

# Mass Diffusion: A Molecular Description

## Introduction

By definition, diffusion is the action to spread a given property i.e. a physical quantity (mass, energy) or a concept (new ideas), outside an initial space zone to the surroundings. It is a transport process that takes its origin in the interaction of a given property with the medium or system (surrounding + initial space zone). This definition is very broad and is used to label situations as either concrete or abstract, and the word itself has been used both in common language since the ancient times (*diffusio* in Latin) and in different fields of knowledge such as biology, chemistry, physics, economy, sociology, etc [1].

The aim of this article is to give a simple description of what is known as diffusion in the physics of mass transfer from the perspective of the molecule (nano-scale), where it originates.

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## A molecular mechanism

In physics, the transfer of mass by diffusion was first described by Brown in 1827, and then subsequently explained by Einstein in 1905 [1]. At a molecular level, matter is heterogeneous and every molecule is in perpetual motion due to interaction with its surroundings. To paint a nice picture, authors say that molecules are dancing in a never-ending ballet [1]. In physics, this is called thermal motion, and the phenomenon increases with temperature. Colliding with other molecules, each one follows a random path and then they tend collectively to fill whatever volume is available to them. In liquids, this spreading effect is counterbalanced by strong attraction interactions between molecules, and the molecules preferentially diffuse inside the liquid itself rather than escaping it. In solids, the difference between the attraction and the effect of thermal motion is even greater as the molecules are trapped between other molecules that act as a cage, meaning diffusion is several orders of magnitude lower than in liquids. The surface acts as a barrier to the transfer of matter. In the gaseous state, the thermal motion is large, the gas diffuses everywhere and the spatial limits of the gas are only given by external properties such as the volume of a container, a liquid or a solid surface, or even an external force like gravity.

The origin of mass diffusion is thus purely stochastic and, like a lot of other physical, chemical and biological properties, it is simply the consequence of instantaneous heterogeneous distributions of matter and energy at a molecular level. As diffusion is due to the perpetual motion of the molecules, it can be studied both under equilibrium, where the distribution of matter is homogeneous at a macroscopic level and no mass

flow can be observed, by Nuclear Magnetic Resonance or Quasi Elastic Neutron Spectrometers (QENS), and under non-equilibrium conditions where the distribution of matter is heterogeneous at a *macroscopic* level and a mass flow can be observed (transient techniques).

In the 19th century, Fick described, at a macroscopic level, the diffusion of molecules from a high concentration zone to a low concentration zone. The flux of molecules in one direction,  $\mathcal{J}$ , due to diffusion processes which are linearly proportional to the gradient of concentration  $c$ ,  $\nabla c$ , along the same direction:

$$\mathcal{J} = -D \nabla c, \quad (\text{equation 1})$$

the coefficient of proportionality  $D$  is called the diffusion coefficient (see appendixes)[1]. Similarly, Fourier found the same linear relation between the flux of energy and the gradient of temperature. These gradients represent the heterogeneous structure of matter and energy at a *macroscopic* level. Temperature and density are thermodynamic properties, that is, their gradients play the same role as a force in mechanics (a driving force) and they are called thermodynamic forces.

## Molecular dynamics simulation [2]

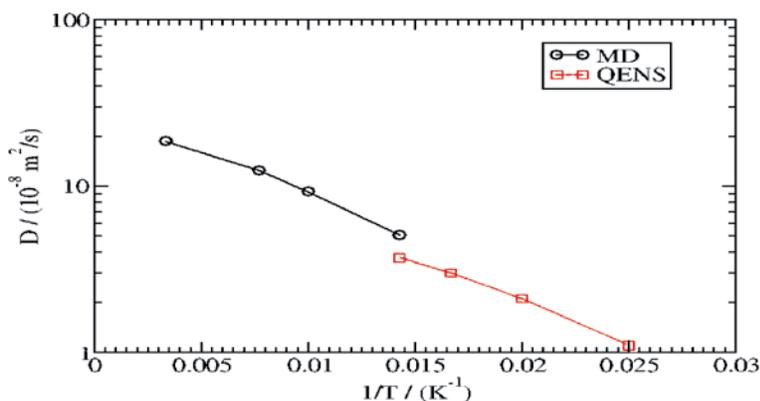
Although the study of the diffusion process from the mechanical point of view was impossible more than 50 years ago, it is now possible by using super computers. In 1957, Alder and Wainwright [2] were the first to use computers to simulate molecular dynamics (MD). The aim of this method is to simulate a system of atoms interacting through analytical potential or forces. The trajectories of all atoms through time are generated by a simple integration of Newton's equation of motion and then analysed using the tools of statistical mechanics. Under equilibrium conditions, the diffusion coefficient can be easily obtained from Einstein's law [1]:

$$D = [r(t)-r(0)]^2 / 2nt, \quad (\text{equation 2})$$

where  $[r(t)-r(0)]$  is the mean distance between position  $r$  of a molecule at time 0 and later at time  $t$ .  $t$  has to be large compared with a characteristic time.  $n$  is the space dimension, and for diffusion on a surface, it equals 2. This MD method is able to provide diffusion coefficients in excellent agreement with experiments; it is also able to explain the molecular mechanism involved in the processes. It is particularly useful to get data when the experiments are dangerous or very costly or perhaps not even accessible, given the present technology. Diffusion properties across and along surfaces are of that sort and they are hardly known although they play a key role in many processes in nature (membranes in biology) as well as in industry (separation processes).

In a recent article [3], we obtained surface diffusion coefficients of hydrogen adsorbed on graphite at different temperatures using the QENS technique. These results are presented in figure 1 and compared with new data we got using MD simulations. The agreement is very good. Additional simulations have shown that the trajectory on the surface before being desorbed was significant, around 5 nanometers, whatever the temperature (a range from 70 to 300K). At 300K, the number of adsorbed  $H_2$  molecules on graphite is very small and their effects are often considered to be negligible, see the recent review paper by Strobel *et al.*

about H<sub>2</sub> storage [4]. This new result suggests that this should not be true. The system studied is a part of fuel cell system and this result gives new insight in their working mechanism. This will be presented fully in a forthcoming article.



**Figure 1:** Arrhenius plot comparing surface diffusion coefficients of H<sub>2</sub> on graphite obtained by MD and QENS techniques [3].

## Conclusion

Mass diffusion is a stochastic process, i.e. a consequence of local heterogeneity of matter distribution and of the energy at a molecular level. It makes a contribution to particle transport and is often coupled with or hidden behind other phenomena. This can make it difficult to analyse, even though its definition is simple.

## References

- [1] For general discussions about diffusion in the context of natural science, the reader is referred to a textbook edited by Jörg Kärger after the first conference: Diffusion Fundamental I, *Leipzig, Einstein, Diffusion*, at the Leipziger Universitätsverlag, Leipzig (2007).
- [2] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press Oxford (1987).
- [3] O.E. Haas and others, *A quasi-elastic neutron scattering investigation of the hydrogen surface self diffusion on polymer electrolyte membrane fuel cell catalyst support*. Accepted by the Journal of Physical Chemistry C.
- [4] R. Strobel and others, *Hydrogen storage by carbon materials*. Journal of Power Sources, vol 159, 781–801 (2006).

## Appendix 1

The gradient of  $c$ ,  $\nabla c$ , in a spatial direction  $x$  is

$$\nabla c = dc/dx$$

In first approximation that can be calculated from the knowledge of the value of  $c$  in two different positions is  $x$ . If in position  $x_1$  we have  $c_1$  and in  $x_2$  we have  $c_2$ .

$\nabla c$  will simply be the difference between  $c$  divided by the distance between the two positions:

$$\nabla c = (c_2 - c_1) / (x_2 - x_1)$$

When the concentration in the system is uniform (i.e. if there is homogeneous particle distribution), the gradient vanishes and the resulting

flux is null (cf. equation 1). On the contrary, when  $\nabla c$  differs from zero, it results in a mass flux from the higher concentration to the lower concentration.

The units of the different variables are:  $x$  and  $r$  in m,  $c$  in mol/m<sup>3</sup>,  $\mathbf{j}$  in mol/(m<sup>2</sup>.s),  $D$  in m<sup>2</sup>/s,  $t$  in s.

### Appendix 2

Diffusion is a result of the heterogeneity of mass distribution and interaction energy with the surroundings. Fick's equation is based on the main term, i.e. the interaction with mass heterogeneity. In its above noted form (equation 1), Fick's equation applies to one phase. At interfaces like, e.g. on the surface of liquids, we saw that this equation is not valid although the difference of concentration is very different (between the liquid and the surrounding gas). It has been shown in fact that the full expression should include energetic terms; the thermodynamic force is then the gradient of the ratio between "chemical potential" ( $\mu$ ) and temperature.  $\mu$  is a function of the energy and temperature and concentration of the molecule. As a consequence a difference of temperature can then lead to a diffusional flux, this is the thermal diffusion effect.