

CAN BIOLOGICAL HOMOCHIRALITY RESULT FROM A PHASE TRANSITION?

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Abstract. The problem of chiral purity in living organisms is still one of the prominent difficulties in the study of the origins of life. In particular the parity non-conservation known to occur in weak interactions could not be related to this lack of symmetry: these physical forces, though universal, are very weak and up to now no amplification process had been proposed.

In 1991, A. Salam remarked that, due to the attractive character of the parity violating force in electro-weak interactions, a phase transition at low temperature should exist, leading eventually to enantiomeric purity.

We undertook then a series of experimental tests, looking for a sizeable change in the optical activity of cystine molecules. We found no evidence for the phase transition down to 0.01 K. The interpretation of these negative results will be discussed, and future experiments proposed.

1. Introduction

As early as 1857, Pasteur was the first to realize that the whole chemistry of life had a preferred handedness. In our present view, there is no mystery in this selective functioning: since most biochemical reactions are strongly dependent on a stereospecific recognition between reactants, it is quite natural that homochirality of molecules perdures as an essential property, and in such an absolute manner as to be considered as a characteristic of the living systems structure. A problem arises, however, when one considers the origins of life: up to now, there was no convincing proposition for a process that would allow to constitute a homochiral medium from a racemic mixture. For sure, there exist many physical processes which might give rise to some asymmetry between the two molecules which are mirror-symmetric of each other, but all the suggested mechanisms are far from accounting for the chiral purity necessary for the good-working of any self-replicating organism. A complete review on the subject was published recently and we will refer to it for information not directly related to our experiment (Bonner, 1991).

The violation of parity discovered in weak interactions (Lee and Yang, 1956) is probably the most promising physical effect for including effects on a macroscopic scale: its constant intensity has been there for eons, and is not subject to modification by any circumstantial event. On the contrary its effects should be very weak, and in fact experiments trying to demonstrate a relation between parity violation in weak interactions and chiral purity in biological matter are generally considered as negative (Bonner, 1991).

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A recent theoretical work (Salam, 1991) has introduced in this context new ideas which might provide a natural solution to the amplification problem. It is briefly described in Section 2. Of the predicted parity-violating phase transition, we only attempted to observe the 'global' signature, mimicking in the crudest possible way the processes which might have been at the origin of chiral purity in prebiotic material. These exploratory experiments are described in Section 3. They brought no evidence for the phenomenon, but this negative result should not be considered as a definitive one: it only eliminates the possibility that the phase transition occurs at any natural low temperature and in our conditions. Other conditions should be explored, if possible in connection with a deeper analysis of the processes at work, which encompass phenomena as diverse as weak interactions and solid state physics. In Section 4, the limits of our experiments are explored and new tests are envisaged. The main uncertainty concerning the Salam's hypothesis, however, lies in the lack of a detailed mechanism relating the proved weak interaction phenomenon and the expected biological one. We briefly attempt to discuss the known and the unknown of this difficult problem.

2. A Simple Test for a New Type of Phase Transition

We do not intend to explore here in details the theoretical work at the origin of this experiment, and we refer to Salam (1991) and Chela-Flores (1991) for a complete account of the ideas which are to be tested. We simply note that weak and electromagnetic interactions have been unified in a single model, called the Standard Model (Glashow, 1980; Salam, 1980; Weinberg, 1980), which allows a quite precise description of the whole set of experimental data produced in these domains of physics. Up to now, there has been no need to go beyond this model, though its limits have been perseverantly searched for. Its direct predictions are then on relatively solid grounds. This is the case for the recent observation (Salam, 1991) that the exchange of a Z^0 boson gives rise to an attractive force between certain pairs of electrons. Since it is a weak interaction phenomenon, the force is minuscule, but there is little doubt about its existence. A second and essential point is that, under some critical temperature T_c at which one should observe a phase transition, the electrons in matter must be sensitive to this attraction and be the seat of a condensation phenomenon. Such a collective process is the equivalent of superconductivity which results from the Cooper pairs interactions. This analogy provides the basis for the amplification of the minute effects classically expected from the weak interaction, since a macroscopic number of particles are then allowed to participate coherently.

The estimate of the critical temperature is much less sure than the existence of the collective effect, and the prudent conclusions in the original publication (Salam, 1991) will be here our credo: 'The best way to determine T_c for a given amino acid is at present experiment'. The fact is that no detailed mechanism exists, which could help the numerical evaluation of the parameter describing the phase

transition. The uncertainty is even so large as to cast doubts on the nature itself of the phase transition, and consequently on its observability by our method. This point will be discussed in Section 4. It seems reasonable however, considering the importance of the prediction for physics as well as for biology, to look for the predicted new type of ordering of matter.

For the time being we will then suppose that the phase transition consists as proposed by Salam (1991) in the transformation of the configurations of mirror asymmetric biomolecules, from the *L* type to the *D* type or the inverse, depending on the precise energy difference between them. The best signature for the phase transition would then be the corresponding inversion of the optical activity when the temperature is lowered under T_c , as already suggested by Salam (1991). We remark further that such a measurement would also supply the most direct and interpretation-free proof for the homochirality problem: the quantity to be measured is precisely the rotatory power which is considered since Pasteur a characteristic signal for life, and in our times as a necessary condition for its emergence (Gol'danskii and Kuz'min, 1989).

3. Experiment

The ideal experiment consists then in measuring the optical rotation produced by a racemic mixture of chiral molecules on a polarized beam of light: as the temperature is slowly lowered, the rotation should abruptly grow at some time from the initial zero value to a sizeable fraction of the nominal rotatory power for the homochiral equivalent preparation. In practice, such a measurement is not easy and we found more convenient to measure the optical rotation outside the cryogenic vessel. We were then faced with the rapid return of the sample to warmer temperature, and eventually the disparition of the expected effect. We devised then our experiment so as to bypass this difficulty: two samples with the same molecular composition but with a different homochirality degree (generally one racemic and one non racemic in our experiments) are simultaneously brought to low temperatures. If the critical temperature is attained, both samples should become identical, possessing now in principle the same high degree of homochirality. When heated back to room temperature, both should follow the same path so that in the end at least one of the two samples should have a chirality different from its initial value, whatever happens when going back above T_c , and provided that the phase transition consists in the predicted change. Let us note finally that the use of two different samples is a necessary condition for completeness of the experiment: it ensures that the phase transition cannot be missed if the right domain of temperatures is explored and if the duration of exposition to them is not too short. This conclusion is not dependent on the direction for the transition (from *L* to *D* or *D* to *L*, nor on its reversibility (when the temperature becomes higher than the hypothesized T_c), and it is not affected by the fact that the new phase can exist only in a temperature band, and not from T_c down to $T = 0$.

A natural choice for our samples would be one of the 4 amino acids for which there exists a parity violating energy difference estimation (Mason and Tranter, 1984). However the rotatory power of these substances is not very high, and we preferred to use a more sensitive detector of their homochirality. A priori, most complex molecules are mirror asymmetric and can then constitute a good target for our experiment, since the weak interaction parity violating energy difference has no reason to be zero, except accidentally. In particular, biomolecules are not expected to present any advantage in this context. We chose nevertheless cystine, because of its similarity with the amino acid cysteine, its high rotatory power [α] = 218 ° at 589.3 nm and 20 °C) and its availability in the pure homochiral states. Two samples were used simultaneously in our experiments: one was racemic and the other left-handed.

The experimental procedure was the following. Polycrystalline cystine powders were brought by pairs (one racemic, one left-handed) to low temperature in a cryostat and kept cold during several days to allow for an eventually slow transition. After that period, the two samples were taken out of the cryostat, dissolved (separately) at room temperature in the 2N HCl solution, and placed for the optical rotation measurement in transparent cells set between polarizers. They were then illuminated with a He-Ne laser at 632.8 nm. At this wavelength, the specific rotatory power of cystine is [α] = 203°.

Different cooling conditions were successively experimented: (1) Three days at 77 K, (2) three days at 4 K, (3) four days at 0.6 K and (4) three days at .01 K. For all initially racemic cystine specimens, absolutely no rotation was observed after cooling. On the other hand, no change in the polarization rotation was measured for the left-handed samples: with a typical concentration of 46 g l⁻¹ of this homochiral cystine, and a light path length of 8 cm, the measured rotation was 7° after as well as before the days inside the cryostat. This value corresponds to a rotatory power [α] = 190°, in good agreement with the specific value 203° if one takes into account our experimental uncertainty, which is about 30' for the measure of the rotation.

In another experiment, we used recrystallized right-handed and left-handed samples. The size of the crystals was close to 5 mm, a much larger dimension than the one of the first received samples. (On the contrary, it was impossible to increase the crystal size of our racemic specimens so that right-handed cystine was used in place of the racemic mixture). After four days at 0.6 K we did not detect any change in the two opposite optical rotations. This points to a relative independence of our conclusions on the detailed state of the macroscopic cystine material.

4. Discussion

In this first exploration, our measures have shown no evidence for a sizeable transition from one state of the molecule cystine to its mirror-symmetric. On the contrary, the existence of some phase transition due to the parity violating sector

of weak interactions is on relatively firm grounds. It is then interesting to compare more in detail what is observed and what is expected.

Our most obvious concern is the temperature range which is to be explored. Estimations, drawn from the analogy with superconductivity, give critical temperatures as high as 300 K, but this number could be varied very easily in any direction (Salam, 1989). On the contrary, an order based on energy differences around 10^{-18} eV would be destroyed by thermal motion as soon as the temperature is higher than 10^{-14} K, i.e. the phase transition would be unattainable before long. Such energy differences should not be considered as characteristic ones, however: the potential barrier between one state and its mirror symmetric is more representative of the transition which produces the chirality change in molecules. A typical energy would then be the dissociation energy, corresponding to temperatures of the order of 5–600 K, but intermediate steps depending strongly on the detailed mechanism could bring T_c to a much lower value: in the absence of a model, experiment stays as the best means of exploration. Our cryostat was brought to 10 mK. Although the cystine powder probably did not attain such a low temperature because of its low conductivity, we are confident that it was during the experiment in conditions colder than anywhere attainable naturally in the universe. A temperature measurement inside the powder will be performed soon for a check. Apart from this restriction, we can then conclude that we found no evidence for the expected phase transition in our experimental conditions.

Another parameter which might be of importance is the duration of the cold period. Here also a theoretical estimate is very difficult: a priori one expects a phase transition to be a relatively rapid phenomenon, but this is a very peculiar one because the interaction is indeed very weak. For sure, the Z^0 exchange is of very short range and quasi-instantaneous, but its probability can vary enormously depending on the atomic conditions in which it is exerted. Let us simply recall here that the periods for β decay, another weak interaction phenomenon, can extend from minute fractions of a second to gigayears. In our case, the Z^0 exchange is limited by the overlap of electron and neutron wave functions, and also by the strength of the potential barrier between the two forms of the molecule, which hinders the tunneling effect necessary for the transformation. Our choice of a three days duration, dictated by practical reasons, can then be at the origin of our negative result. Obviously we cannot wait much longer and the only possible way to collect pertinent data is then the analysis of outerspace material. The search for homochirality of complex molecules formed in extraterrestrial space is then a natural extension of our present work. In this context, one may find encouraging the recent find (Engel *et al.*, 1990) that the ratio D/L for alanine (and also for other amino acids) in samples of the Murchison meteorite is significantly lower than 1. If confirmed, it would constitute a first indication for the existence of a non-racemic chemistry outside our planet, which might take its origin in the phase transition that we were looking for in this experiment. In effect, the main consequence of the existence of the phase transition at some low or very low

temperature might be to displace the origins of life, or at least some of its primordial steps from the earth to extraterrestrial space – with obvious consequences for all prebiotic chemistry researches.

The third question arising from our analysis concerns the choice of cystine. This biomolecule is the association of two cysteines linked by a disulfide bridge. No theoretical calculation is available for the amino acid cysteine, and even less for cystine, but the generality of the argument for the existence of a phase transition implies that cystine is a priori as good a candidate for a test as amino acids. The presence of sulfur atoms in this molecule is even an advantage, a priori, because of the Z^6 dependence of the parity-violating energy difference (MacDermott and Tranter, 1989). Our choice might be unlucky, however: the structure of the molecule as an arrangement of two identical pieces may lead in this case to a particular and unpredictable lack of sensitivity of our measures. A check of our results with alanine will then be our objective in the near future.

These uncertainties are mainly due to our ignorance of the mechanism which might transfer the parity violation from the particle level to the molecular one. However, it has been known experimentally for more than 10 years now that the weak force, and more particularly the Z^0 exchange, is felt measurably by the outermost electrons in atoms (Bouchiat and Pottier, 1984). Thus, the problem reduces to know if the collectivity of electrons in the medium is sufficient to produce a phase transition involving energies as high as the potential barrier between left and right-handed configurations. This is a complex matter from which arise many and various questions: is the dependence with Z of the parity violation effect valid for atoms still applicable for complex molecules? What is the importance of the medium density and of the crystal structure? What can be the intermediate states between the two enantiomers, and consequently how high is the effective potential barrier? Finally, what is the characteristic time necessary for the establishment of the phenomenon? None of these is really easy to answer at present or even to formulate so as to lead to clear experimental tests. The problem is nevertheless so important, and the recently provided answer so elegant, that more work is needed along these lines both on the theoretical and on the experimental sides.

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