated in fig. 2. It can be observed that accordingly the interaction potential is expressed through the sum of two

contributions, one attractive inversely proportional to the sixth power of  $r$ , mainly due to the so called dispersive forces, and the other repulsive inversely proportional to the twelfth power of the distance. The former prevails at large distances between the molecules while the latter is prevailing at short distances.

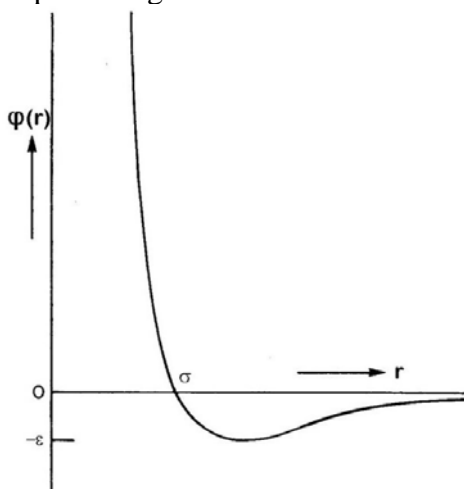


Figure 2. Behaviour of the intermolecular potential, i.e. the potential energy of two molecules when a distance  $r$  apart.

## 2. Microscopic behaviour of ideal gases

Let us start by considering a system in which the particles are assimilated to structureless non interacting objects. Then the motion of each of them is independent from the others. It is advisable to refer to a cubic box of size  $\ell$  in which  $N$  particles are present. If a mole of gas is considered,  $N$  is equal to the Avogadro number  $N_A$ , given by  $6.023 \times 10^{23}$  molecules.

First of all we want evaluate the energies of the stationary states of a particle with mass  $m$  confined within the square-box shaped volume, where:

$$0 < x, y, z < \ell$$

being  $x, y, z$ , the three Cartesian axes that define the position of the particle.

Let us assume that within the box the potential is zero and outside it is infinite. Within the box each particle moves freely and its motion is described by the time-independent Schrödinger equation (see Schrödinger Equation and Quantum Chemistry):

$$-\frac{h^2}{8m\pi^2} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = \varepsilon \psi \quad (3)$$

being  $h$  the Planck constant equal to  $6.624 \times 10^{-27}$  erg-s and  $\psi(x, y, z,)$  the particle wave function.

A simple solution yields the following expressions of wave function and energy

respectively:

$$\begin{aligned}\psi(x, y, z) &= \sin(k_1x)\sin(k_2y)\sin(k_3z) \\ \varepsilon &= \frac{h^2}{8m\pi^2} (k_1^2 + k_2^2 + k_3^2)\end{aligned}\quad (4)$$

being  $k_1, k_2$  and  $k_3$  three integration constants.

Outside the box the wave function must vanish since the potential is infinite. To make it continuous, it must also vanish at the faces on the box. Therefore  $\psi(x, y, z,)$  must be equal to zero when:

$$x = 0 \quad , \quad y = 0 \quad , \quad z = 0$$

$$x = \ell \quad , \quad y = \ell \quad , \quad z = \ell$$

The first three conditions are satisfied for the characteristics of the sine function, while the last three conditions impose restrictions on the allowed values of  $k_1, k_2$  and  $k_3$ :

$$k_1 = \frac{n_1\pi}{\ell} \quad , \quad k_2 = \frac{n_2\pi}{\ell} \quad , \quad k_3 = \frac{n_3\pi}{\ell}$$

being  $n_1, n_2, n_3$  equal to 1,2,3, ...,  $\infty$ . Thus the wave functions are:

$$\begin{aligned}\psi_{n_1, n_2, n_3}(x, y, z) &= \\ \sqrt{\frac{8}{\ell^3}} \sin\left(\frac{n_1\pi x}{\ell}\right) \sin\left(\frac{n_2\pi y}{\ell}\right) \sin\left(\frac{n_3\pi z}{\ell}\right)\end{aligned}\quad (5)$$

The factor  $(8/\ell^3)^{1/2}$  has been included in order to satisfy the normalization condition:

$$\int_0^\ell \int_0^\ell \int_0^\ell |\psi_{n_1, n_2, n_3}(x, y, z)|^2 dx dy dz = 1 \quad (6)$$

The energy of each particles can then assume only a set of discontinuous values given by:

$$\varepsilon_{n_1, n_2, n_3} = \frac{h^2}{8ml^2} (n_1^2 + n_2^2 + n_3^2) \quad (7)$$

Then an infinite set of states exists, each of them defined by the values of three integer numbers  $n_1, n_2, n_3$ . In the gas the particles are distributed differently and randomly among the energy levels, consistently with the total values of energy and particle number of the system itself.

Our aim now is to focus the attention on a isolated ideal gas, and then with a constant value of the overall energy. Let us indicate with  $\varepsilon_j$  the energy of the  $j$ -th state. Not all molecules of course will have the same energy and then they will be distributed over the possible available energy levels. Let us assume further that the time average of a property of a system should be the same as the average of that property over the collection, or ensemble, of the large number of replicas, or virtual copies, of the system itself, all alike in nature but with the particles in their different states. Such a statement relies on the following ergodic hypothesis:

***The time average of a property of a system is the same as the average of that property over the ensemble of system replicas.***

The advantage is that it is easier to compute ensemble average than time average.

Then if we indicate with  $N_j$  the average number of molecules in the state  $j$ , for an isolated system the following relationships must be satisfied:

- the number of particles

$$N = \sum_j N_j \quad (8)$$

is constant.

- The energy of the system:

$$E = \sum_j \varepsilon_j N_j \quad (9)$$

is constant.

In the specific case of an ideal system its total energy is equal to the sum of the kinetic energies of the different particles. The total number  $\Omega$  of states which are consistent with the preceding restrictions, or that belongs to the mentioned ensemble of copies of the system, depends on the values of number of particles  $N$ , volume  $V$  and energy. The derivation of the corresponding expression is not straightforward and therefore we will mention only the final result:

$$\Omega(E, V, N) \approx A^N \left( \frac{E}{N} \right)^{3N/2} V^N \quad (10)$$

being  $A = \left( 4\pi m e / 3h^2 \right)^{3/2}$ , where  $e$  is the base of the natural logarithm. It is obtained by the expression of the number of translational quantum states of the whole system when their total energy is less than  $E$ . Then a reasonably approximate value of  $\Omega$  is given by the increase of the number of quantum states, passing from an energy level to the one adjacent to it. The previous equation refers of course to a system of structureless

particles, but it can be shown that the value of  $\Omega$  for a generic thermodynamic system depends on energy through a similar expression, that is:

$$\Omega(E) \propto E^{\nu}$$

being  $\nu$  the number of the degrees of freedom of the system itself:  $(3/2)N$  for a simple perfect gas,  $3N$  for a collection of oscillators, and so on.

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### **Biographical Sketch**

**Sergio Carrà** was born in Milano in 1929 and he is married with two sons and one grand-son. He obtained the doctorate in Industrial Chemistry at the University of Milano in 1953 .

He has been assistant professor and associate professor at the University of Milano. In 1968 Sergio Carrà become full professor of physical chemistry at the University of Messina and two years after at the University of Bologna.

At the present he is full professor of Chemical Engineering Thermodynamics at the Polytechnic of Milano. Some of his research and teaching activity has been made in USA.

Sergio Carrà has been President of the Italian Association of Physical Chemistry, Vice President of the Italian Chemical Society and is member of the "Accademia Nazionale dei Lincei" and of the "Accademia Europeaea. He won in 1991 the "Antonio Feltrinelli" award, in 1997 the "Mario Giacomo Levi" and in 1999 the "Bonino" of the Divisione di chimica fisica della Società Chimica Italiana, and the Gold Medal by Scuola Normale Superiore di Pisa.

Sergio Carrà had important charges in the organization of research activities performed with public financial support. Besides he has been consultant of different companies (Montedison, ENI, SnamProgetti, ENEL, SISAS, Atochem, Dow and others) for the development of industrial projects.

His research interest focuses on some aspects of molecular thermodynamics, applied chemical kinetics, catalysis, modeling of chemical processes.

Sergio Carrà published about 370 papers, 6 patents and 7 books.