

Committee 1
Symmetry in Its Various Aspects:
Search for Order in the Universe

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The Enigma of Asymmetry

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Introduction

It is stated in many eastern philosophies that opposites unite to constitute a single reality. So it is with symmetry and asymmetry: symmetry is the fundamental in nature's laws, but it is to asymmetry we owe our very existence. For decades, physicists have found symmetry to be a powerful and unfailing guide in their quest for the fundamental laws of nature. But the perfect symmetry between matter and antimatter is broken in our universe which seems to contain only matter and practically no antimatter. It is now thought that, early in the evolution of the universe, a small asymmetry between the properties of matter and antimatter resulted in the generation of one excess proton per every billion antiprotons. As the universe evolved, the mutual annihilation of protons and antiprotons pairs resulted in a universe in which the small excess of matter remained¹. This small excess makes up all the visible and invisible matter in the universe, the visible galaxies and the dark invisible matter that surrounds them.

Asymmetry also appears in other forms. The most ubiquitous of asymmetries is that between the left and the right. Nature shows a clear and persistent preference for one hand over the other -- as we see for instance, in most people being right-handed and not ambidextrous. Remarkably, such preference is everywhere; we can see it in elementary particles, atoms, molecules, proteins, DNA, morphology of plants and animals and in animal behavior. The all pervading nature of this asymmetry is astonishing and many questions come to mind immediately: What processes created these asymmetries? Did these asymmetries arise independently or are they related? What processes could relate asymmetry at one level to that at a higher level? In this article I shall present an overview of our current state of understanding of this asymmetry and the processes that generate asymmetry.

Objects that are not identical to their mirror images possess a sense of handedness; they cannot be superimposed on one another so that every point of one coincides with the corresponding point of the other. They are said to be *chiral* – a term proposed by Lord Kelvin with the Greek root $\chi\epsilon\iota\rho$, which means hand. The property of handedness is termed *chirality*; the asymmetry between the left and the right is thus *chiral asymmetry*.

We shall begin by outlining the known chiral asymmetries from elementary particles to the biosphere. Then, we shall look at our current understanding of the origin and relationship between asymmetries at various levels.

Chiral Asymmetry in Elementary Particles

Chiral asymmetry in nuclear processes responsible for β -radioactivity was discovered in 1957 by Chen-Shiung Wu and her colleagues. Some unstable nuclei "decay" to a lower state of energy by emitting electrons or positrons, also called β -particles. The isotope of cobalt, ^{60}Co , for example, emits electrons. The nucleus of ^{60}Co has spin but a stationary particle with a spin is not chiral; it does not possess handedness unless there is a direction associated with it that could be used to define chirality. The usual "right-hand-rule" used to define the "north pole" is a convention; right and left cannot be defined using a stationary spinning object. If there is an additional direction associated with the spinning object, however, one could define left and right. For example, if the two hemispheres of a spherical spinning object are different, say red and green, then we can define a direction as the movement from red to green; this movement when combined with the spin could be used to trace a helical path. We then obtain either left-handed or right-handed helix, which can be used to identify the chirality of the spinning object. In the case of radioactivity in ^{60}Co , when the nuclei are placed in a magnetic field, their spin axes line up along the direction of the magnetic field. Under these conditions, more electrons were emitted from one of the hemispheres. This reveals a chiral asymmetry in this fundamental process. As in the above example of a sphere consisting of red and green hemispheres, we may combine the direction in which the larger number of electrons are emitted with the spin to define a helix. In the case of the ^{60}Co shown in Fig. 1, we have left-handed helix.

Further studies of β -radioactivity revealed that the emitted electrons themselves exhibit asymmetry. Since electrons have spin, one can associate left- or right-helicity to each electron, as shown in Fig.2, when the spin is combined with the direction of the electron momentum. It was

found that the electrons emitted by radioactive nuclei are predominantly left-helical. Chiral asymmetry in β -radioactivity appears in other ways as well. The emission of β -particles is accompanied by the emission of elusive particles called the neutrinos, which also have spin. All neutrinos generated in β -radioactivity are left helical, and antineutrinos are right helical. Neither right-helical neutrinos nor left-helical antineutrinos have been detected; they are presumed not to exist. If there were equal number left-helical neutrinos and right-helical anti-neutrinos then we might say that left-right symmetry is restored, but this would require a balance between matter and anti-matter. As far as we can tell, there is matter in the universe but not antimatter. The consequence is that present universe is filled exclusively with left-helical neutrinos.

Optically Activity in Atoms

Before the forces that held the particles in the atomic nucleus were discovered, physicists knew two fundamental forces in nature: gravity and electromagnetism. With the discovery of the nucleus, in which positively charged protons and uncharged neutrons were held together, new forces came to light. Soon after, studies in nuclear physics showed that there were basically two types of nuclear forces, which were termed, “strong” and “weak” forces. The weak forces were responsible for β -radioactivity, while the strong force was responsible for nuclear fission and fusion. Now physicists faced a world ruled by four forces: gravity, electromagnetism, the nuclear weak and strong forces. This state of affairs was not satisfactory to a physicists who sought simplicity in nature’s most fundamental laws. Inspired by Einstein’s quest for one unified theory of all the forces, a whole generation of elementary particle physicists has set out on a quest for a single theory that unifies these four forces. Its first triumph was in unifying the electromagnetic and weak forces, which necessitated the coining of the term “electroweak” force.

The exact nature of this unification is not important for us, but the chiral asymmetry this unification revealed is. One of the predictions of the electroweak theory, the credit for which is given to Steven Wienberg, Abdus Salam and Sheldon Glashow, is that the electron interacts with

the neutrons and the protons in the nucleus with a force that depends on its helicity. Left- and right-helical electrons (in the sense shown in Fig. 2) are acted upon by a different forces. This fact brings the chiral asymmetry to the level of atoms, because it ultimately results in the atoms having a property called “optical activity”. As shown in Fig. 3, polarized light is rotated clockwise or counter-clockwise by a chiral medium. This property is called optical activity. Optical activity is a clear expression of chiral asymmetry. The directions of propagation and rotation define a helix, which is either left- or right-handed. Since the time of its discovery, optical activity has been observed only in compounds whose molecules have a chiral structure but never in atomic vapors. Atoms were thought to be spherically symmetric entities with no chiral attributes until electroweak force was discovered.

A tube filled with a vapor of the element bismuth, for example, is found to rotate light in the counter-clockwise direction, when the beam is viewed from the front. Materials that rotate light in this manner are termed “levo”, while those that rotate light in the opposite direction are termed “dextro”. Due to electroweak interactions we only find levo-bismuth in nature, its mirror-image twin does not exist. The optical activity of atoms, though very small, has been measured and found to be as predicted by the electroweak theory.²

Chiral Asymmetry in Molecules

Asymmetry of the electroweak force extends its reach past the atomic level to the level of molecules. Chemical bonds that hold atoms together as a molecule are such that they give a definite geometrical structure to the molecule. A carbon atom attached to four other atoms or groups of atoms, for example, has a tetrahedral structure. If the four atoms or groups of atoms attached to the carbon atom are distinct, then the molecule is not identical to its mirror image, and hence chiral (Fig. 4). Since chirality appears in such a simple way in carbon compounds, the chemistry of carbon compounds is replete with chiral compounds. Indeed, as we shall discuss in more detail later in this article, the very building blocks of life, amino acids and nucleic acids, are chiral molecules. Chemists call the mirror image twins of a chiral molecules “enantiomers”. Molecules

consisting of a given set of atoms can be bonded to each other in different ways and may have different geometric shapes. These different versions of a molecule are called “isomers”. Enantiomers are a particular case of isomers in which the two versions of the molecule are mirror images of one another, they are the left- and right-handed versions of the molecule. Following a particular convention for naming a molecule, which was proposed by R.S. Chan, C. Ingold, and V. Prelog in 1956, chemists identify the two enantiomers as R (from the Latin root, *rectus*, meaning right) and S (from the Latin root, *sinister*, meaning left). This identification is purely on the basis of the geometric structure, not a chemical or physical property. Prior to that, before methods of determining the geometric structure of a molecule were developed, the two enantiomers of a chiral molecule were distinguished by their optical activity. The two enantiomers rotate light in opposite directions, i.e., if one rotates it clockwise the other rotates it in the counter-clockwise direction, and by the same amount. Based on this property, the two enantiomers are also called levo- or dextro-rotatory, “l” or “d” for short. There is no simple relation between the optical activity and the geometrical structure of a molecule, i.e. there is no simple way to predict if the R-enantiomer of a molecule will be levo-rotatory or dextro-rotatory.

In general, isomers may differ in their physical properties, such as melting point or solubility. Not so with enantiomers, they have identical melting points and solubilities. The optical rotation caused by each enantiomer, though opposite in direction, was found to be identical in magnitude within the experimental accuracy. And, before the discovery of the electroweak asymmetry, there was no reason to expect the magnitude of the optical rotation of enantiomers to be different, though they were opposite in sign. Phenomena caused by electromagnetic interactions show no chiral asymmetry or preference for one handedness. If we see a phenomenon resulting from electromagnetic interactions we can be sure that the mirror image of such a phenomenon will also occur. Physicists call this fundamental mirror-image symmetry, conservation of parity. Electromagnetism conserves parity. Electromagnetic interaction between light and molecules that causes optical rotation must conserve parity. For example, if a solution made with one enantiomer of a chiral compound rotates the plane polarized light clockwise through

2.3 degrees, then the mirror image of this phenomenon will show the opposite enantiomer rotating the light in the counter-clockwise direction, by the same amount, 2.3 degrees. Since electromagnetism conserves parity, we can expect an experiment corresponding to the mirror image to yield a counter-clockwise rotation of 2.3 degrees.

In addition to optical rotation, conservation of parity in electromagnetism implies many other equivalencies. For example, the energies of the two enantiomers of a chiral molecule should be identical, and so must the wavelengths of light they absorb or scatter. Also, chemical reactions that produce chiral molecules from achiral reactants produce the two enantiomers of the chiral product in equal amounts. All this was validated within experimental accuracy and there was no reason to expect any deviation from this perfect symmetry between the left and the right until a unified theory of the electroweak interactions was formulated in the 1970's. Prior to that, it was thought that chemical reactions and molecular properties were solely a consequence of electromagnetic interactions, unaffected by nuclear forces that caused β radiation. Therefore molecular properties and chemical reactions were not expected to show any chiral asymmetry.

According to the electroweak theory, however, molecules do not exhibit perfect chiral symmetry. When the electron is very close to the nucleus, the "weak component" of the electroweak force comes into action; this is in addition to the electromagnetic force between the electron and the particles in the nucleus, the protons and the neutrons. The weak component of the electroweak force, however, is asymmetrical: it acts on left-helical electrons but not their right-helical twins. Due to this asymmetrical interaction, a left-helical electron in an R-enantiomer will have a different energy when compared to its energy in an S-enantiomer. Consequently, the energies of the two enantiomers are not equal. According to the principles of statistical mechanics, at a given temperature, more molecules will be found in a state of lower energy. This means, in a sample of a chiral compound in which the R- and S-enantiomers can interconvert, we must find unequal amounts of the two enantiomers, the amount of enantiomer with the lower energy being larger. Of course, this electroweak energy difference between the enantiomers of a chiral molecule had always existed, but it wasn't detected in chemical experiments because it was very very small.

In fact it is so small, that it is yet to be experimentally detected. Theoretical calculations show that, at room temperature, the excess of the lower energy enantiomer is about 1 in 10^{17} for molecules such as amino acids. This small excess is very hard to detect but, because so many predictions of the electroweak theory have been confirmed by experiments, there is no doubt that this small energy difference between enantiomers exists. Like most such challenges in science, confirming the existence of this chiral asymmetry at the molecular level by experiments is only a matter of time.

The energy differences between enantiomers due to the electroweak force, usually termed as "parity violating energy differences", or PVED for short, can also be expected to change the rates of formation of chiral compounds from achiral reactants by a very small amount, about 1 part in 10^{17} . Because of this extremely small magnitude, this difference in the rates of formation of enantiomers has not been observed in the laboratory.

The First Unifying Principle of Biochemistry

Long before the formulation of the electroweak theory, which predicts a small energy difference between enantiomers, Louis Pasteur's serendipitously discovered the most spectacular chiral asymmetry of all: the chiral asymmetry in the chemistry of life. During the 19th century, when Pasteur did his famous experiments, chemists were still debating the existence of atoms and the structure of molecules. To talk about molecular structure in this world was to advocate avant garde science. Optical activity was already of great interest when Pasteur began his scientific investigations. In 1857, Pasteur was working with the salts of sodium ammonium tartrate, a chiral compound. Two types of tartrates were known at that time; both had identical chemical properties, but one exhibited optical activity and was dextro-rotatory, while the other had no optical activity at all. The tartrate that did not exhibit optical activity was called "racemic" – because it was extracted from grapes. It was also observed that molds could grow in an aqueous medium that contained the tartrate. They metabolized the compound or "fermented" it, in other words used it for their own purpose. The popular account has it that Pasteur, in one of his characteristic ways, decided to

examine the consequences of microbial action on a solution of racemic tartrate, the tartrate that showed no optical activity. To his amazement, he found that the action of microbes converted the initially optically inactive solution to an optical active one. In Pasteur's own words, "The originally inactive liquid has appreciable levo-rotatory power that gradually increases until it reaches a peak."³ Pasteur's simple and clear explanation revealed to him a profound difference between living and dead matter: the racemic compound contained equal amounts of dextro- and levo-rotatory tartrate; the microbes acted only on the dextro-rotatory tartrate leaving the levo-enantiomer in the solution. The chemistry of life showed a preference for one enantiomer. It was asymmetric.

Even in those days when the very existence of atoms and geometrical shapes of molecules were still being debated, Pasteur rightly regarded this discovery as one of the most fundamental aspect of the chemistry of life. In fact he regarded it as, "perhaps the only well-marked line of demarcation that we can at present draw between the chemistry of dead and living nature"⁴.

During the nineteenth century, with time and effort, it became evident that molecules indeed have well-defined geometrical structure and today it is a matter of routine for undergraduate chemistry students to determine the structure of a molecule by the many theoretical and experimental tools available to them. What then is the molecular nature of life's asymmetry that Pasteur discovered? Modern biochemistry gives a very clear and universal picture. All living cells contain proteins, large molecules that are responsible for the function of the cell, and DNA and RNA that contain the genetic blue print for the synthesis of the proteins. Proteins are large chains, or polymers, made of twenty different building blocks called *amino acids*, while DNA and RNA are also polymers made of four types of building blocks, called *nucleotides*. Both sets of building blocks, amino acids and nucleotides are chiral molecules and the two enantiomers are commonly called L- and D-enantiomers. Remarkably, from bacteria to the largest living creature, proteins consist exclusively of L-amino acids (Fig. 5) and DNA consists of only the D-nucleotides. In the words of Francis Crick, "The first great unifying principle biochemistry is that the key molecules have the same hand in all organisms". Organisms do use D-amino acids in rare circumstances, but

dominance of L-amino acids is overwhelming. The origin of this fundamental asymmetry is still unknown and we shall discuss the current thought on this matter later in this article. We now move on to asymmetry at the next level, morphological asymmetry.

Morphological and Behavioral Chiral Asymmetry

Chiral asymmetry in the morphology of plants and animals and in animal behavior is all too visible, though not always noticed. The most obvious asymmetry is, of course, humans being predominantly right handed. Though, due to cultural bias against the left hand -- the "sinister hand" -- many left-handed people are forced to use their right hand, simple experiments on dexterity can reveal the true handedness of a person. Regardless of region and culture, we find roughly 10% of all human population is left handed.

And there is the internal asymmetry in the placement of the organs that breaks the external bilateral symmetry of most mammals: the heart is more to the left, the liver is on the right and so on. Very rarely, some humans are born with positional inversion of their internal organs, a condition referred to as *situs inversus*. Their hearts are a little to the right and their liver is on the left. This occurs with a frequency of about one in 10,000. This condition is often accompanied by several abnormalities collectively called Kartagener's syndrome.

Helical sea shells, whose beautiful shapes fascinate us, are mostly right helical. Of all the species of sea shells that show some form of helicity, well over 90% of them are right helical. The helicity of the shell is maintained in a species through inheritance, except for mutations. A few species, such as the Lightning Whelk which can be found on the Atlantic coast of the United States, are predominantly left helical. Collector of shells in the west call them sinistral shells, but they have a special religious status in Buddhist cultures.

Chiral asymmetry can also be found in plants that wind around a tree for support. Each species, winds in one particular manner: the honeysuckle, for example is left helical while the bindweed is right helical. It is very rare for a honeysuckle to be right helical or a bindweed to be

left helical. Chiral asymmetry can also be found in the shapes of bacterial colonies. The colonies of a bacterium called *bacillus subtilis* are right-helical in shape.

The above are but a few examples of morphological asymmetries we find in the living world. In his book, *Animal Asymmetry*, Neville has catalogued a large number of chiral asymmetries that can be found in the animal kingdom⁵. This asymmetry is clearly an inherited quality, but we do not yet know the exact mechanism through which chiral asymmetry is transmitted from one generation to the next.

Morphological asymmetry can give rise to behavioral asymmetry. Though the brain looks somewhat symmetric, it is well established that the two hemispheres perform very different functions. The predominant use of right hand in humans can be traced to this asymmetry between the two hemispheres of the brain. The same is true for much less noticed dominance of one eye over the other. We all have a dominant eye which we use more than the other to make visual judgments. A simple experiment tells which of your eyes is dominant. With both eyes open, stretch your hand in front of your face and hold your thumb so that it obstructs a distant object from view. The object will not be completely blocked from view, but you can judge when your thumb is obstructing the view. Now if you close one eye, you may see that the object is completely blocked from view: the open eye is your dominant eye. You use the dominant eye to decide if your thumb is in front of the object. If you close this dominant eye and open the other, you will see that the thumb is not blocking the object from your view. Again this asymmetry can be traced to the asymmetry between the left and right-hemispheres of the brain.

Extraterrestrial Chiral Asymmetries

Recently, two important interstellar chiral asymmetries have been discovered. One is in meteorites and the other in the light we receive from nebula. Meteorites that survive their fiery entry into the earth's atmosphere bring us valuable information about the forms of matter that exists outside the bounds of the earth. It is found that some of these meteorites, called carbonaceous chondrites, have carbon compounds in them. In one such meteorite that fell in Murchison,

Australia, amino acids and other biologically significant molecules were found. This clearly showed that the building blocks of life can be synthesized in extraterrestrial chemical processes. This is a remarkable discovery in itself, but even more curious is the recent discovery that in the Murchison meteorite there is a small excess of L-amino acids. This excess ranges from 3 to 6% but it still points to an asymmetry whose origin is a matter of speculation at this time.

Another extraterrestrial chiral asymmetry was discovered by the Anglo-Australian team of astronomers in the nebula Orion. Light reaching scattered by this nebula towards our planet was found to contain a large component of circularly polarized light. Though this does not reveal a cosmic asymmetry, it shows that there could be large regions in space that are “bathed” in circularly polarized light. Chemical reactions occurring in such an environment could generate a small excess of one of the two enantiomers. The implications and significance of this discovery are currently being debated.

Many Questions but Few Answers

Once we become aware of the ubiquity of chiral asymmetry in our world, many questions naturally come to mind. Why does nature have a preference for one hand over the other in its fundamental laws? Are the asymmetries at various levels related to one another? Does the molecular asymmetry of life have its origin in the asymmetry of the electroweak force? Can chemical reactions spontaneously generate asymmetry from symmetry? These and other questions have been vexing physicists, chemists and biologists alike for decades. Some progress has been made but we do not yet have clear unambiguous answers to such questions. In the remainder of this article, I shall give an overview of our current understanding of the physical and chemical processes that may one day provide answers to these questions.

Why asymmetry appears in electroweak forces, and why the universe is filled with left-helical neutrinos, remains a complete mystery. We have no deeper explanation. But we have seen that this asymmetry “propagates” to the level of atoms and molecules, but because the energy differences between enantiomers due to electroweak force is so very small, it used to be thought

that biological asymmetry must have had an independent origin. But this not necessarily so, as we will see in the following sections.

Spontaneous Generation of Asymmetry in Chemical Processes

Can asymmetry spontaneously arise from an initial state that is symmetric? In the context of chemistry, can achiral molecules react to form chiral molecules in such a way that one of the two enantiomers is produced in excess even though there is no preference for the production of either enantiomer? The answer to this basic question is an unequivocal yes. Such a process has been called “spontaneous symmetry breaking” by physicists. In the context of chiral asymmetry in chemistry, in 1953 Sir Charles Frederick Frank showed how asymmetry could be generated from reactions that have no preference for one or the other enantiomer through a simple model reaction scheme. His model assumes that each enantiomer, which is produced by a reaction between achiral molecules, can catalyze its own production, i.e. there is chiral autocatalysis. In addition, if the two enantiomers encounter each other, they would form an inactive product, i.e. mutual destruction. Such a reaction scheme is capable of generating chiral asymmetry by amplifying a small excess of one of the enantiomers that might arise due to random fluctuations. This is because, due to chiral autocatalysis, the rate of growth of each enantiomer is proportional to its concentration. Hence, the enantiomer whose concentration is larger grows more rapidly – it is like the rich getting richer. Not only that, as its concentration grows, the dominant enantiomer is also able to make its chiral twin inactive through the mutual destruction reaction. Thus, if the concentration of one of the enantiomers exceeds that of the other through a random fluctuation, then that concentration grows more rapidly and soon becomes dominant. Of course, in this scheme, which of the two enantiomers will dominate is entirely random, but one will dominate. Asymmetry can emerge from symmetric conditions spontaneously in system that has the mechanism to amplify small random asymmetries.

In order to elucidate the thermodynamic nature of this model and to assess the impact of small external asymmetries on such models, George Nelson and I modified Frank’s model. This

modified model is shown in Fig. 6. In this modified model, achiral molecules, S and T react to form a chiral molecule X_L or X_D . The molecule X is chirally autocatalytic: X_L catalyzes the production X_L and X_D catalyzes the production X_D . In addition, X_L and X_D react to form an inactive product P. In our model, the system consists of a “reaction chamber” into which there is an inflow of reactants S and T and an out flow of P. For a given set of flows, the system reaches a stationary state in which the concentrations of all the reactants remain constant. The flows maintain the concentration of S, T at a constant value. If the flows are reduced to zero, the system reaches thermodynamic equilibrium in which the concentrations of X_L and X_D are equal. If the flows are slowly increased from zero, the concentrations of S, T as well as X_L and X_D increase but still the concentrations of X_L and X_D remain equal until the concentrations of S and T reach a critical value. Above this critical value, the system becomes “unstable” in the sense any small difference between the concentrations of X_L and X_D grows; the system no longer maintains the symmetry between X_L and X_D . In the terminology of non-equilibrium chemistry, the system undergoes a “bifurcation”. If the concentrations of S and T surpass the critical value, the system will be forced to make a transition to a state in which concentrations of X_L and X_D are not equal. Which one will be greater is entirely random, but one of the two enantiomers will dominate. This symmetry-breaking bifurcation is summarized in the lower part of Fig.6

The study of many such theoretical models followed the model of Sir Charles Frederick Frank but experimental demonstration of spontaneous generation of asymmetry remained elusive for decades. Though the theoretical models were simple, they required the reacting chiral compounds to have two properties: chiral autocatalysis and some form of competition through which each enantiomer suppresses the other. Chemists were hard put to find these two properties in chiral compounds. My own discussions with many chemists, though always interesting, did not result in the identification of any reaction that could be studied in the laboratory.

Then, in 1990, my students and I unexpectedly discovered⁶ spontaneous generation of symmetry in the extremely simple process of crystallization of NaClO_3 (sodium chlorate). Though the molecules are not chiral, the crystals of this compounds are chiral. The two enantiomeric forms

of crystals of NaClO_3 can be easily detected through their optical rotation. An aqueous solution of NaClO_3 is not optically active, it has no chirality. But if we prepare a saturated solution of NaClO_3 and allow the solvent to evaporate so that crystals form, each crystal is either levo- or dextro-rotatory (l- and d-crystals for short). When we performed crystallization, as is usually done, in a crystallization dish, without in anyway disturbing the solution, we found statistically equal number of l- and d-crystals. This was as expected. The surprise came when we crystallized the compound while the solution was continuously stirred: each crystallization generated an extraordinary amount of asymmetry. In almost every stirred crystallization we found more than 98% of the crystals were either l or d! Far from being equal, the number of l- and d-crystals generated by stirred crystallization showed a total breakdown of symmetry. Fig. 7 shows some of our experimental results. This was the first clear experimental demonstration of the phenomenon of spontaneous chiral symmetry breaking. The details of the mechanism, the needed chiral autocatalysis and mutual competition, were elaborated in our later studies. We now have a fairly good theory to describe such systems.

The spontaneous symmetry breaking that we found in NaClO_3 is not an isolated phenomenon. Our more recent work showed that this is a general phenomenon which can occur in several compounds; it also occurs in the crystallization from a melt. Other similar chemical systems were also identified by researchers in Japan. Though all this is still far from providing an answer to the question of the origin of biomolecular chiral asymmetry, it provided us with some insight into nature's ways of generating chiral asymmetry.

The Origin of Biomolecular Chiral Asymmetry

In spite of the great advances in our understanding of the chemistry of life, we only have a rudimentary understanding of the chemistry from which life originated. There is an abundance of suggestions and theoretical models such as Frank's, but no clear consensus as to which of these mechanisms is most likely. Some contend that the particular choice of L-amino acids and D-sugars was a matter of chance; if similar life originated in another planet, it could have the opposite

chirality. Others contend that Pasteur's conjecture that life as we know is a result of some cosmic and universal asymmetry must be true, that somehow the symmetry of the electroweak force must have found its way into the chemistry of life. But the great difficulty with this theory used to be that electroweak chiral asymmetry is extremely small at the level of molecules, only one part in 10^{17} . Is there a natural process that can amplify even such small but systematic asymmetry and aid the electroweak-favored amino acids to dominate the prebiotic chemistry? An analysis that George Nelson and I conducted⁷ answered this question in the affirmative. We found that on a very large scale (such as reactions that occur over time period of tens of thousands of years, in waters several square kilometers in area and hundreds of meters deep) chemical reactions can indeed show the effects of the electroweak force in the outcome of symmetry breaking transition. Our analysis showed that under the above conditions, if L-amino acids are favored by the electroweak force, and if they underwent a symmetry breaking transition as in the model described in Fig.6, then there is 98% chance that L-amino acids will dominate the state of broken symmetry. In the presence of a chiral asymmetry such as the electroweak force the bifurcation diagram is modified as shown in Fig. 8.

Once this excess of L-amino acids has been established, evolution of homochiral proteins would be greatly facilitated. But does the electroweak force favor the L-amino acids? Theoretical calculations performed by Steven Mason, George Tranter and Alexandra MacDermott indicate that this may indeed be the case. They found that for all the amino acids for which they calculated the electroweak energy difference between the two enantiomers, it is the L-enantiomer that has the lower energy. According to a basic principle of physics, molecules will appear in greater proportion in states of lower energy. This implies L-enantiomers of amino acids will appear in a slight excess, about one in 10^{17} . This result also implies that the rates of production of the two enantiomers will also be unequal and perhaps favor L-amino acids.

So we can identify prebiotic chemical processes, which occur in large bodies of water over a long period of time, that could link the electroweak asymmetry to the biomolecular asymmetry. But it is not a proof that such a process was indeed responsible for the biomolecular asymmetry of

life on our planet. Alternative theories have been proposed which, in one form or the other, assert that the dominance of L-amino acids is purely a matter of chance. One theory, proposed by Bill Bonner and Mayo Greenberg, points to circularly polarized radiation from neutron stars. They note that in a cone along the axis of neutron star, there is strong circular polarization of light. Interstellar chemistry exposed to such radiation might produce an excess of one of the two enantiomer. Other theories point to the left-helical electrons emerging from β radioactivity.

A more recent theory proposed by Albert Eschenmoser is based on polymerization of chiral molecules. Eschenmoser has demonstrated that when certain chiral molecules polymerize, they tend to be homochiral, i.e., all the units of the polymer tend to be the same enantiomer. This is entirely due to stereo specificity of the polymerization reaction. If we consider long polymers made of say 10 different subunits, due to the enormous number of possible polymer sequences, no two samples will have identical set of molecules. In particular, the homopolymers made of the L-enantiomer and those made of D-enantiomers will not be identical. Thus their properties will be somewhat different. It is then conceivable that only one of the homopolymers had the properties the led to the evolution of life, while the other was left behind.

None of these theories have won compelling support from related experiments or from the researchers in the field. The origin of the chiral asymmetry of life remains a challenging question.

Origins of Morphological Asymmetry

The full details of the mechanism that establishes morphological asymmetry are still unknown. We do know that this trait is genetic and, in some cases, some of the genes whose expression results in the establishment of morphological asymmetry have been identified. But still, this does not explain how the chiral asymmetry is consistently established. We are still unsure if, in the final analysis, morphological chiral asymmetry is related to molecular chiral asymmetry.

On thing we do know is that the information about chirality cannot be transmitted by a linear sequence of entities, that is, it is impossible to code chirality into a sequence of letters such as GCCTTACGA Merely be relaying such a sequence, by whatever means, it is impossible

to specify what is “left” what is “right”, unless the receiver already knows what is meant by “left” and “right”. The reason for this is not difficult to see. Suppose a process exists that does not have a built-in ability to distinguish the left from the right but that it can nevertheless read a linear sequence, such as GCCTTACGA..., and produces only a left-helical object. If we look at the same process in a mirror, it will be reading the same sequence but producing a right-helical object. Since the process has no built-in ability to distinguish left from the right, it must be identical to its mirror image. This leads us to a contradiction: the process that was assumed to produce only a left-helical object must also be able to produce a right-helical object. Hence such a process cannot exist. The only way to specify left or right is through three dimensional structure that is chiral. This means, that the information about morphological chirality cannot be simply be coded in a sequence of DNA. Morphological chiral asymmetry must be transmitted through a chiral structure. Might this be in the very chiral asymmetry of the D-sugars of DNA or the L-amino acids in the proteins? In other words, does the morphological asymmetry of life have its origins in its molecular asymmetry? Quite possibly, but there is no experimental evidence for this. The origin of morphological asymmetry is not fully understood.

And there are more open questions. The most basic question of all, why the universe, at its most fundamental level of matter and antimatter, is asymmetric remains an enigma.

Notes and References

¹ The excess of protons over anti-protons is only one in a billion. This can be ascertained from the ratio of photons to protons, which is about 2×10^9 in the present universe. The annihilation of a proton-antiproton pair produces two photons and the excess protons are left behind

² The rotations measured in the lab are of the order of 10^{-7} radians.

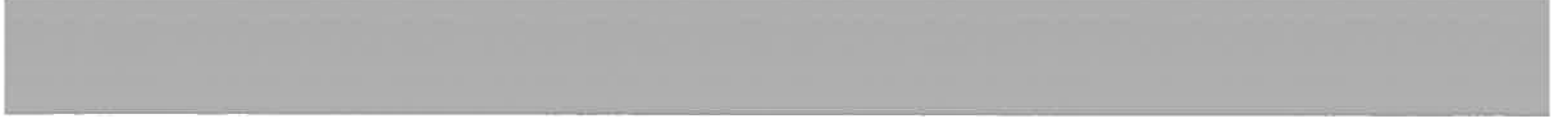
³ Jean Jacques, *The Molecule and its Double*, 1993, McGraw-Hill (page 92)

⁴ Gerald L. Geison, *The Private Life of Louis Pasteur*, (1995, Princeton Univ. Press, Princeton, NJ) (page 105)

⁵ A.C. Neville, *Animal Asymmetry*, (1976, Edward Arnold, London)

⁶ D.K. Kondepudi, R.. Kaufman and N. Singh, *Science*, **250** (1990) 975-976

⁷ D.K. Kondeoudi and G. Nelson, *Nature*, **314**, (1985) 438-441



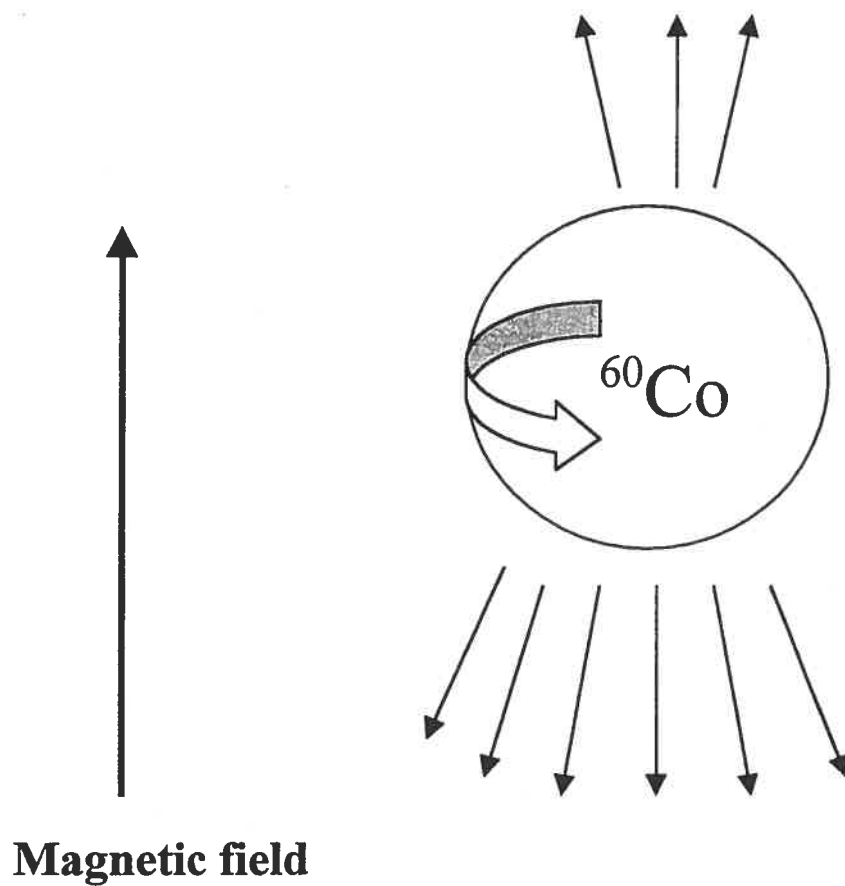


Fig. 1. β -radioactivity observed in the isotope of cobalt, ^{60}Co , shows a fundamental asymmetry in nature. When the spin of the nuclei of ^{60}Co are aligned using a magnetic field, it was found that more electrons were emitted from one hemisphere. The asymmetry in the number of emitted electrons shows a preference for one handedness.

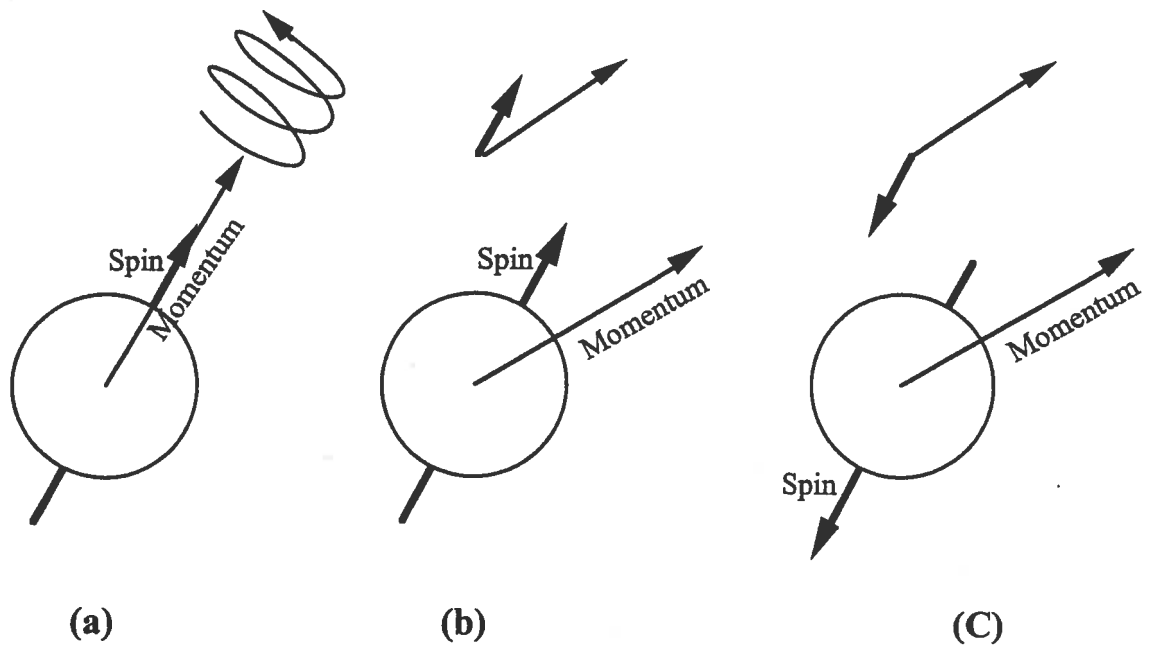


Fig. 2 If the axis of spin and the direction of momentum of a particle coincide, the combined motion of spin and momentum defines helical motion or helicity. Such particle can be right-helical, as shown in (a), or left-helical. If the axis of spin and the direction of momentum do not coincide, one can still assign a helicity depending on the projection of the spin vector on the momentum vector. If the projection is positive, as in shown (b), we call the particle right helical, and if it is negative as shown in (c), it is left helical.

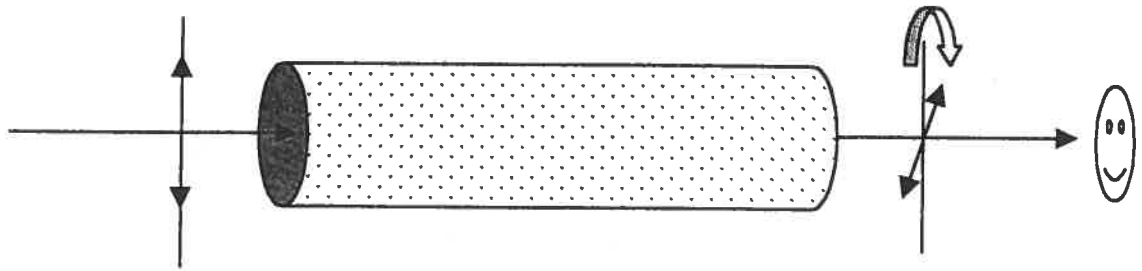


Fig. 3. In polarized light, the direction of vibration of the electric field is in one particular direction, perpendicular to the direction of propagation. When polarized light propagates through a chiral medium, its direction of propagation rotates as shown. A solution of sugar, for example, rotates the polarized light in the clockwise direction as the beam approached the viewer. One of the consequences of the chiral asymmetry of the electroweak force is to endow optical activity to atomic vapors. For a particular element, the rotation is clockwise or counterclockwise.

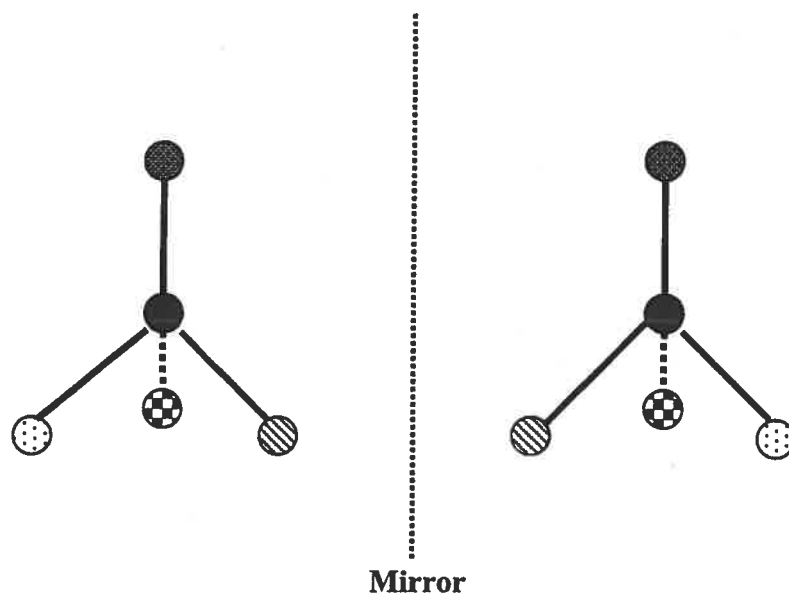


Fig. 4 A carbon atom attached to four other atoms or groups of atoms is tetrahedral in structure. Such a molecule is not identical to its mirror image and hence it is chiral.

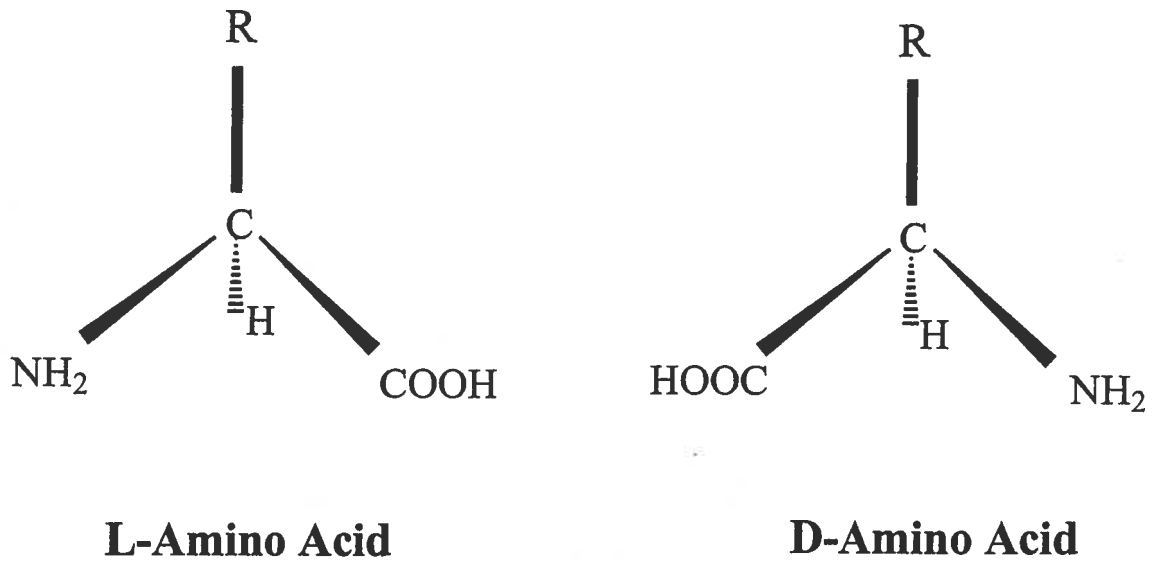
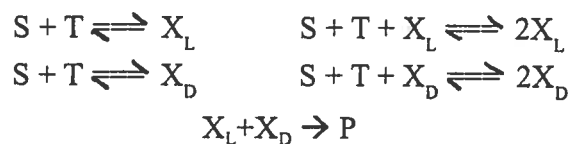


Fig. 5 The structures of L- and D-amino acids are as shown. The group of atoms "R" attached to the carbon atom varies between amino acids. Each R group represents a distinct amino acid. Of the hundreds of possible amino acids, only 20 are incorporated in the chemistry of life. Of these twenty amino acids, only the L-forms are used to construct the proteins. The D-amino acids

Reaction scheme:



$$\lambda = [S][T] \quad \alpha = [X_L] - [X_D]$$

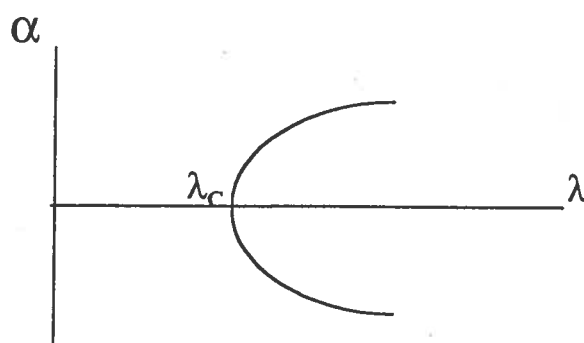
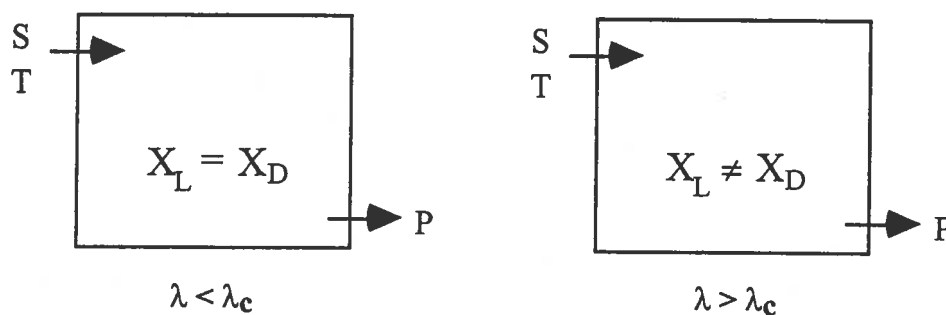
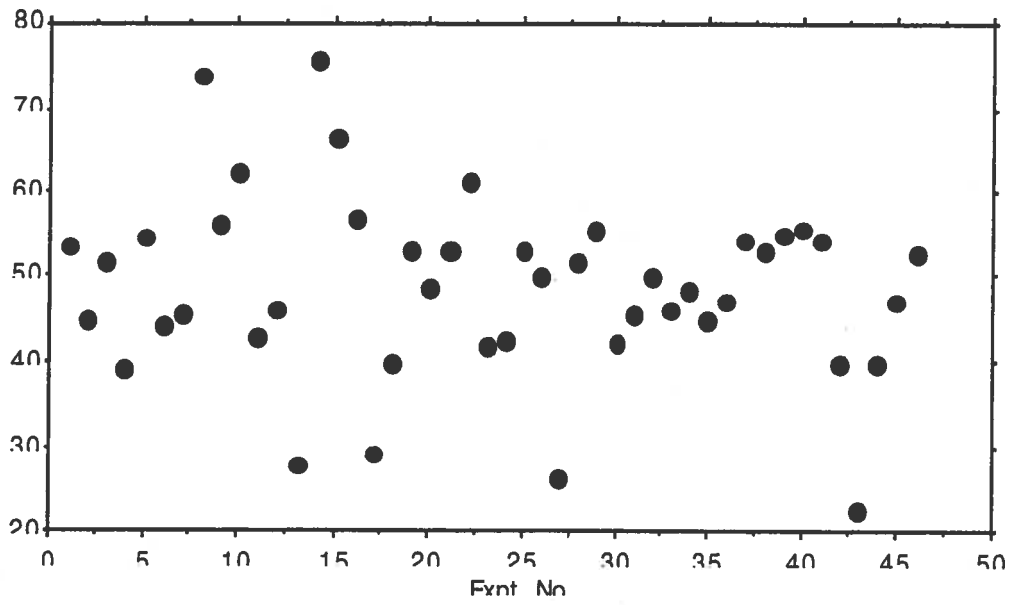
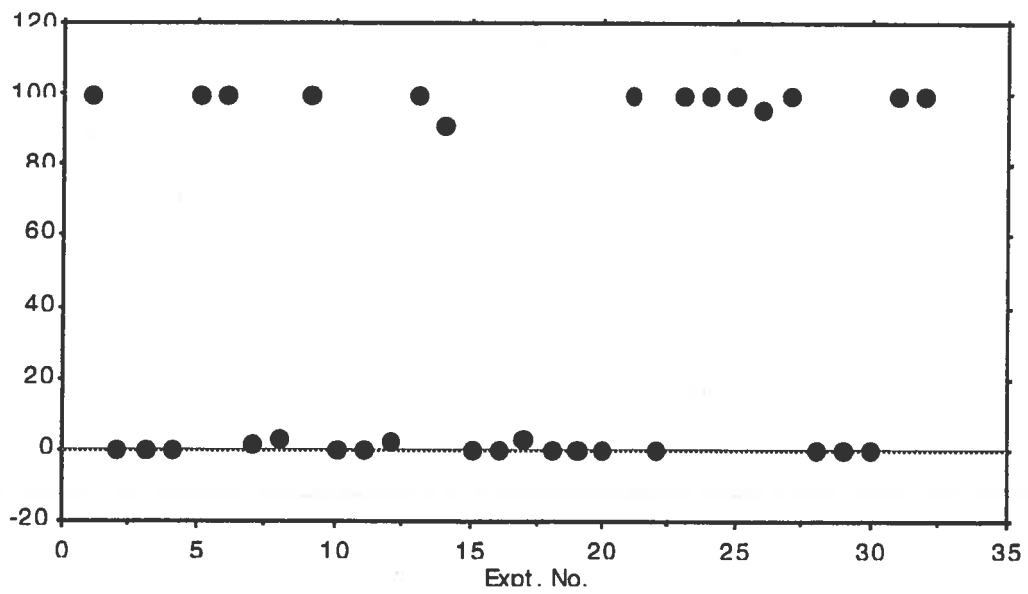


Fig. 6. A simple autocatalytic reaction scheme in which X_L and X_D are produced with equal preference. However, in an open system, this leads to a state of broken symmetry in which $X_L \neq X_D$. Below is a bifurcation diagram showing some general features of transitions to asymmetric state. The parameter $\alpha = X_L - X_D$ is a measure of the asymmetry. $\lambda = [S][T]$, the product of the concentrations of S and T, is the bifurcation parameter. When the value of λ exceeds λ_c the system becomes unstable and makes a transition to an asymmetric state in which α is not zero.



(A)



(B)

Fig 7. (A) Percent of l-crystals obtained in unstirred crystallization of NaClO₃.
 (B) Percent of l-crystals obtained in stirred crystallization of NaClO₃

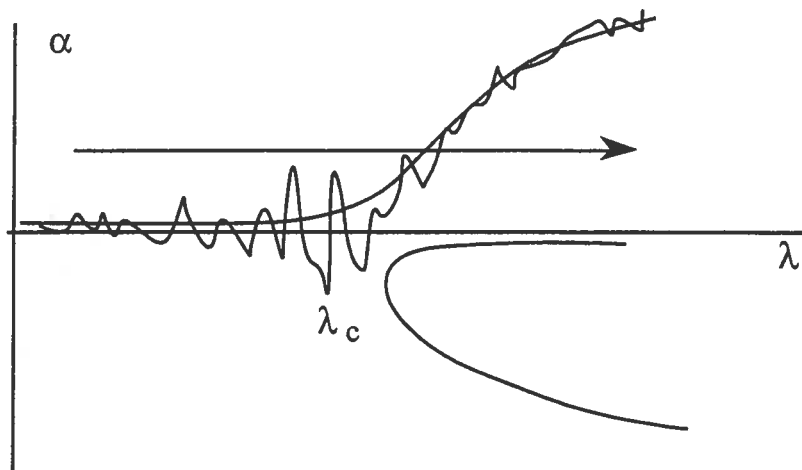


Fig. 8 In the presence of a chiral preference for one enantiomer, the bifurcation diagram shown in figure 6 is modified as shown. As λ increase from a value below λ_c to a value above λ_c , the system makes a transition to the upper branch, which is favored. The above figure shows a trajectory of α including fluctuations. This process is very sensitive to small chiral asymmetries. Such processes occurring on a prebiotic scale can link electroweak chiral asymmetry to biomolecular chiral asymmetry. Whether such a process did occur during the evolution of life, is still a matter of speculation.