Fresnel as Seen by Chemists: Circular Birefringence in Optically-Active Media

by Jeanne Crassous, Director of Research at CNRS,
at the Institute of Chemical Sciences, Rennes (F), (UMR CNRS 6226)

Augustin Fresnel, who was born in Broglie (Eure, northern France) in 1788 and died in Ville-d'Avray (currently in the Hauts-de-Seine department) in 1827, began his education at the *Ecole polytechnique* in Paris at the age of 16. Five years later, he became a member of the *Corps des ponts et chaussées* [Corps of Bridges]. Unanimously elected as a member of the Academy of Sciences in 1823, he accomplished in his short life first-class work on the study of light, highlighting its wave-like nature and opposing the corpuscular theory strongly defended by Isaac Newton (1643-1727) and, among others, Jean-Baptiste Biot (1774-1862) and Siméon-Denis Poisson (1781-1840). Like the work of Thomas Young (1773-1829), Fresnel carried out experiments on the diffraction of light, which could only be explained by the wave theory. He subsequently managed to apply his theory to polarisation and formulated it mathematically.

As of 1819, he was a French commissioner of lighthouses, and developed a new headlamp lighting system based on a type of compact lens (nowadays known as Fresnel lens) and catadioptric systems which are used to this day in lighthouses around the world.[1] Fresnel had very poor health and eventually died of tuberculosis. He received the Rumford Medal for his work, awarded by the *Royal Society of London*, of which he had been a member since 1825. He therefore received the long-sought recognition from the United Kingdom, which had tended to ignore his contribution to the field of the diffraction of light.

His paper, *La double réfraction que les rayons lumineux éprouvent en traversant les aiguilles de cristal de roche suivant les directions parallèles à l'axe* [The double refraction of rays of light when passed through crystals according to the directions parallel to the axis], presented to Academy of Science on 9th

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1. See the *BibNum* analysis of *Mémoire sur un nouveau système d'éclairage des phares* [On a new system for headlights] (Fresnel 1822).

December 1822, is an important milestone in the midst of many discoveries made during the nineteenth century, concerning certain solids, liquids or gasses with optical rotation. The Fresnel theory of double refraction in these systems, commonly known by chemists as "circular birefringence" can explain the interaction between polarised light and media with optical activity.

The history of optical rotation most likely begins with Denmark's Erasmus Bartholin (1625-1698), who discovered the double refraction of Iceland spar in 1669. This strange duplication of images transmitted by the crystal helped Christiaan Huygens (1629-1695) to back up his wave theory of light. However, it was Étienne-Louis Malus (1775-1812), more than a century later (1808), who complemented the discovery with his observation: that light reflected by a glass surface has a *polarisation* of which the direction can be determined by the double refraction of an Iceland spar crystal.

From Birefringence to Polarisation

Birefringence (or double refraction) is a phenomenon whose effects were observed early on (Bartholin 1669), but one which has been difficult to analyse ever since the polarisation of light was discovered more than a century later (Malus 1808).

Figure 1: Double refraction through an Iceland spar crystal (calcite $CaCO_3$). *The image of letters passed through the crystal is shifted in relation to the original image (effect of refraction); the image is also divided into two images (effect of double refraction).*

This property of birefringence is maximised when the ray of light is perpendicular to the "optical axis" of the crystal, and is non-existent when it is parallel. As Fresnel explained (p. 732): "There are positions of the rhomboid in which one of the two rays disappears entirely and the incident light experiences solely one single mode of refraction when passed through the crystal."

Fresnel also recounts this history in his paper (Introduction, p. 731):

Before the wonderful discoveries made by Malus, it had long been observed that the two rays in which light is split when passed through a spar calcite rhomboid receive this singular modification to which the term polarisation has been given, in accordance with the ideas of Newton on the physical cause of the phenomenon. Strictly speaking, Malus did not discover the polarisation of light; instead, he demonstrated that rays of light can be reproduced, by their mere reflection onto a transparent body at a suitable incidence, or by their oblique passage through a series of diaphanous blades, which produces the same change that they would receive when they are divided into two distinct rays by crystals with double refraction.

The Polarisation of Light

Natural light is not polarised; this is only achieved after reflection (precisely what Malus revealed). The plane of polarisation is perpendicular to the direction of propagation of the light: this plane carries the electric fields E and the magnetic fields B of the light's electromagnetic wave.
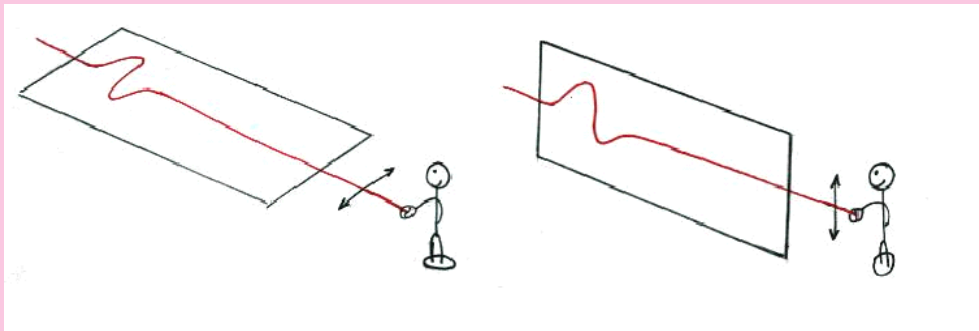

*Figure 2: **The polarisation of a vibrating cord** (image: e-scio.net). With this analogy, polarisation is easily understood: to the left, the figure of Malus makes a horizontal movement, and the wave of propagation is polarised horizontally; to the right, he makes a vertical movement, and the wave of propagation is polarised vertically. In both cases, the wave's direction of propagation is the same, in front of the figure.*

Polarisation can be rectilinear (in the above diagrams, E oriented in a fixed direction in the plane of polarisation) or circular (E drawn as a circle in this plane). It can also be elliptical, a combination of both rectilinear and circular polarised light.

Polarised light, highlighted in this way by Malus, had quickly become a subject of study for physicists. In 1811, François Arago (1786-1853) observed that quartz blades, properly cut, and arranged on the path of a ray of light polarised by reflection, produces a rotation of the plane of polarisation in relation to its original

orientation[2] : quartz crystals have *optical rotation*. Soon after, in 1812, the physicist Biot completed the observation made by Arago by showing that certain quartz crystals deflect the plane of polarisation towards the right (they are *dextrorotatory*), others to the left (*levorotatory*).[3] In 1815, Biot demonstrated that optical rotation is not the appanage of crystalline bodies, but is in addition observed in liquid solutions of natural organic substances, such as camphor, turpentine, sugar and tartaric acid. This property also exists in the gas state, as was revealed by a particular experiment (in 1817) which highlighted the optical rotation of turpentine vapour. Biot was a strong advocate of Newton's corpuscular theory of light and never managed to explain his experimental observations. It was Fresnel who eventually applied his mathematical formulation of polarised light. He developed an experimental apparatus which allowed the manufacturing of circularly polarised light, the Fresnel rhomb (§2, text p. 733):

> *In one paper, which I had the honour to read to the Academy towards the end of 1817,[4] I introduced a new modification of light, which is just as general, or rather, just as uniform as polarisation itself, in that all the rays of different colours that form white light receive this change, at the same time and at the same degree, as is what happens in the case of ordinary polarisation. This process comprises the following: after having already polarised the beam of light, either by passing it through a spar calcite rhomboid, or by reflecting it onto a non-tin reflective surface, and tilted 35°, it is introduced into a glass parallelepiped, where it experiences successively, on two opposite sides, two total internal reflections, at around 50° incidence, and in accordance with a plane inclined 45° relative to the original plane of polarisation. The angle of the entrance and exit sides of the parallelepiped, both of which are reflective, must be such that they are approximately perpendicular to the incident and emergent rays, so that they do not apply onto them any polarising effect.*

Fresnel describes an experiment that produces circularly polarised light from linearly polarised light. He understood that circularly polarised light is the sum of two linearly polarised waves, orthogonal to each other and shifted from a quarter wave (text p. 734):

> *These are the experiments that have made me realise that light changed in this way could be considered as composed of two beams that follow the*

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2. Arago, *Mémoires de l'Institut des sciences, lettres et arts (Classe des sciences mathématiques et physiques)*, vol. 12 (1811), p. 93-134.

3. Biot, "Expériences sur les plaques de cristal de roche taillées perpendiculairement à l'axe de cristallisation", *Mémoires de l'Institut des sciences, lettres et arts (Classe des sciences mathématiques et physiques)*, vol. 13 (1812), p. 218.

4. Fresnel, "Mémoire sur les modifications que la réflexion imprime à la lumière polarisée" and "Supplément", N° XVI and XVII.

same route, but are polarised in different rectangular directions as they reach a quarter of a wave.

Fresnel observed that the phenomenon of double refraction does not exist solely in some crystals but also in some substances (§3, text p. 735):

These consequences, which seemed to lift all theoretical difficulties concerning the colouring of turpentine, naturally led me to suppose that this liquid, in which I had demonstrated the existence of double refraction by several experiments of interference, has its particles formed in such a way that each of them has double refraction, and also reproduces rays of light, at their entrance and exit, which is the same change that they would receive by two total reflections in a glass parallelepiped.

As was presupposed by Biot at that time, optical rotation is a molecular action depending on their individual formation; as for crystals, optical rotation results from the mode of aggregation of its components (§3, text p. 735-736):

In order to faithfully represent the phenomena, it had to be assumed that in these particles the double refraction is very different for rays of different colours, and in inverse proportion to their wavelength, according to Biot's law on the deviation of the plane of polarisation of total light passed through a tube filled with turpentine. This is because, assuming that the double refraction of each ray type in the particles of this liquid is in inverse proportion to their wavelength, it appears that by the formulas of interference that I have employed, the deviation of the plane of polarisation of the total ray of homogeneous light, upon leaving the liquid, is in inverse proportion to the square of the length of access, or wavelength, as Biot concluded in his observations.

Fresnel observed "the dispersion of double refraction," which appears much stronger for red rays than purple rays (§9, text p. 744):

According to the only consideration of the facts, the term rectilinear polarisation can be given to that which was long observed in the double refraction of the spar calcite, and that which Malus first noticed in light reflected onto transparent bodies, while circular polarisation goes to the new change, whose characteristic properties I have just described: it is naturally divided into circular polarisation from left to right, and circular polarisation from right to left... Between rectilinear and circular polarisation is a host of intermediate degrees of various polarisations, pertaining to two other characters, and to which the term elliptical polarisation is given.

Fresnel has shown that while decomposing a rectilinearly polarised wave into the sum of two circularly polarised waves from right to left, these do not propagate at the same speed in a chiral medium[5]. Fresnel's law on circular birefringence is

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5. See the note on the following page.

used, connecting the optical rotation of a chiral substance to the index of refraction of two right and left lights. Fresnel's law gives the expression of the angle according to the difference (n_L – n_R), where n_L and n_R respectively are the indices of refraction for left-handed circularly polarised light and for right-handed circularly polarised light, the length of the tank l, and the wavelength studied λ. The quantity (n_L – n_R) is known as circular birefringence.

$$\alpha = (n_L - n_R) \frac{\pi \times l}{\lambda} \qquad \text{(Fresnel's law)}$$

Fresnel was not aware of the molecular nature of optical rotation. While William Herschel (1792-1871) showed in 1820 that optical rotation is linked to the direction of hemihedral crystals (known then as plagiohedral−see figure below) and that it is possible to distinguish the direction of the quartz's facets due to its dextrorotatory or levorotatory nature. It was Louis Pasteur (1822-1895) who eventually introduced in 1848 molecular asymmetry, proposing the link between the hemihedry of a crystal and its molecular nature. Observing more closely the double salt in sodium ammonium tartrate, Pasteur demonstrated that the crystals of this salt are in fact made up of two types: hemihedral crystals to the right and hemihedral crystals to the left. He separated them by hand, and when he dissolved them again in alcohol, he showed that solutions of crystals to the right rotated light in one direction and those of crystals to the left in the other direction Pasteur therefore carried out the first spontaneous resolution! However, it was not until 1874 when Joseph Achille Le Bel (1847-1930) and Jacobus Henricus van't Hoff (1852-1911, first Nobel Prize in Chemistry in 1901) independently invented "chemistry in space" and the carbon asymmetry theory. Stereochemistry was finally born! The term "chiral[6] " was proposed in 1902 by William Thomson (1824-1907), better known as Lord Kelvin, during the conferences in Baltimore: "I term *chiral* any geometric figure or set of points which cannot be superimposed onto its own mirror image. I therefore speak of *chirality*".

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6. From Greek "kheir", meaning *hand*: the hands are indeed a chiral system (this Greek root has also given words such as *chiromancy* and *chirurgy*).

Stereochemistry: Chemistry in Space

The term stereochemistry is a generic term used to describe chemistry in three-dimensional space. In 1874, Le Bel and van't Hoff discovered that a carbon with four different substituents had two different structures in space, which are mirror images (Figure 3, C). It was understood that the two double tartrates separated by Pasteur in 1848 had three-dimensional chemical structures and mirror images (Figure 3, D). The term "chirality" was then introduced by Lord Kelvin in 1902 for this particular type of stereochemistry. Careful: there is also a third type of tartrate, meso-tartrate, which is not chiral (it is superimposable on its mirror image). Quartz crystals (A) are hemihedral because they have facets which together are mirror images. In quartz, hemihedry results in the coiling of tetrahedra SiO$_4$ helices, which can be produced in both directions, left and right.
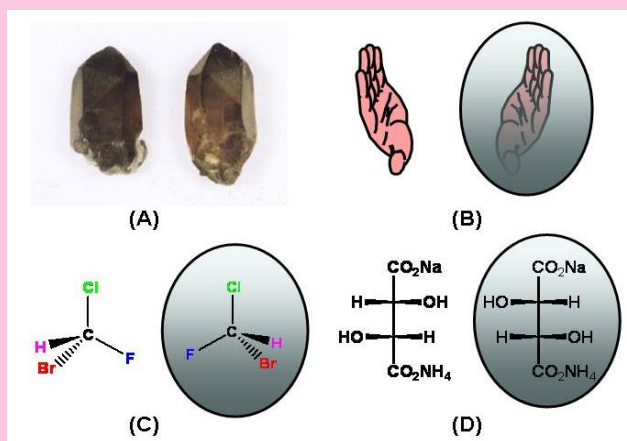

Figure 3. *Chiral objects and their specular images. (A) Hemihedral (or plagiohedral) quartz crystals. (B) Specular image of a left hand is a right hand. The origin of the term "chiral" is the Greek term "kheir", meaning "hand". (C) An example of a molecule (bromochlorofluoromethane) with an asymmetric carbon. The C-H and C-Br bonds are directed backwards or forwards, respectively shown by dashes or in bold. (D) The double chiral sodium ammonium tartrate and its mirror image.*

Enantiomers are two chiral molecules that are mirror images of each other. Two enantiomers rotate the linearly polarised light in opposite directions.

What about medicine? In the nineteenth century, chiral active substances were already being used, including morphine extracted from poppy, and quinine extracted from cinchona bark and used as an antimalarial. The chemical and three-dimensional structure of these molecules, however, was not known. Despite the ideas made by Pasteur in late nineteenth century, it was necessary for chemists to understand that chirality had a great impact on living organisms. It was not

until the 1960s and the *Thalidomide* disaster, a drug which had been given to pregnant women as an anti-emetic and which caused serious malformations among new-borns. Today, it is believed that the cause of this outcome is that while one of the enantiomers is indeed an anti-emetic, the other enantiomer is a teratogenic! Many drugs have different therapeutic properties depending on their enantiomeric form. Aromatic carboxylic acids such as naproxen and ibuprofen are known for having an anti-inflammatory and antipyretic[7] effect in an enantiomeric form (but have no significant effects in the other). Similarly, propranolol is known for having a blocking effect β[8] in an enantiomeric form as well as being a male contraceptive in the other form. Tastes and smells also have to do with chirality: for example, asparagine has the bitter taste of asparagus in an enantiomeric form, but it has a rather sweet taste in the other form. The measurement of enantiomers in a chiral solution therefore is "an important piece of information for pharmaceutical laboratories, since the enantiomers of some drug substances are very toxic" *[article from La Recherche n°404 January 2007].*

Finally, sugars and amino acids that are core components of the living world (i.e., animals and plants) are chiral and exist in one single enantiomeric form! It has been said that the living world is dissymmetrical. The link between this dissymmetry and the origin of life remains a fascinating research topic!

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7. Antipyretic = to counter fever (from Greek *puretos,* fever, and *pur,* fire).

8. A substance that blocks the action of adrenaline, used for example in the treatment of high blood pressure.