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On the Selection of Biomolecular Chirality during Chemical Evolution
(Addendum)

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The Role of Chirality in the Origin of Life

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"Any man who, upon looking down at his bare feet, doesn't laugh, has either no sense of symmetry or no sense of humour" (Descartes, cf. Walker 1979)

Summary. The role of chirality in the theories that determine the origin of life are reemphasized—in particular the fact that almost all amino acids utilized in living systems are of the L type. Starting from Z^0 interactions, I speculate on an explanation of the above fact in terms of quantum mechanical cooperative and condensation phenomena (possibly in terms of an $e-n$ condensate where the $e-n$ system has the same status as Cooper-pairing), which could give rise to second-order phase transitions (including D to L transformations) below a critical temperature T_c . As a general rule, T_c is a low temperature. From this, it is conceivable that the earth provided too hot a location for the production of L amino acids. I suggest laboratory testing of these ideas by looking for the appropriate phase transitions.

Key words: Prebiotic chirality — Origin of life — Condensation

Section 1

One may summarize the presently accepted view of the origin of life as occurring in three stages: the cosmic stage; the prebiotic chemical stage, and the biological stage:

1) The cosmic stage concerns itself with the early history of the universe where electroweak forces made a phase transition into two forces, electromagnetic and weak, 10^{-12} s after the universe was born. The temperature was then 250 GeV and the

carriers of the neutral weak force—the Z_0 particle—acquired mass.

2) Chemistry became important after the planets were formed (some 10 billion years later), though it may have played a role in the presolar epochs as well (long after the quarks of the early cosmic era had condensed into protons and neutrons and much after the recombination with electrons, which took place some 10^5 years following the big bang). Molecules of future life could thus have formed even before the origin of the Earth itself (Orò et al. 1990a).

3) The biological era concerns itself with the replication of nucleic acid polymers and protein synthesis. The biological era may have started some 3.8 billion years ago.

Section 2

Classically, a chiral molecule and its mirror image [defined by left (L) or right (D) optical/rotatory dispersion] have been considered energetically equivalent. However, the parity-violating weak interactions give rise to L and D configurations (Mason and Tranter 1984), and ensure that this equivalence is no longer exact—one of the two molecules, L or D, being energetically stabilized, with energy differences on the order of 3×10^{-19} eV.

In living systems, protein molecules are composed of 20 L amino acids (although some amino acids of the opposite D type do occur in cell walls of certain bacteria). Of the 74 amino acids, for example, found in samples of the Murchison meteorite, only 8 are present in proteins, 11 have other biological roles, and the remaining 55 have been found only in extraterrestrial samples (Knervolden et al. 1971; Cronin 1989).

The polynucleotides contain sugars in D configurations only. Clearly, once living processes had selected handedness, the complex machinery of protein synthesis and stereoselectivity of enzymes could have assured that such handedness was perpetuated.

Section 3

The most significant of the parity-violating weak interactions are the weak-neutral, these being mediated by the Z^0 bosons (Harris et al. 1978). These interactions are of exceptionally short range by atomic and strong nuclear physics standards, and to a very good approximation may be taken as contact phenomena. Recent calculations (Mason and Tranter 1984; Tranter and MacDermott 1989) indicate that four of the amino acids in aqueous zwitterionic conformation—essentially all the ones for which these calculations are available: alanine, valine, serine, and aspartic acid—are L stabilized relative to their unnatural D mirrors for configurations in aqueous media. (A minor triumph, for the sugars—particularly for D-glyceraldehyde—the calculations show that the right-handed variety is the more stable.)

This stability affects 1 out of 10^{17} molecules at room temperatures (since $10^{-17} \approx (3 \times 10^{-19} \text{ eV}) / 300^\circ\text{K})k_B$. It is the smallness of this figure that has prompted many chemists to wonder if this mechanism could indeed be responsible for the ultimate optical asymmetry.

The crucial problem is that of amplification of this electroweak advantage over the course of time so that, for example, the 20 amino acids (which make up the proteins) convert almost entirely from D into L types. This problem has been considered by Kondepudi and Nelson (1985) following the seminal ideas of F.C. Franck.

Consider, for example, quartz crystals that may be taken as nonequilibrium statistical mechanical systems at ambient temperatures on the order of $T = 300^\circ\text{K}$. Using an autocatalytic mechanism and theory of delayed bifurcations, one can show that a lake 1 km² and 4 m deep would need 10^4 years to produce the necessary electroweak advantage so far as quartz is concerned. Kondepudi and Nelson give a general theory of spontaneous chiral symmetry breaking in nonequilibrium chemical systems and the possible influence of weak-neutral currents in such a process. They conclude that on a long time scale (10^4 years), for reactions occurring in large volumes, such as the oceans, the effects of parity violations due to weak-neutral currents cannot be considered small.

Objections to this work have been voiced (Goldanski in Avetisov et al. 1987). For one thing, these

authors (as well as L. Orgel, personal communication) maintain that the electroweak advantage takes place by repetitive steps in these calculations and that there are $n = 10^{17}$ steps involved. The earth must therefore have contained $n^2 \approx (10^{17})^2 \approx 10^{34}$ chiral molecules to take proper account of the resulting fluctuations. This, these authors (Goldanski in Avetisov et al. 1987) find difficult to credit, and conclude that “the role of weak neutral currents in the origination of the biomolecular chirality should not be considered essential.” Kondepudi (personal communication) agrees with this estimate (10^{34}) but maintains that “this number of molecules need not all be reacting at the same time. This is the total number that is fluxed through the nonequilibrium flow system in 1.5×10^4 years.”

Without necessarily disagreeing with the work of Kondepudi and Nelson (particularly at high temperatures where the equations they use may be considered part of the renormalization group), we speculate on an alternative mechanism. The discussion in this note is mainly physical in character. The enhancement due to phase transitions is discussed in Appendices A–E.

I would like to treat this quantum mechanically as an equilibrium problem. The quantum mechanical formalism treats the phenomenon as a cooperative one where condensation aspects are emphasized and the transitions D to L are accomplished below a critical temperature T_c .

In general, when global cooperative and condensation phenomena do take place, low temperatures (or high densities, e.g., as for neutron stars) are necessary; now if T_c for the amino acid turns out to be very small, then it would be plausible that the origin space in which production of chiral amino acids takes place, was larger than the Earth. This problem is discussed below.

Section 4

A modern version of the phenomenon of condensation has been described by Leggett (1990) giving a uniform treatment of a superfluid (like liquid helium II), where T_0 —the so-called degeneracy temperature—is $\approx 3^\circ\text{K}$, as well as of metallic superconductivity for Cooper-paired electrons below a transition temperature T_c . The latter is more relevant for our purposes as we shall see below.

What is condensation?

Imagine that you are on a mountain-top looking down at a distant city square. The crowd is milling around at random, and each individual is doing something different: Now suppose, however, that it is not market day but the day of a military parade, and the crowd is replaced by a battalion of well drilled soldiers. Every soldier is doing the same thing at the same time, and it is very much easier to see (or hear)

from a distance what that is. The physics analogy is that a normal system is like the market day crowd—every atom is doing something different—whereas in a Bose condensed system the atoms (or, more accurately, the fraction of them which is condensed at the temperature in question) are all forced to be in the same quantum state, and therefore resemble the well drilled soldiers: every atom must do exactly the same thing at the same time (Leggett 1990).

The analogy of the behavior of the crowd with racemicity and of the well-drilled soldiers with L amino acids is apt. The number of particles in any given energy level is fixed as a function of temperature, and as a result the total number of particles occupying the levels cannot be greater than some number $N_{\max}(T)$ (which decreases along with T). At some temperature T_0 the quantity N_{\max} becomes equal to the total number of particles in the system N , whereas below T_0 we have $N_{\max} < N$. At such temperatures there are simply not enough quantum states available to accommodate all the particles. "The resolution of the problem is remarkably simple: below T_0 the system adjusts by taking all the particles which cannot be accommodated by the distribution formula and putting them in the single quantum state which has the lowest energy" (Leggett 1990). Because these surplus particles are a finite fraction of the whole (in fact, at zero temperature all of them), we reach the remarkable result that a macroscopic number of particles (of order N , which typically is of order 10^{23}) occupy a single quantum state. This phenomenon is known as Bose condensation.

Section 5

The necessary conditions for condensation have been studied by L. Landau (Landau et al. 1980). Landau distinguished between Bose superfluids and Fermi superfluids (even for Fermi superfluids like superconductors the "superfluidity" is produced by bosonic condensates like those for Cooper pairs). [A condensate is the constant part of a spin zero field (φ) that can arise for some theories (provided the potential for φ is like an inverted Mexican hat). This is achievable for parts of fields that carry zero frequency (zero energy and zero momentum).]

"A Fermi gas with attraction between the particles must have the property of superfluidity . . . howsoever weak the attraction is" (Abrikosov 1987). To clarify this point further, consider the following situation (Goodstein 1985):

Imagine two people on an old sagging, nonlinear mattress. They tend to roll toward the middle, even if they don't like each other. That is, there is an attractive interaction. The cause of this interaction . . . is that the people create distortions in the mattress, and the distortions try to merge. The electrons in the metal do not stand still but rather zip through the lattice at something like the Fermi velocity. The ions are

attracted to the electrons but, owing to their large mass, move very slowly compared to the much lighter electrons. By the time the ions respond the electron is long gone, but it has, in effect, left behind a trail of positive charge, which is the lattice distortion we mentioned above. Another electron, transversing the same path, would find that its way has been prepared with the positive charge that it finds so attractive. We can imagine that the first electron created a phonon, which the second happily absorbs. Notice that the interaction is strongest if the two electrons traverse exactly the same path—that is, if they have, say, equal and opposite momenta.

Section 6

For $T = T_c$ the phase transition is present with all its aspects of suddenness. For $T < T_c$ the "superfluidity" persists, reaching its climax at $T = 0$. The question arises as to what happens when $T > T_c$. To answer this question, let us consider cooperative phenomena. The main features of cooperative phenomena can be illustrated by considering with Atkins (1959), the semiclassical treatment of ferromagnetism. At 0°K the electron spins are aligned parallel to one another to give a resultant magnetization even in the absence of an external magnetic field. However, at a finite temperature thermal agitation is able to turn over some of the spins and the average magnetic moment in the direction of magnetization is thereby decreased. "As soon as this process starts, an electron chosen at random is likely to have neighbors pointing against the direction of magnetization as well as with it and this reduces the energy needed to reverse the spin of the electron, so that as the temperature increases and more spins are turned over, it becomes increasingly easier to turn over the remaining spins and the disordering process develops with ever-increasing rapidity. At the Curie point the disordering is eventually complete and the spins point equally in both directions" so that only a 50–50 racemic state survives.

The results of this section will be used in Appendix B to obtain one estimate of T_c for most amino acids.

Section 7

How important are the effects of the parity-violating weak interactions for specific amino acids? This question may be answered by setting $(1 - 4 \sin^2\theta) \approx 0$; the resulting elegant expression for the Hamiltonian has led to molecular conformation-dependent values for parity violation, which for Ala, Val, Ser, and Asp have been calculated to give (Mason and Tranter 1984; Tranter and MacDermott 1989) -3.0 , -6.2 , -2.3 , and -4.8 , in units of 10^{-19} eV. These authors express the energy values in atomic units (1 atomic unit = 1 Hartree = 27.2 eV) corresponding to the L configuration of the aqueous

zwitterionic amino acids. The simplest amino acid, glycine (residue $R = H$), is not resolvable into optical isomers. On account of the further symmetry implied by $R = H$, parity violation, when averaged over a complete rotation of the carboxylate group through all configuration angles, turns out to be zero, in agreement with experimental results. For the sugar glyceraldehyde the value is $+1.8 \times 10^{-19}$ eV corresponding to its D configuration [see section 1, Appendix E].

The classical chemist has hitherto used the electromagnetic force as the only fundamental force that can produce chemical effects. He has not considered the electroweak force, and in particular its Z^0 component, because the effects due to Z^0 are supposedly very small at low temperatures. I shall now show that the electroweak interactions (for which there is nothing comparable in classical chemistry) can give rise to phase transitions.

The superconductivity phase transition can be attributed to the attractive force due to the parity nonconserving effective interaction produced by the spin-0 part of Z^0 , which is itself caused by spontaneous symmetry breaking associated with the condensate $\langle \varphi \rangle \neq 0$.

Like all phase transitions, this one will have a behavior like $(T_c - T)$, $T - T_c$. This makes the amplitude (or derivatives thereof) an infinite quantity.

To compute T_c exactly is difficult (for one thing, on account of the incompleteness of the standard model of elementary particles), but T_c can be measured without much difficulty. In the sequel it is assumed that T_c does exist and that it has been measured for each amino acid.

Section 8

Because the ambient temperature of the Earth's surface is $\approx 300^\circ\text{K}$ (the maximum temperature on the surface being $\approx 350^\circ\text{K}$), if $T_c < 300^\circ\text{K}$, the present formalism may not apply to the Earth. The fact that the prebiotic temperatures may indeed be less than 300°K was the content of a paper by Sanchez et al. (1966); these authors claim that tetramer formation in 0.01 M HCN is accelerated by lowering the temperature from 300°K to 250°K . The authors conclude that "we may have to replace the usual picture of a warm dilute prebiotic medium with one more cold and much more concentrated at least for some syntheses." Thus in the language of the present note, the data of Sanchez et al. may perhaps be interpreted as advocating $T_c \lesssim 250^\circ\text{K}$. On the other hand, K.D. Kondepudi (personal communication) has suggested that unless $T_c \lesssim 2.7^\circ\text{K}$ —the ambient universal temperature—the entire interstellar space could be

optically active provided, of course, the density of amino acids is not too dilute over most of space.

In this case, there could be several possible scenarios:

1) Presolar contributions may be necessary to get low enough temperatures.

2) Major contributions come from the more distant and the cooler parts of the solar system with ambient temperatures less than T_c . In this context it is good to remember that the maximum surface temperatures have been estimated at 135°K for Jupiter, 120°K for Saturn, 85°K for Uranus, 55°K for Neptune, and 20°K for Pluto (see section 2, Appendix E).

3) If T_c is considerably less than 300°K , then one could entertain the (somewhat odd) notion that the Earth only acted as a junction place where L amino acids came together with D sugars and nucleotides for the replication phenomena to get started for the biotic stage mentioned in Section 2 to be implemented.

In order for the biotic alternative to prevail, it is necessary to invent a mechanism to deliver organic molecules to the Earth from the cooler locations mentioned above. This was considered by Orò (Orò 1961; Orò et al. 1990a), and in greater detail recently by Chyba et al. (1990). The latter authors conclude that:

1) "The Earth did accrete prebiotic organic molecules important for the origins of life from impacts of carbonaceous asteroids and comets during the period of heavy bombardment 4.5×10^9 to 3.8×10^9 years ago" (cf. the Chiron comet?).

2) For plausibly dense (10-bar carbon dioxide) early atmospheres, these authors find that 4.5×10^9 years ago the Earth was accreting intact cometary organics at a rate of at least $\approx 10^6$ to 10^7 kg per year—a flux that thereafter declined with a half-life of $\sim 10^8$ years. These results may be placed in context by comparison with terrestrial oceanic and total biomasses, $\sim 3 \times 10^{12}$ kg and $\sim 6 \times 10^{14}$ kg, respectively.

3) Contrary to the general impression, alanine molecules could withstand temperatures as high as $\approx 700^\circ\text{K}$ for 1 s whereas other amino acids could withstand temperatures in the range of 600 – 800°K for a like period of time and remain stable and intact upon impact with the Earth.

It is tempting to assume further that this material ($\approx 10^6$ to 10^7 kg) maintained its chirality at delivery (particularly if T_c had a small value near zero). This follows from the formula

$$-\frac{\partial \Delta}{\partial T} \approx \frac{3.06}{2} \times \sqrt{\frac{T_c}{T_c - T}}$$

(see Appendix B.2) if the formula applies to the case

of amino acids. At this juncture life could have started and the chirality perpetuated in accordance with the biotic picture mentioned in Section 2.

Section 9

Is the laboratory testing of the central hypothesis of this note feasible? This can be tested by taking a racemic mixture of crystalline L and D amino acids.

The crystalline conformations of L and D amino acids do not differ much from the zwitterionic forms except for the absence of water molecules inside the lattice cell. Barring for alanine, there are no definite calculations which show that it is indeed the L configuration that prevails for these crystals. However this may not affect the laboratory testing of the hypothesis of this paper because lowering of the temperature below the transition temperature would eventually convert all amino acids into that particular configuration that only partially predominated before. Conversely, a raising of temperature through T_c would show that a pure configuration below T_c can be converted into a racemic mixture for $T > T_c$.

To conclude, note that ideally one should be able to compute the values of T_c when electroweak theory is fully worked out. The numerical value of this quantity could lie anywhere around 2.7°K (the ambient temperature of outer space) or beyond 350°K but below the dissociation temperatures.

One could contemplate reaching 0°K, but this would have to be strictly local. The best way to determine T_c for a given amino acid is at present by experimentation. The analogy of the "superfluidity" exhibited by amino acids and sugars is to "superfluidity" in superconductors and not to the liquid helium. In the case of superconductivity, one has to apply an external magnetic field and look for the Meissner effect to determine T_c . Likewise, the "superfluidity" of amino acids (or sugars) is measured by shining on these external light sources (see section 3, Appendix E).

One direct way to test for evidence of the hypothesis (regarding the existence of such a phase transition) is to lower the temperature while measuring optical activity when polarized light is shined upon a racemic mixture of a particular amino acid. If the polarization vector gets rotated, one may be sure that the appropriate phase transition has taken place.

The process itself could perhaps be detected by optical rotatory dispersion (ORD) for circular dichroism (CD) (see section 4, Appendix E). An alternative means of detecting the process may be by measuring differences of specific heats and looking for anomalies in the curve $C = \gamma T + \beta T^3 + \dots$ like

what has been done (see Appendix D) for the non-amino acids like melanins and tumor melanosomes (Mizutani et al. 1976).

Section 10

I have shown that chirality may provide a boundary condition for theories of the origin of life and that Z^0 interactions—as well as what comes beyond the standard model of fundamental interactions (CP violation, for example)—ought to play a central role in this story. In this context, the following quotation from L. Pasteur (who did not even know of Z^0 particles) is perhaps prophetic: "Life as manifested to us is a function of the asymmetry of the Universe and of the consequences of this fact. The Universe is asymmetrical. Life is dominated by asymmetrical actions. I can even imagine that all living species are primordially in their structure, in their external forms a function of cosmic asymmetry" (Pasteur 1860).

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Appendix A

Section A.1

To implement these ideas for L amino acids we start with the Z^0 interaction

$$L_{em} = \frac{e}{\sin \theta \cos \theta} [(T_{3L} - \sin^2 \theta J_{em})_L Z^0] \quad (A.1)$$

(units $\hbar = c = 1$). Here J_{em} is the electromagnetic current, T_{3L} is the left-handed third component of the weak isospin consisting of the (anomaly-free) combination of the proton-neutron (p, n) and neutrino-electron (ν_e, e) left-handed doublets (of weak isospin), i.e., $T_{3L} = \bar{\psi} \gamma_5 \left(\frac{1 + \gamma^3}{2} \right) \tau_3 \psi$ where $\tau_3 = 1/2(1, -1)$ where ψ stands either for the doublet of protons (p) and neutrons (n), or for the doublet of neutrinos (ν_e) and electrons (e). Proton and neutron (composite) fields have been used in preference to the elementary quarks, as this illustrates the point that for our present calculations (up to certain energies and temperatures), it is not important to know the elementary entities themselves. In addition there is the Higgs field ϕ , with a known nonzero expectation value $\langle \phi \rangle$, which is needed to give masses to the protons, neutrons, and electrons as well as the Z^0 particle. Choosing the value of $\langle \phi \rangle \neq 0$ is the same as spontaneous symmetry breaking. The Higgs particles on account of their nonzero expectation value ($\langle \phi \rangle \neq 0$) can act as perfect condensates at zero temperatures. In terms of this quantity ($\langle \phi \rangle = 250$ GeV) the electron mass m_e turns out to be a very tiny number ($\approx 2 \times 10^{-6} \times \langle \phi \rangle$). [It is perhaps worth remarking that this number is very large for the top quark if its mass is in excess of 100 GeV. Thus the terms that give this, look like $b\phi\bar{t}t$ where $b \geq 3/4$. Some physicists, like Y. Nambu, take this as the defining property of the field ϕ , i.e., ϕ is considered as a $t\bar{t}$ composite.]

Let $(1 - 4 \sin^2 \theta) \approx 1/3$, with the present empirical value of the parameter $\sin^2 \theta \approx 0.231$. Unlike some authors (Harris et al. 1978; Mason and Tranter 1984; Tranter and MacDermott 1989) let us not assume this quantity to equal zero. Neglecting neutrinos (and Higgs), the right-hand side of (A.1) can be written in the form:

$$\frac{e}{4 \sin \theta \cos \theta} (V_\mu - a_\mu) Z_\mu \quad (A.2)$$

Here

$$V_\mu = (1 - 4 \sin^2 \theta) J_{em\mu} + (-\hbar \gamma_\mu n) \quad (A.3)$$

and

$$-a_\mu = (\partial \gamma_\mu \gamma_5 p - \hbar \gamma_\mu \gamma_5 n) - (\partial \gamma_\mu \gamma_5 e) \quad (A.4)$$

To this must be added the purely electromagnetic terms (which are parity conserving)

$$e J_{em\mu} \times A_\mu \quad (A.5)$$

Section A.2

In order to address the question of the existence of a finite critical temperature T_c for the phase transition into a condensed mode, we recall that our picture of amino acids is as follows:

Amino acids consist of a backbone made up of atoms of

carbon (2 in number, one of which C_α acts as the center for the mirror transformations), oxygen (2), nitrogen (1) and hydrogen (4), plus a residue that may consist of hydrogens (up to 15), carbons (up to 8), nitrogens (up to 3), oxygens (up to 2), and sulfur (up to 1). The electrons interact with protons and neutrons essentially (in fact with the quarks contained inside the nucleons) at the location of these objects; they in particular interact with neutrons.

The amino acid gets its L or D configurations through mirror arrangements of the atoms contained in the backbone structure. It has been shown that L or D configurations are correlated with left or right chirality (Mason and Tranter 1984).

The state of a given amino acid as composite of p , n , e , and ν will be shown in the sequel. It must be remembered that the amino acids are not metallic compounds. Thus there is no concept of Fermi energy nor of wandering electrons for them. The electrons from the inner shells interact with the nucleons, in particular with the neutrons and quarks inside them.

Appendix B

Section B.1

Consider the pseudoscalar terms in the effective interactions, which, after integrating out the Z^0 field, is proportional to $V_+ \times A_+ + A_+ \times V_+ \approx \psi \gamma_5 \psi' \gamma_5 \gamma_3 \psi' + \dots$. A part of these terms is proportional to $(1 - 4 \sin^2 \theta)$. Such terms have been set equal to zero by some authors (Harris et al. 1978; Mason and Tranter 1984; Tranter and MacDermott 1989). I shall not make this approximation. These terms contain 4-Fermi interaction of electrons that are proportional to the pseudoscalar quantity $\sigma \cdot p$ in the nonrelativistic approximation, where only large components are kept. Such terms are proportional to $(1 - 4 \sin^2 \theta)[(e^+ e^- \times e^+ \frac{\sigma \cdot p}{m_e} e) + (e^+ e^- \times n^+ \frac{\sigma \cdot p}{m_n} n)] + n^+ n \times e^+ \frac{\sigma \cdot p}{m_e} e$. The important point for our purposes is that this part of the parity-violating sector of $e-e$ coupling is negative for half the states of the system, i.e., for states that have the opposite eigenvalue for the operator $\sigma \cdot p$ before and after the interaction—and positive for the remaining half of the states.

I concentrate on the attractive set among the parity-violating terms. Because of the absence of such terms in the parity-conserving (in fact repulsive) Coulomb force, this would allow us to develop the analogy for metals within the theory of superconductivity. The situation is analogous to that of BCS theory where the 4-Fermi effective interaction of the electrons is attractive. According to Landau's criterion, the electron fluid must therefore exhibit "superfluidity" (Abrikosov 1987).

Section B.2

The ideas and results from BCS theory, which may be of interest to us in developing our analogy, are next emphasized.

The condensate wave function for a metallic superconductor is the "gap" function $\Delta(0) = \omega_D \exp\left(\frac{-2}{g\nu}\right)$. Here ω_D is the Debye cutoff $\approx 10^2 K$ for most metals, p_F stands for the Fermi momentum, ω_F is the corresponding Fermi energy, and g is the effective 4-Fermi coupling parameter for electrons, which in general is given by $\nu = \frac{p_F m}{\pi^2}$, whereas $g\nu \approx 1$ represents an approximation.

Thus the expression for the exponent may be taken to be of order unity (as $g\nu \approx 1$). I shall continue to make this approximation. Empirically, one finds that $\omega_D \approx (10^{-3} - 10^{-4})\omega_F$. [The fact that the interaction spreads over an energy interval $\Delta\omega_D$ implies, according to quantum mechanics, that it is retarded, or in other

words, it operates during a finite time interval $\Delta t \approx (\Delta\omega_D)^{-1}$ (Abrikosov 1987). This implies that for the electron-phonon interaction, the time interval is given by approximately 10^{-13} s for $T_c = 10^2 K$ for the case of niobium (superconductivity) and 10^3 s for the case of amino acids if $\omega_D \approx 3 \times 10^{-19}$ eV.]

Using the methods of Gorkov and Sakita for the nonrelativistic electron case, an equivalent Landau-Ginzburg equation for the BCS theory is written down. This gives the following results for the superconductivity case:

1) T_c , the critical temperature is given by $T_c \approx (1.76)^{-1} \times \Delta(0)$.

2) The dependence of $\Delta(T)$ on temperature is approximately given by $\Delta(T) \approx \pi \left(\frac{8}{7\zeta(3)}\right) [T_c(T_c - T)]^\alpha = 3.06[T_c(T_c - T)]^\alpha$ for $T < T_c$; here $\zeta(x)$ is the Riemann zeta function: $\zeta(x) = \sum_{n=1}^{\infty} n^{-x}$. $\Delta(T)$ decreases with increasing temperature. Its derivative with respect to T becomes infinite at $T \approx T_c$ (Abrikosov 1987).

3) $C_v(T) = C_n(T) + \frac{4}{7\zeta(3)} \frac{p_F m}{k^3} T_c$. Here C_v corresponds to specific heat for the superconducting phase, whereas C_n denotes the corresponding quantity for the normal case. From this, the result that $[C_v(T_c) - C_n(T_c)]$ is proportional to T_c is obtained. The same formula seems to apply for some of the organic materials as shown by Mizutani et al. (1976).

4) The expression 2 above, for $\Delta(T)$, holds for $T < T_c$. What happens in general for $T > T_c$? Goodstein states that for the (analogous) case of magnetic susceptibility, this expression is of the form $f_+ \times \epsilon^{-\gamma}$ for $T > T_c$, provided the susceptibility for $T < T_c$ has the form $f_-(-\epsilon)^{-\gamma}$, where $\epsilon = \frac{T - T_c}{T_c}$.

One consequence of scaling laws of physics is that $\gamma = \gamma'$ (Goodstein 1985, p. 481).

If these results can be carried over to the amino acid case, a racemic mixture starts forming for $T > T_c$, completing, in general, the process to a 50-50 mixture for $(f_+ + f_-)T_c$. Because the melting point (m.p.) represents the dissociation limit for the amino acids, one expects that $(f_+ + f_-)T_c$ is less than $T_{m.p.}$. Mr. P. Agbedjro, to whom thanks are due, has compiled from the 1988-1989 "Handbook of Chemistry and Physics," the following table of the melting points of the amino acids: Ala 568°K, Arg 537°K, Cys 533°K, Glu 497°K, Gly 535°K, His 560°K, Pro 511°K, Ile 557°K, Leu 566°K, Lys 497°K, Met 554°K, Phe 557°K, Pro 493°K, Ser 519°K, Try 563°K, Tyr 615°K, and Val 571°K. These numbers uniformly lie between 500°K and 600°K except for Tyr, which is $\approx 615^\circ K$.

This could give 250-300°K if $f_+ = f_- = 1$ [compare the work of Sanchez et al. (1966), cf. Section 8] for one estimate of T_c . However this estimate could vary between a very wide range of values if $f_+ \neq f_- \neq 1$.

5) The present BCS theory applies to the low temperature case. How are the ideas of this theory utilized for the case of high T_c ? Our interest is in the critical temperatures for amino acids that may well be in excess of 350°K. Such a model beyond BCS might, for example, follow more the analogy of high T_c superconductivity where present experiments take T_c to values as high as 125°K. There is, as yet, no accepted theory (Randjbar-Daemi et al. 1990) of these high T_c superconductors and it is not clear what, if anything, is the analogue of Cooper pairs.

Two of the mechanisms suggested that high T_c superconductivity may possibly be of relevance to the case of "superfluidity" for amino acids. These are: (1) The use of the electrons of inner shells of atoms that are retained in the lattice ions. ω_D could be as high as $\approx 10^4 K$, and (2) an attempt to find a transmitting system of electrons with high polarizability: molecular organic crystals, polymers, for example C_m (where C stands for carbon and x represents a multiple repetition of the group). Unfortunately, as far as high T_c superconductivity is concerned, neither

of these two suggestions have proven very effective in increasing T_c to higher values.

Appendix C

To proceed for the case of amino acids from these expressions is not that easy: the difficulties in carrying this program through are recounted below.

Section C.1

For the amino acids, let us take an expression for T_c that is similar in form to the expression for superconductivity $T_c = \Delta E \exp(-1/\lambda)$. " ΔE is the energy difference between the states A and A^* . A is the ground state, A^* is the excited state of the . . . system (it can easily be shown that such an interaction is necessarily an attraction if it is not strong)." λ depends on the interaction of electrons for the case of superconductivity, and ΔE is related to ω_D , and $\lambda \propto gv$. Let us designate $\exp(-1/\lambda)$ as the probability factor for the transition A to A^* to take place. The major problem will be to secure $gv \approx 1$ so that this probability factor is not too small.

1) A nonperturbative calculation like the one used by Sakita (1985) is needed for the case of superconductivity but for attractive parity-violating interactions. The difficulty in this case lies in choosing what the analogy is for the Fermi energy.

2) The electrons in the inner shells of atoms are probing much more deeply into the quark structure of the nucleon. In Appendix B such electrons were observed to give rise to 10^{26} K in the superconductivity case. Chemical phenomena are probing deeply into the centers of nucleons (and the quarks within them), the energies involved being much higher than one is used to.

3) $gv \approx 1$ may be difficult to achieve. Because $\lambda \propto gv$ the fact that $gv \neq 1$, in general, may mean a diminution of probability represented by $\exp(-1/\lambda)$.

Section C.2

There is another possibility, that is, to consider the relativistic term $\hbar\gamma_n \times \partial\gamma_n\gamma_e$. This term does not have the factor $(1 - 4 \sin^2 \theta)$ in front of it.

Could we utilize this term to invent a condensate model of e - n pairing like the Cooper pairing? The answer is clearly yes, as can be seen by the fact that an interchange of particles 2 and 4 by a Fierz reshuffle can be made, so that the term reads $\hbar e \cdot \partial\gamma_n\gamma_e$. Both factors contained here are scalars and a field φ' can be invented that could have the effective coupling $[\varphi' \times (\hbar e + \partial\gamma_n\gamma_e)]$. From the calculations previously made (Mason and Tranter 1984; Tranter and MacDermott 1989), for this particular case if $T_c \approx \omega_D \exp(-2/g'v')$ and if $g'v' \approx 1$, ω_D can be taken as 3×10^{18} eV.

What field does φ correspond to? Clearly an e - n pairing (with $\Delta B \neq 0$, $\Delta L \neq 0$) brings back the memories of proton decays and baryon number violation. The question would then be, is this triggered off by a grand unification mass $\approx 10^{16}$ - 10^{19} GeV or does it rely upon the work of Rubakov and his collaborators (Kuzmin et al. 1985; Arnold and McLerran 1987; Ringwald 1990), which ascribes baryon violation to the standard model with $\langle \varphi \rangle = 250$ GeV? In other words is $\langle \varphi \rangle = \langle \varphi' \rangle$? I would tend to favor this, but this does bring us to the modern unresolved controversies that are the substance of present-day theoretical particle physics.

There is a further uncertainty that comes about because of the uncertainty in physics of the standard model. This theory (with Z^0 particles) violates P and C but conserves CP. If parity violation P is accompanied by CP (\approx T) violation (and this seems to be the case from the K^0 system), this is accomplished by writing

down a mass matrix of the Cabibbo-Kobayashi-Maskawa type. Such a mass matrix has been shown to involve necessarily a phase factor if there are three generations. A different procedure would be to build this violation as a consequence of extra terms as in Weinberg's new theory that uses gluons. It could also be built in by postulating the existence of invisible axions, where the appropriate mass terms may be greater than 10^{12} GeV, or by enhancing the symmetry of theory to left-right symmetry, or of the idea above of considering the condensate $\langle \varphi' \rangle \neq 0$ of spin-0 particle, which has interactions with $\hbar e$ and $e\gamma_n$. This may mean the addition of extra terms to the standard model, and more terms added for T_c like the ones already included.

Section C.3

The value 250°K obtained in Appendix B.4, if correct, could provide one of the better possibilities physically. It would mean that the Earth had a reasonable chance of being the site of prebiotic L amino acid production. [The very best possibility is, of course, $T_c \geq 350^\circ\text{K}$. This would mean that the Earth suffices for the production site of amino acids, in general. This is a possibility that should not be ignored if laboratory tests are made for amino acids in accordance with what is suggested in Section 9.]

All that may reasonably be inferred at this stage is the existence of a nonzero T_c due to the attractive forces mentioned before.

Be that as it may, consider the case of 4-Fermi interactions with electrons. Because this term comes together with the factor $(1 - 4 \sin^2 \theta)$, the form to be expected is of the type

$$T_c \approx \frac{\langle \varphi \rangle}{10^3} \exp[-2/gv(1 - 4 \sin^2 \theta)] \\ \approx 2.5 \times 10^{26} \text{K} \quad (\text{C.1})$$

Here ΔE is taken to be $\approx \langle \varphi \rangle$ multiplied by the old familiar factor of 10^{-3} , while gv is still taken ≈ 1 . The exponential factor gives $\exp -26 \approx 10^{-10}$, so that altogether one has $10^{-13} \times \langle \varphi \rangle$.

Because the only quantity that has the right transformation character (for such parity-violating interactions) is Z_μ^0 , or its longitudinal part where $\partial Z_\mu^0 / \partial x_\mu \approx M\varphi$, therefore 250 GeV must somehow play a role of in the formulae that have been set up.

To emphasize the arbitrariness in the calculation so far shown, it is worth remarking that T_c comes out to be $T_c \approx \omega_D \exp -2/(1 - 4 \sin^2 \theta) = 5^\circ\text{K}$ if one takes $\omega_D \approx m_e \approx 2 \times \frac{\langle \varphi \rangle}{10^6}$.

Appendix D

After this paper was completed, Dr. J. Chela-Flores provided the following quotation to be inserted into the text. I gladly do so:

Perhaps the earliest suggestion of the possible occurrence of condensation in biology was made almost three decades ago by Delbrück, who was concerned as to "whether or not something very peculiar from the quantum mechanical point of view, like superconductivity or superfluid helium, will come up. If strange cooperative phenomena can happen at room temperature in very special molecules . . . , then certainly life will have discovered this (Delbrück 1963). Within the context of the origin of life, condensation was conjectured to occur in the earliest riboorganism (Chela-Flores 1985)

* This is such an important point that I shall discuss it further in a separate note to be published in a physics journal. The top quark is necessary to get $gv = 1$. The reason for this is that g contains m_2^2 , which is of the order of m_2 .

under the effect of low temperatures estimated to be approximately 160°K.

Regarding the laboratory tests mentioned in the text, I thank Dr. A.J. MacDermott for sharpening the suggestion regarding the polarization measurements, and Dr. J. Chela-Flores for the suggestion regarding the use of specific heats.

Appendix E consists of four clarifications that occur in places in the text.

Appendix E

1) It may be noted in passing that if $(1 - 4 \sin^2 \theta) \approx 0$ uniformly, one is taking the contribution of the neutrons inside the nuclei into account, but not of the protons, except when deuterons substitute for protons. Also note that the isotope C^{13} should give a different contribution than C^{12} . This is the peculiar hallmark of Z^0 interactions. Such behavior has been attributed in the past to presolar cosmic abundances. For example, "the discovery that amino acids from the Murchison meteorite are as a group highly enriched in deuterium ($\delta D = 1370\%$) strongly suggests that the amino acids or their precursors were formed at low temperatures in interstellar clouds" (Chyba et al. 1990). This pathway reportedly supports the hypothesis of a direct relationship between organic-rich interstellar grains, comets, dark asteroids, and carbonaceous chondrites (Cruikshank 1989). It is clearly important to get the precise ratios of D/H, tritium/hydrogen, as well as C^{13}/C^{12} separately in order to distinguish the effects of Z^0 from the contributions due to abundances in the early universe. This has been done for the Murchison meteorite (Engel et al. 1990); these authors conclude that optically active materials were present in the early solar system before life began.

2) Such extraterrestriality had been anticipated on different

grounds. Some 40 years ago, Stanley Miller performed fundamental experiments demonstrating that the action of electrical discharges on a mixture of water vapor, methane, and ammonia could produce reasonable yields of simple amino acids (glycine and alanine). Subsequent experiments along the same lines by Orgel, Ponnampereuma, and others have confirmed Miller's findings. The Miller–Orgel–Ponnampereuma "experiments simulated an environment rather similar to the lower atmospheric regions of Jupiter, where it is known that there are violent thunderstorms. Jupiter (or one of its satellites like Europa) may well be the best candidate in the solar system for rudimentary extraterrestrial life!" (Oró 1961; Ponnampereuma and Molten 1973; Mitton 1977; Hanel et al. 1979a; Oró and Mills 1989; Oró et al. 1990b). It is also conceivable that chemical evolution and synthesis of biochemical compounds have occurred and are occurring now in Titan—the largest satellite of Saturn. Titan has a reducing atmosphere—a desirable feature. This may explain in part, "some of the darker spots observed in Europa's outer surface and more recently in Triton, the remarkable satellite of Neptune" (Oró et al. 1990b). [Triton's surface temperature apparently is $\approx 38 \pm 4^\circ K$ (Soderblom et al. 1990).]

3) The difference between superconductivity and Bose superfluidity for He^4 lies in the fact that the Cooper pairs (which are bosons) are rather large objects ($\sim 10^{-4}$ cm) compared with the interparticle distance ($\sim 10^{-6}$ cm), i.e., there is a significant overlap between Cooper pairs.

4) It is conceivable that the experiments are best done where a heavy atom substitutes for one of the light atoms. The analogy could be with the Patterson phases in normal x-ray diffraction analyses where one uses atoms of gold, platinum, or mercury. I find that amino acid crystals have been made with nickel, iron, or copper, for example, crystals of silver glycine $AgOOC-CH_2-NH_2$ or copper DL- α -aminobutyrate $Cu(OOC-C_2H_4NH_2)_2$ (Wyckoff 1966).

Comments on a Novel Approach to the Role of Chirality in the Origin of Life

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ABSTRACT We review a recent paper²⁰ in which a specific enhancement factor (i.e., a phase transition into a condensed Bose mode) is proposed to account for the observed amplification of the ground state energies of the L- and D-amino acid enantiomers; the difference between these energies is assumed to be due to the neutral parity-violating electroweak interaction. This physical effect initially shifts the enantiomer energies by about 3×10^{-19} eV. The proposed phase transition is characterized by a critical temperature T_c , which may be studied theoretically by enlarging the standard electroweak theory to include either the top quark or supersymmetry.²¹ Possible experimental means of finding T_c are discussed.

KEY WORDS: chirality, origin of life, Bose condensation, organic superconductivity, electroweak interaction

THE SOURCE OF BIOMOLECULAR HANDEDNESS

The first unifying principle in biochemistry is that the key molecules—amino acids, sugars, and natural lecithins (phospholipids)—have the same handedness or chirality.^{5,24} Chiral molecules and their corresponding mirror images may be defined by left (L), or right (D) optical/rotatory dispersion. Remarkably, this is true for all organisms with the exclusion of bacterial cell walls, which contain D-amino acids, as in the case of *Bacillus brevis* or *Lactobacillus arabinosus*.²² However, we may state in general that living systems translate their genes into proteins composed of 20 L-amino acids.

In a recent paper a search for the physical bases of this principle in biochemistry has been attempted.²⁰ This work has been preceded by a long history of efforts investigating the chief cause of the molecular evolution from racemic mixtures of amino acids to enantiomorphous-biased L-amino acids.¹⁶ In a substantial group of previous work, the parity-violating electroweak neutral current has been suggested as the main physical force inducing the observed biochirality. The new approach to the origin of chirality that concerns us here once again invokes the electroweak interaction, but is original in appealing to further physical concepts which we shall discuss in turn.

First of all, Salam considers that at the end of chemical evolution a particular cooperative phenomenon did take place, namely, a phase transition beneath a certain critical temperature T_c : Amino acids that had been synthesized earlier from various precursors entered into a new phase, which was a Bose condensed mode. Since this concept is well understood in physics, but has only been used a few times before in the context of biochemistry, we shall use some simple examples drawn from the new publication, which illustrate adequately the main ideas to a reader whose background is in the life sciences.

COOPERATIVE PHENOMENA, CONDENSATION, AND PAIRING: POSSIBLE FACTORS INFLUENCING CHEMICAL EVOLUTION

In order to understand how the amino acids may behave as the temperature exceeds the critical value, it is somewhat sim-

pler to consider with Salam²⁰ a well known physical system where analogous *cooperative phenomena* may occur.¹

At absolute zero temperature the electron spins are aligned parallel to one another to give a resultant magnetization even in the absence of an external magnetic field. However, at a finite temperature thermal agitation is able to turn over some of the spins and the average magnetic moment in the direction of magnetization is thereby decreased. As soon as this process starts, an electron chosen at random is likely to have neighbours pointing against the direction of magnetization as well as with it and this reduces the energy needed to reverse the spin of the electron, so that, as the temperature increases and more spins are turned over, it becomes increasingly easier to turn over the remaining spins and the disordering process develops with ever increasing rapidity. At the Curie point (i.e., at the critical temperature) the disordering is eventually complete and the spins point equally in both directions, so that only a 50–50 racemic state survives.

In his study of amino acids, rather than of electron spins, Salam has done a service by bringing attention to a specific form of cooperative behaviour at the microscopic level: *Bose condensation*. This phenomenon is being proposed as a quantum mechanical enhancing factor in the molecular evolution from the initial racemic mixture to the present day chiral amino acids. The concept of condensation is not new in biology; indeed it goes back some 30 years.⁷ In the context of the origin of life condensation in the nucleic acids was suggested to have played a role in the origin of Darwinian evolution.³ However, since the concept still remains unfamiliar in the life sciences, in spite of its extensive use made in studies of the cell membrane,⁹ we cite an interesting introduction to this singular phenomenon:^{13,20}

Imagine that you are on a mountain top looking down at a distant city square. The crowd is milling around at random,

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and each individual is doing something different. Now suppose, however, that it is not market day but the day of a military parade, and the crowd is replaced by a battalion of well-drilled soldiers. Every soldier is doing the same thing at the same time, and it is very much easier to see (or hear) from a distance what that is. The physics analogy is that a normal system is like the market day crowd—every atom is doing something different—whereas in a Bose-condensed system the atoms (or, more accurately, the fraction of them which is condensed at the temperature in question) are all forced to be in the same quantum state, and therefore resemble the well-drilled soldiers: "every atom must do exactly the same thing at the same time."

The necessary conditions for condensation have been studied by Lev Landau, who distinguished between Bose superfluids and Fermi superfluids. It should be noticed that even for Fermi superfluids, like superconductors, the phenomenon of bosonic condensates still occurs; in this case the condensate consists of *Cooper pairs*, which brings us to the third of the physical concepts that we set out to introduce with simple examples. In this case Salam chose another analogy from the work of Goodstein:¹⁰

Imagine two people on an old sagging, nonlinear mattress. They tend to roll toward the middle, even if they don't like each other. That is, there is an attractive interaction. The cause of this interaction is that the people create distortions in the mattress, and the distortions try to merge. The electrons in the metal do not stand still but rather zip through the lattice at something like the Fermi velocity. The ions are attracted to the electrons but, owing to their large mass, move very slowly compared to the much lighter electrons. By the time the ions respond the electron is long gone, but it has, in effect, left behind a trail of positive charge, which is the lattice distortion we mentioned above. Another electron, transversing the same path, would find that its way has been prepared with the positive charge it finds so attractive. We can imagine that the first electron created a phonon, which the second happily absorbs. Notice that the interaction is strongest if the two electrons (i.e., the Cooper pair) traverse exactly the same path—that is, if they have, say, equal and opposite momenta.

ALTERATIONS IN THE CHEMISTRY OF CHIRAL MOLECULES DUE TO THE PARITY-VIOLATING NEUTRAL WEAK INTERACTIONS

The above three physical concepts—cooperative phenomena, condensation, and (Cooper) pairing—have led Salam, with arguments developed in considerable detail, to suggest that the electromagnetic force is not the only force which can produce chemical effects: The Z^0 component of the electroweak force, in spite of the fact that its effects appear to be negligible at low temperatures, may play an active role in chemistry.

The reasons for the proposed chemical role of the parity-violating weak interactions may be found in some calculations in quantum chemistry.¹⁶ The results of these calculations indicate that four amino acids, for which calculations have been completed, taken in aqueous zwitterionic conformation, are L-stabilized relative to their D-partners for configurations in aqueous media (the above-mentioned amino acids are alanine, valine, serine, and aspartic acid). This stability affects 1 out of 10^{17} molecules at room temperature, since

$$10^{-17} \approx (3 \times 10^{-19} \text{ eV} / 300 \text{ K } k_B),$$

a small quantity that has deterred many chemists from accepting the effects of the electroweak interactions as a possible source of optical symmetry; nevertheless, in Salam's most recent calculation²¹ new work has been reported on the proposed phase transition, in which he has found sufficiently large effects by the inclusion of the top quark (t) and top antiquark (\bar{t}) in an enlarged version of the standard theory. He has also found evidence for the extinction of further macroscopic quantum mechanical effects below T_c , such as the value of the critical magnetic field H for the Meissner effect, which becomes extinct for temperatures above T_c . He finds that the phenomena of polarization will occur, as explained in the recent paper. For temperatures below T_c he finds no evidence for polarization (since $\mathbf{H} = \mathbf{0}$ and, therefore, $\mathbf{H} \cdot \mathbf{E} = \mathbf{0}$ inside the specimen, where \mathbf{E} denotes the electric field).

In modelling the phase transition Salam used the condensate wave function as $\omega_D \exp(-2/gv)$, where ω_D is the Debye energy, p_F stands for the Fermi momentum, while g is the effective 4-Fermi coupling parameter for electrons and v is given by the expression $(p_F m/\pi^2)$. The approximation $gv \approx 1$ is important in the postulated phase transition. This needs justification. We now understand this approximation as follows (Salam, private communication): The g parameter contains the term $1/m_x^2$, so there must be a large mass coming in the picture in order to cancel m_x^2 . This mass can only be $t\bar{t}$, or due to the supersymmetry partners of the old quarks and old mesons being heavier than the original ones by m_x^2 , where $m_x \approx 1 \text{ TeV}$. To sum up, Salam now believes that the approximate equality $m_x^2 \approx (1 \text{ TeV})^2$ is responsible for the very important approximation $gv \approx 1$.

POSSIBLE SCENARIOS FOR THE ORIGIN OF BIOCHIRALITY

An important aspect of the origin of biological chirality concerns the thermal conditions that may have existed in the Hadean Earth, when presumably the presently observed handedness of amino acids originated. Since the ambient temperature of the Earth's surface is approximately 300 K, if T_c is much smaller than this temperature, Salam's theory may not apply to the Earth, in which case at least three scenarios may be possible:

1. Presolar contributions may be necessary to get low enough temperatures.
2. Major contributions come from the more distant and cooler parts of the solar system with ambient temperatures less than T_c (typically all the outer planets have temperatures smaller than liquid nitrogen).
3. If T_c is found to be considerably less than 300 K, one would be led to accept that the Earth only acted as a junction place where L-amino acids came together with D-sugars and nucleotides, in a (field theoretic) self-consistent fashion, so as to give rise to early replication.

Salam feels that for the biotic alternative to prevail, it may be necessary to invoke a mechanism for delivering to the Earth the constituents of the biomolecules from the cooler locations (1) and (2). It may be reasonable to assume the following:^{4,19}

The Earth did accrete prebiotic organic molecules important for the origin of life from impacts from carbonaceous asteroids

and comets during the period of heavy bombardment in the Hadean Earth.

Remarkably, we may also assume that the alanine molecules, for instance, could withstand temperatures as high as about 700 K for 1 sec, whereas the other amino acids could withstand temperatures in the range 600 to 800 K for a similar period of time, and remain stable and intact upon impact with the Earth.

CAN PHASE TRANSITIONS OCCUR IN THE MOLECULES OF THE LIVING CELL?

The Occurrence of Phase Transitions Is Possible in Biochemistry and in Genetics

Perhaps one of the deepest questions raised by Salam is whether phase transitions of the type of Bose condensation may occur in the living cell. To a certain extent the answer must be positive, since we may recall that in the case of certain specific macromolecules relevant to living processes, this subject has been studied in both biochemistry as well as in genetics during the last 30 years.

In biochemistry, the ability of lipids to adopt a variety of phases is well documented.¹⁴ This has been called lipid polymorphism; an important aspect of this topic is that the macroscopic structure adopted by lipids depends on the experimental conditions; for instance, temperature is an important parameter which determines the macroscopic structure of hydrated membrane lipids.⁶ At present a conservative position is still that the possible biological significance of some of the polymorphic membrane transitions is striking, but we have not yet bridged the gap between these transitions and physiological phenomena.¹⁴

On the other hand, evidence for phase transitions in the life sciences is not limited to biochemistry, but a separate line of research in genetics also suggests the occurrence of phase transitions: A factor that may influence the onset of DNA replication is intracellular ion concentration.^{8,15} In fact, experiments with rat liver-cell nuclei may indicate that chromatin structure and nuclear volume display abrupt transitions as a function of ion concentration in the nuclear environment.¹⁸ This experiment has suggested to its authors that the chromatin structural changes may be discussed in terms of phase transitions.

Experimental Tests of the Possible Occurrence of the Superconducting-Like Phase Transition in Amino Acids

These results from the biochemistry of the cell membrane and from the genetics of chromatin structure lead us naturally to raise the question: What direct evidence is there for a clear hallmark of the phase transition underlying the origin of chirality?

Salam's paper provides a sample of alternatives:

1. Melanin—a dark brown pigment of many animals—is the product of tyrosine metabolism. It is often located in melanosomes (cells with permanent radiating processes lying superficially in vertebrates). Data taken from natural melanins, as well as from melanosomes isolated from human melanoma, clearly indicate that it undergoes a phase transition. In fact, its heat capacity shows a discontinuity near 1.9 K. This anomaly, though relatively small, is significant beyond the scatter of the data points. It is probably associated with a magnetic transi-

tion possibly from paramagnetism to antiferromagnetism.¹⁷ In an analogous manner, a means of detecting the putative phase transition may be by measuring differences of specific heats and looking for anomalies in the curve $C = \gamma T + \beta T^3 + \dots$ as has already done for the above-mentioned non-amino acids.

2. One direct means of testing the new theory for the origin of chirality in amino acids is by taking a 50–50 racemic mixture of crystalline L- and D-amino acids and lowering the temperature. Salam has discussed extensively an experiment involving a 50–50 racemic mixture subjected to a temperature gradient ranging from the melting temperature for the amino acids to the absolute zero temperature. In Figure 1 we have illustrated the Salam picture for the evolution of the D/L ratio.

3. In view of the discovery of organic superconductors with critical temperatures similar to metals and alloys (cf. below), an alternative experimental procedure may be to test directly for conductivity and magnetic (Meissner effect) properties of amino acid crystals.

The suggestion has been made that a superconducting-like phase transition may actually occur in amino acids. Physics has been rather slow in studying alternative candidates for superconductors. The first class of (low-temperature) superconductors was discovered in 1911; these early superconductors were unlike any form of matter that occurs in living systems. In fact, they were metals and alloys. The discovery of a radically new class of superconductors had to wait some time. In 1986 a more interesting superconductor from the point of view of chemistry was identified in certain ceramics. Finally, this year, the simple potassium-doped fullerene K_3C_{60} ¹² has been shown to be superconducting with a reasonably high critical temperature, i.e., the onset of the critical temperature is 18 K.

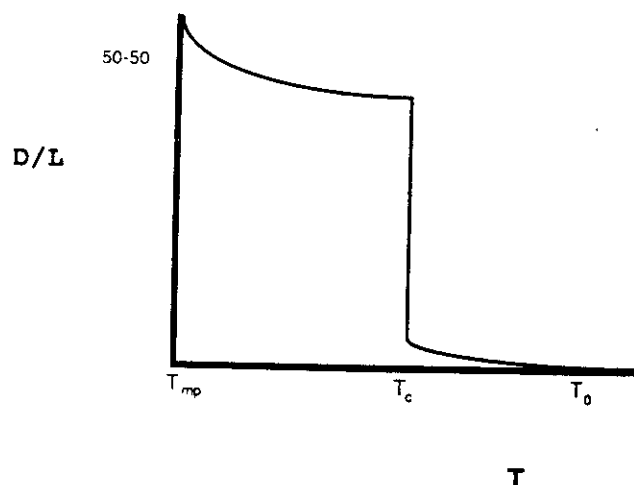


Fig. 1. Evolution of the D/L parameter in the Salam picture for an experiment involving a 50–50 racemic mixture subjected to a temperature gradient. The temperature T ranges from the melting temperature (i.e., melting point) for the amino acids (T_{mp}) to the absolute zero temperature ($T_0 = 0$ K). Here T_c denotes the critical temperature for the phase transition. The part of the curve from the melting point to the critical temperature has been conjectured in analogy with Atkins' semiclassical treatment of ferromagnetism; this is not in disagreement with the expectation of Bada and Miller² that with increasing temperature the D/L ratio increases (as it does in the tail from T_0 to T_c). The phase transition has not been assumed to be of the "reentry" type, as it may happen in some superconductors, in which case the phase transition may occur only in a thermal range defined by two critical temperatures.

However, we should recall that organic superconductors have been known for some time, such as graphitic compounds with typical formulae C_8A ($A = K, Rb, Cs$) with values of T_c smaller than 1 K;¹¹ another example is that of the organic superconducting metal bis(ethylene dithio)tetrafulvalene triiodide with formula $(C_{10}H_8S_8)_2 I_3$ ²³ with a value of $T_c \approx 1.5$ K at normal pressure. Hence, the discovery of the most recent superconductor, K_3C_{60} in a simple organic compound of relatively high critical temperature, if confirmed in many laboratories, would be yet another small step in the direction anticipated by those of us who have maintained that superconductivity, or superfluidity-like effects may occur in biology.

DISCUSSION AND CONCLUSIONS

The relevance of testing Salam's rationalization of the origin of chirality cannot be overemphasized. Some of the same experiments that may test his original theory for the origin of amino acid chirality are indeed experiments which suggest searching for superconductivity-like effects in one of the main carbon-based molecules constituting the living cell, namely, amino acids; earlier, this possibility was also raised for nucleic acids, as previously pointed out regarding the origin of evolution.³

To sum up, one way to interpret Salam's contribution is as a proposal for a solid-state candidate for a superconductivity-like phenomenon in a novel class of organic molecules, namely, the amino acids.

The essence of the analogy used by the author is that the "superfluidity" exhibited by amino acids is to "superfluidity" in superconductors and not to liquid helium. In the case of superconductivity, one has to apply an external magnetic field and look for the Meissner effect to determine T_c ; likewise, the "superfluidity" of amino acids may, in principle, be measured by shining external light sources on these molecules. The calculation of critical temperatures in terms of an electroweak lagrangian including the top quark, as mentioned above, may serve to restrict the value of the critical temperature from the wide range of the ambient temperature of outer space and the dissociation temperature for amino acids. However, in view of the considerable theoretical difficulties still to be overcome, perhaps the best way to determine T_c may be by means of the experiments suggested above, or by other experiments that may have escaped our attention.

ACKNOWLEDGMENTS

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Is the Salam Phase Transition Relevant to the Causal Origin of Homochirality⁽⁺⁾ ?

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Abstract. From the point of view of (a) chemical evolution and (b) exobiology (the origin of life in the universe), we discuss the possibility that phase transitions of the type postulated by Salam in 1991 to occur in a racemic mixture of amino acids, may play instead the role of an amplification mechanism in the novel context of chirally-pure samples of amino acids. Salam's seminal contribution referred to the role of phase transitions in the induction of the observed homochirality of protein amino acids. This was assumed to occur in a racemic mixture that, as a consequence of the conjectured phase transition, turned homochiral beneath a certain critical temperature T_c . In the present review we discuss selected theoretical aspects of the question of homochirality. The relevance of starting a new generation of experiments is pointed out, as suggested by the present author in 1991 [1]. These experiments should test a form of condensed matter that has so far not been at the forefront of research from the point of view of the phase transitions. We discuss those aspects of the origin of homochirality which are still valid and require verification.

1. Introduction

1.1. Chemical Evolution and the Origin and Evolution of Life

The preliminary questions that are raised when we attempt to lay the scientific bases of the origin of life are: Where did the biomolecules come from? Were they synthesized on Earth or, is there a need to study this problem in the context of exobiology (i.e., within a systematic search for life beyond the Earth)? In order to gain some insights into these fundamental questions it is important to recognise molecular relics of earlier stages of chemical and biological evolution. This review is devoted to one of the most important relics amongst them, but we should beware from the beginning about the broad spectrum of conditions in which biomolecules can present themselves in the universe. Although the extensive searches for extraterrestrial intelligence (SETI) have not been rewarded with a positive result, in spite of the enormous progress in the equipment used in the Project Phoenix [2], interstellar organic molecules have in fact been detected by microwave and infrared techniques since 1969. (Prior to that date it was known that simple carbon compounds such as C_2 and CO were formed in the atmospheres of relatively cool stars). Now we are aware of the existence of interstellar ammonia, water, formaldehyde and hydrogen cyanide. Altogether about one hundred molecules have been identified, about 75%

are organic [3]. These discoveries have made the conjecture of Oro more plausible [4], namely, that comets may have been relevant in the formation of biochemical compounds on the primitive Earth. From the old studies of the Alais meteorite in 1834, to the extensive studies of the meteorite that fell in Murchinson, Victoria (Australia) on September 28, 1969, important information about possible sources of life on Earth has been gathering. The Laboratory of Chemical Evolution (LCE) of the University of Maryland was directed by Ponnamperna until his death in 1994. It played an important role in analyzing the Murchison meteorite, at a time when LCE was preparing to receive the first Moon samples [5]. The results of that investigation have an important bearing on the biochemical relic that we shall discuss presently (cf., Sec. 2.2').

1.2. Chemical and Atmospheric Evolution in the Solar System

In the early Earth atmosphere the most abundant element, hydrogen, may have combined with carbon to form methane (CH_4), with oxygen to form water (H_2O), and with nitrogen to form ammonia (NH_3). In such an environment, under the influence of an abundant source of energy, Calvin and co-workers were able to synthesize (in a model of a paleoatmosphere consisting of carbon dioxide, water and molecular hydrogen) some

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organic molecules including formaldehyde, which is relevant in the synthesis of sugars (ribose) and glycerol (cf. Sec. 2.1). Other significant successes were the synthesis of amino acids [6], nucleotides [7,8]. Another early success was the synthesis of protenoids by thermal heat in possible primitive Earth conditions [9]. In other words, all the basic building blocks of life can, in principle, be synthesized in the laboratory. The question of how such synthesis may have occurred in the early Solar System is not an idle one:

Firstly, four satellites with atmospheres resembling the Earth's paleoatmosphere exist in the Solar System. Io is the first (closest) of the Galilean satellites of Jupiter (which has altogether 16 satellites). Io has a thin atmosphere of sulphur dioxide. The second Jovian moon, and the smallest of the Galilean satellites) Europa has some oxygen in its atmosphere [10]. Titan, perhaps the most intriguing component of the Solar System (cf. below), is a satellite of Saturn. It is surrounded by mainly molecular nitrogen atmosphere, but there is also a substantial component of methane. Finally, the last satellite known to have an atmosphere is Triton, the largest of the eight known moons of Neptune. It has a tenuous atmosphere with surface pressure of 15 microbars, mainly of nitrogen but with a trace of methane. It is remarkable that one of the components of the model paleoatmospheres of the chemical evolution experiments (ammonia) does not seem to be present in appreciable quantities in any of the satellites that have an atmosphere.

Secondly, chemical evolution is turning into an important chapter of the space sciences. This development may be illustrated with the questions raised by current studies of Titan. In the atmosphere of this satellite, the largest of Saturn's 18 confirmed satellites (bigger than even Mercury), biopolymers may possibly arise in this planet-like satellite. Indeed, under the action of sunlight it is possible that there may be liquid bodies of mixtures of ethane or methane on its surface. The Cassini-Huygens mission, under preparation at present, will attempt to obtain more reliable information on Titan. It includes a spacecraft (Cassini, built by NASA) bearing the atmospheric probe Huygens (built by the European Space Agency). The mission is due for launch in October, 1997 [11].

1.3. Chemical Evolution in the Early Earth Atmosphere

Chemical evolution on Earth seems to have taken place from 4.6-3.9 thousand million years before the present (Gyr bp), a geologic time interval which is known as the Hadean subera within the Archean era. It should be noticed, however, that considering the impacts by large asteroids in the early Earth does not

necessarily exclude the possibility that the period of chemical evolution may have been considerably shorter. Indeed, the Earth may have been continuously habitable by non-photosynthetic ecosystems from a very remote date, namely since approximately 4.44 Gyr bp [12]. In subsequent suberas of the Archean (3.9-2.5 Gyr bp) life, as we know it, certainly was present. This is well represented by fossils of the domain bacteria, which is particularly well documented by many species of the phylum Cyanobacteria [13].

Once again, it should be kept in mind that the content and the ratios of the two long-lived isotopes of reduced organic carbon in some of the earliest sediments (retrieved from the Isua peninsula, Greenland, some 3.8 Gyr bp), may convey a signal of biological carbon fixation [14]. This reinforces the expectation that chemical evolution may have occurred in a brief fraction of the Hadean subera, in spite of the considerable destructive potential of large asteroid impacts during the same geologic interval in all the terrestrial planets, as well as on the Moon.

2. The Search for the Origin of Homochirality

2.1. What is Homochirality?

This broad knowledge of early life has allowed a search for relics that may show the common thread of evolution from our last common ancestor. At the beginning of the 1990s Abdus Salam's deep interest in the role of asymmetry in the living state gave a strong impulse to the topic of the asymmetry of the biomolecules [15,1].

The first unifying principle in biochemistry [16] is that the key biomolecules have the same handedness: this phenomenon occurs when molecules are asymmetric, in such a manner that they are able to exist in two configurations, both partners (isomers) being mirror images of each other. These two possibilities are referred to, according to the response of a mixture of them to the incidence of a plane-polarized light. More precisely, the angle α through which the plane of polarization is rotated can be given a sign as follows: when looking towards the incoming beam of light, for a clockwise rotation of α , we would assign the term right-handed or dextrorotatory (D); if such a rotation is anticlockwise we say that the rotation is 'left-handed', or laevorotatory (L).

Molecules that respond to beams of light in the above-mentioned manner are said to be optically active. Examples of single-handed biomolecules that will concern us in this review are the monomers of proteins, which are only L-amino acids, while the ribose and 2-deoxyribose monomers of the nucleic acids are all in

the D-configuration. Phospholipids are no exception. These are biomolecules of the cell membrane having a phosphate group and one or more fatty acids. Indeed, the plasma membrane of the organisms of the domains bacteria and Eukarya contain exclusively D-glycerol [17].

Thus, the key biomolecules have the same handedness, or, we say more often that biomolecules have the same 'chirality or, preferably that they are homochiral'. (These words are taken from the Greek language, as *cheir* means hand.) Finally, an equimolar mixture of both isomers is called a racemic mixture. Chiral molecules have non-superposable D, or L three-dimensional mirror image structures or enantiomers' (once again, these are words derived from the Greek *enantios morphe*, whose meaning is 'opposite shape').

It is important to distinguish between the truly chiral influences (such as the electroweak interaction, cf., Sec. 2.3), from other physical effects that have been proposed since Pasteur's famous resolution of tartaric acid crystals. (These are crystalline naturally occurring carboxylic acids, with melting point of 170C, which Pasteur showed to be optically active). In fact, Barron defines a truly chiral system, as one in which there are two enantiomers that may be interconverted by space inversion, but not by time reversal [18]. Optical rotation changes its sign under parity reversal, but not under time reversal, therefore satisfying Barron's criterion. The electroweak interactions provide an example of a truly chiral influence, and for this reason in this review we shall restrict our attention to this elementary interaction (cf., Sec. 2.3).

However, under kinetic control irreversibility destroys T-invariance, a situation which allows further possibilities in the context of the life sciences, since life itself is to be understood as a non-equilibrium phenomenon.

Homochirality is valid for all organisms, but some care must be taken with the concept of homochirality as we consider the highest taxa:

- 2.1.1. Exceptionally, in the domain Bacteria (encompassing thermotogales, the flavobacteria and relatives, the cyanobacteria, the purple bacteria, the Gram-positive bacteria, and the green nonsulfur bacteria) cell walls may contain D-amino acids, as in the case of *Bacillus brevis* or *Lactobacillus arabinosus*.
- 2.1.2. A second exception concerns another one of the three highest taxa, the domain Archaea encompassing the kingdoms Crenarchaeota (which, for instance, includes the genus *Pyrodictium* and the genus *Thermoproteus*) and

Euryarchaeota (for instance, the extreme halophiles and archaeobacteria capable of producing methane as a byproduct of the reduction of carbon dioxide). Organisms in this domain contain L-glycerol in their membrane phospholipids, instead of the standard D-glycerol, as we mentioned above, which is characteristic of the phospholipids of the cellular membranes of the other two domains, Eukarya (the animals, the ciliates, the green plants, the fungi, the flagellates and the microsporidia) and Bacteria.

2.2. *Is the Origin of Homochirality Extraterrestrial?*

The property of homochirality is particularly relevant in the identification of microorganisms for the in situ search for extraterrestrial homochirality (SETH). This recent research proposal may eventually be implemented by means of an apparatus denominated the 'SETH cigar' [19]. The most useful physical techniques that may be used in this context are circular dichroism (CD) and optical rotatory dispersion (ORD, the functional relationship between the angle of rotation and the wavelength of the polarized light). Normally these techniques imply equipment that is too bulky. Both techniques, CD and ORD may allow the determination of the sign and magnitude of the optical rotation to be measured, as well as the identity of the putative homochiral molecule.

MacDermott and Tranter propose instead to miniaturize the equipment by just restricting the search to the optical rotation that would be produced by a chiral molecule. Their idea is based on the property of some crystals (dichroism) of being able to absorb selectively light vibrations in one plane, but allowing the vibrations at right angles to go through. Two polarized films at right angles are introduced in the presence of small electronic devices consisting of regions (p-n junctions) in which on semiconductors are present on either side, so that their conductivity is due to the flow of electrons ('n-type') and mobile holes ('p-type'), respectively. This device is called a light-emitting diode. In addition, a detector is used, which consists of a semiconductor diode that produces a significant photocurrent when illuminated (photodiode). With this arrangement no light should reach the detector unless the plane of polarization is rotated. In this manner racemic mixtures will not be capable of allowing light to reach the detector. Hence a signal in the detector is certain proof that the sample tested is homochiral.

Homochirality may be considered as a signature for life anywhere in the universe. Due to the progress in

research and the availability of a whole series of forthcoming space missions (towards the end of this decade and the beginning of the next), the problem of chemical evolution has been virtually transferred from the laboratories of organic chemistry to the space sciences.

In this context we may recall the intriguing ideas of sonner and Greenberg. These authors suggest, independently, that circularly polarized light from neutron stars on passing clouds of interstellar dust may selectively eliminate one or the other enantiomer in the dust mantle, if mirror image molecules are originally present [20,21]. Another possible astrophysical source of homochirality may be the supernovas, according to some recent work [22]. We may state in general that living systems translate their genes, following the rules of the genetic code, into proteins composed of relatively a small number of L-amino acids. The strength of this statement may be illustrated with the discovery that out of the 74 amino acids that were found in the Murchison meteorite (cf., Sec. 1.1), only 55 have been found in extraterrestrial samples and none of them has been shown conclusively to have a chiral bias [23]. These numbers give us considerable insights, when we recall that the protein monomers are chosen from a very restricted set of twenty amino acids.

2.3. Homochirality and the Electroweak Interaction

The search for the origin of homochirality from the point of view of the effects of the weak interactions started in the 1950s. This has led to the proposal of various mechanisms that have been postulated in order to account for homochirality. Amongst them we should recall the differential decomposition and resolution of enantiomers under beta-irradiation (the Vester-Ulbricht hypothesis). The experimental confirmation of this theoretical conjecture has been much discussed over the last three decades [24]. More ingenious mechanisms have been recently postulated, such as the possible relevance of molecular decay in the origin of homochirality [25].

In the standard model of Glashow, Salam and Weinberg, the electroweak interactions arise by the exchange of photons, massive charged W^+ and neutral Z^0 bosons of spin 1 between quarks (u,d,s,c,b,t) and leptons (electron, muon, the tau particle and three types, or 'flavours', of neutrinos). Within the framework of this model, a substantial body of previous work has suggested the parity-violating electroweak neutral current (mediated by the Z^0 boson) as the main physical force inducing the observed homochirality [26]. Neutral current weak interactions are predicted to induce small energy differences, equal in magnitude

but opposite in sign between the enantiomers. Such a 'parity-violating energy' difference between the enantiomers (twice the small induced energy difference in each enantiomer) may induce energy shifts to both enantiomers, which in spite of being small effects they are, nevertheless, subject to calculation as well as to the eventual effect of amplification mechanisms [27]. We shall return to this topic more fully in Sec. 5.1.

Salams approach (1991) also invoked the electroweak interaction, but was original in appealing to further physical concepts that may apply during chemical evolution. He pointed out a particular cooperative phenomenon that may have taken place, namely, a phase transition beneath a certain critical temperature T_c . Amino acids that had been synthesized earlier from various precursors entered into a new phase assumed to be a Bose condensed mode.

These concepts: cooperative phenomena and condensation led to the suggestion that the electromagnetic force is not the only force producing chemical effects. The Z^0 component of the electroweak force, in spite of the fact that its effects appear to be negligible at low energies, may play an active role in biochemistry. The reasons for the proposed chemical role of the parity-violating weak interactions may be found in quantum chemistry calculations (QCCs) of, amongst others, Mason, MacDermott and Tranter [28] and, independently, by Bakasov, Ha and Quack [29]. We refer the reader to the reviews of Bonner [20], Cline [22] and Keszthelyi [26] and for a comprehensive list of earlier references.

These calculations indicate that four amino acids, for which results have been obtained, are L-stabilized relative to their D-partners for configurations in aqueous media. (The above mentioned amino acids are alanine, valine, serine, and aspartic acid.) Although the result of the calculations give only a small energy shift in the ground state energies of the L- and D-amino acids, nevertheless, in the conjectured phase transition, sufficiently large effects may still have to be taken into account, such as the inclusion of the top quark (t) and its antiparticle, in an enlarged version of the standard model [1].

2.4. Physical Criteria for the Genesis of Homochirality

An important aspect of the origin of homochirality concerns the thermal conditions that may have existed at 'a time when chemical evolution took place. Although the geological record is unknown on Earth, as metamorphism has destroyed all evidence, the corresponding period in Moon stratigraphy is well documented (the Nectarian, 4.2-3.8 Gyr bp), when presumably the presently observed homochirality of

amino acids originated on the Earth-bound biomolecules. Solid evidence of the heavy bombardment period is known from the rocks retrieved by the Apollo missions. (Even samples from the pre-Nectarian period are known, as the Apollo 17 mission succeeded in retrieving a dunite-an intrusive igneous rock of ultramafic chemistry - some 4.4 Gyr bp.)

Since the ambient temperature of the Earth's surface is approximately 300K, if T_c is much smaller than this temperature, Salam's theory may not apply to the Earth, in which case some options are still open:

- 2.4.1. Pre-solar contributions may be necessary to get low enough temperatures. We may assume that such contributions may have arisen from a molecular cloud of dust and gas (predominantly in molecular form) out of which the Solar System originated. Since over seventy organic molecules have been detected in the last 25 years (cf., Sec. 1.1), it is possible that the effects that we are discussing in this review may have taken place in amino acids at a time prior to the formation of the Solar System. In those early stages the temperatures may indeed have been low enough (possibly in the range 10-20K, as in current small molecular clouds).
- 2.4.2. Major contributions come from the outer Solar System with ambient temperatures less than T_c . (For instance, the surface temperature of Uranus, which is some three billion km from the Sun, is well below -200C, a temperature in which both methane and nitrogen condense.) In the heavy-bombardment period (i.e., prior to about 3.8 Gyr bp) the Earth and Mars, for instance, may have exchanged matter and if life originated in Mars first, it is conceivable that it may have been transferred to the early Earth. So the assumption that chemical evolution of the Earth biomolecules may have been influenced by interplanetary exchange of chemicals cannot be ruled out.
- 2.4.3. If T_c is found to be considerably less than 300K, one would be led to accept that the Earth only acted as a junction place, where L-amino acids came together with D-sugars, so as to give rise to early replication. This option is in agreement with the Oro hypothesis (cf., Sec. 1.1).

It may be reasonable to assume that the Earth did accrete prebiotic organic molecules important for the origin of life from impacts from carbonaceous asteroids and comets during the period of heavy bombardment in the Hadean Earth [30]. Remarkably, we may also assume that the alanine molecules, for instance, could withstand temperatures as high as about 700K for one second, whereas the other amino acids could withstand temperatures in the range 600 to 800K for a similar period of time, and remain stable and intact upon impact with the Earth.

Another physical question is whether phase transitions of the type of Bose condensation may occur in the living cell. We may recall that in the case of certain specific macromolecules relevant to living processes, this subject has been studied in both biochemistry, as well as in genetics, during the last thirty years.

In biochemistry, the ability of lipids to adopt a variety of phases is well documented [31,32]. This has been called lipid polymorphism: an important aspect of this topic is that the macroscopic structure adopted by lipids depends on the experimental conditions; for instance, temperature is an important parameter which determines the macroscopic structure of hydrated membrane lipids [33]. At present a conservative position is still that the possible biological significance of some of the polymorphic membrane transitions is striking, but we have not yet bridged the gap between these transitions and physiological phenomena.

On the other hand, evidence for phase transitions in the life sciences is not limited to biochemistry, but a separate line of research in genetics also suggests the occurrence of phase transitions in the living state: A factor that may influence the onset of DNA replication is intracellular ion concentration [34,35]. In fact, experiments with rat liver-cell nuclei may indicate that chromatin structure and nuclear volume display abrupt transitions as function of ion concentration in the nuclear environment [36]; this experiment has suggested to its authors that the chromatin structural changes may be discussed in terms of phase transitions.

The phenomenon being proposed may be thought of as a quantum mechanical enhancing factor in molecular evolution from the initial racemic mixture to the present day chiral amino acids. The concept of condensation is not new in biology; indeed, it goes back some 30 years [37]. In the context of the origin of life condensation in the nucleic acids had already been suggested to have played a role in the origin of Darwinian evolution [38].

3. Experimental Tests of the Putative Superconducting-Like Phase Transition in Amino Acids.

3.1. *What Direct Evidence is there for a Clear Hallmark of a Phase Transition that may Underly the Origin of Homochirality?*

These results from the biochemistry of the cell membrane and from the genetics of chromatin structure lead us naturally to raise the question: What direct evidence is there for a clear hallmark of the phase transition underlying the origin of chirality? There are some alternatives: 3.1.1. Melanin- a dark brown pigment of many animals- is the product of tyrosine metabolism, which causes pigmentation of eyes, skin and hair in vertebrates. It is often located in melanophores (cells with permanent radiating processes lying superficially in vertebrates). Data taken from natural melanins, as well as from melanosomes isolated from human melanoma, may indicate that it undergoes a phase transition. In fact, its heat capacity shows a discontinuity near 1.9K. This anomaly, though relatively small, is significant beyond the scatter of the data points. It is probably associated with a magnetic transition, possibly from paramagnetism to antiferromagnetism [39]. In an analogous manner, a means of detecting the putative phase transition may be by measuring differences of specific heats and looking for anomalies in the curve for specific heat (a cubic polynomial) as has already been done for the above-mentioned non-amino acids.

3.1.2 One direct means of testing the new theory for the origin of chirality in amino acids is by taking a 50-50 racemic mixture of crystalline L- and D-amino acids and lowering the temperature. Salam has discussed extensively an experiment involving a 50-50 racemic mixture subjected to a temperature gradient ranging from the melting temperature for the amino acids to the absolute zero temperature.

3.1.3. In view of the discovery of organic superconductors with critical temperatures similar to metals and alloys, an alternative experimental procedure may be to test directly for conductivity and magnetic (Meissner effect) properties of amino acid crystals.

3.2. *Phase Transitions in Organic Materials*

The suggestion has been made that a superconducting-like phase transition may actually occur in amino acids. Physics has been rather slow in studying alternative candidates for superconductors. The first class of (low-temperature) superconductors was discovered in 1911; these early superconductors were unlike any form of matter that occurs in living systems. In fact, they were metals and alloys. The discovery of a radically new class of superconductors had to wait some time. In 1986 a more interesting superconductor from the point of view of chemistry was identified in certain ceramics.

The simple potassium-doped fullerene [40] has been shown to be superconducting with a reasonably high critical temperature i.e., the onset of the critical temperature is 18K. However, we should recall that organic superconductors have been known for some time, such as graphitic compounds with typical formulae C_8A ($A = K, Rb, Cs$) with values of T smaller than 1K [41].

Another example is that of the organic superconducting metal bis(ethylene dithiolo) tetrathiofulvalene triiodide with formula $(C_{10}H_8S_8)_2 I_3$ [42] with a value of T_c 1.5K at normal pressure. Hence, the most we can say at present is that superconductivity-, or superfluidity-like effects may not be excluded from organic materials. This suggests to extend the search for quantum liquid behaviour observed in the organic materials to a particular form of organic materials, namely, amino acid crystals. This point will be discussed further in Sec. 5.5.

3.3. *Biomolecular Relics of Evolution*

The search for physical mechanisms underlying the causal origin of homochirality are mainly motivated by the fact that the most characteristic of all relics of evolution is provided by the chiral nature of the biomolecules.

Other relics, however, are known. This may be illustrated with the widespread use of the standard genetic code by a very large number of organisms. (Exceptionally some protozoans and Mycoplasma use a modified code.)

The general question of whether it is possible for further relics of the earliest stages of evolution to have survived till the present has been raised in the past by various authors. Some well known examples are certain nucleotide sequences (introns) in genes of mainly eukaryotic organisms; they do not code for the gene product (neither proteins nor nucleic acids). The presumed antiquity of these sequences is based on

the finding that some introns are ancient [43]. More recently, the question of further molecular relics from one of the earliest stages of the evolution of life on Earth (the RNA world) has been raised in the context of the origin of RNA plant pathogens, such as the viroids [44]. The relevance of this putative relic has been discussed recently [45].

Inserted in this broad range of problems regarding biomolecular relics, the all-important question of homochirality of amino acids as an evolutionary relic has been recently reviewed, particularly from the point of view of experiments [46,26,22], while the relevance of chirality in biology has also been discussed extensively in an excellent review [47].

The continued efforts to come to terms with the experimental question of Salam's two conjectures (cf., Sec. 5.3 below), have not been completed so far, but these set of experiments [48,49,50,51] are, nevertheless, illuminating an area of condensed matter physics which has so far not been extensively studied, and which potentially may be of wider interest than strictly within the domain of chemical evolution and the origin of life.

The preliminary tests of Wang and co-workers in Beijing (1995) have faced the first part of the task (to test for the specific heat curves; these experiments await confirmation and should be repeated), but the complementary magnetic properties should also be urgently explored and tested by independent groups. The intrinsic importance of testing new materials for the key technologies of the future should be emphasized, as technological innovation should not stop at ceramics, which already produced the revolution of the high TC superconductors in 1986 [52], but biological materials should be thoroughly discussed and tested, as we already emphasized in our earlier paper [1].

4. Asymmetric Adsorption of Amino Acid at Crystal Surfaces

4.1. *L*-Amino Acids may be Adsorbed on *L*-Quartz Crystals

There is a long history of experimental efforts with inorganic substances which have the ability to rotate the plane of polarization of light passing through a crystal (cf., Sec. 2.1). This ability is due to their chiral crystal structure. In this respect quartz, the most common of the six polymorphs of crystalline silica (SiO_2) is found in nature in the form of well defined enantiomorphic crystals, in which chirality is caused

by the spiral structure of linked silicon-oxygen tetrahedra.

Quartz, therefore, is an obvious candidate for the stereoselective adsorption of a given enantiomer from a racemic mixture. A long series of experiments has led to the conclusion that asymmetric adsorption on quartz is a well authenticated phenomenon, but it is also equally clear that in this process, quartz acts merely as a passive filter of homochiral domains, passive in the sense that quartz itself does not induce any catalytic process that may convert racemic or achiral reactants into optically active products [20].

Asymmetric adsorption of amino acids at the surface of chiral crystals is a possible physical mechanism that may have led to the onset of homochirality in one class of biomolecules. It is well documented that about one per cent more *L*-amino acids than *D*-amino acids are adsorbed on *L*-quartz crystals [53].

This experimental fact may be taken together with the theoretical work that has shown that due to the effect of the weak interactions, *L*-amino acids (and similarly, *D*-sugars) have smaller ground-state energy than their corresponding enantiomers, a property that has been shown by independent QCCs (cf., Sec. 2.3). The experiments on the stereoselective adsorption of amino acid enantiomers on the surface of either *D*-quartz or *L*-quartz suggest (together with the QCCs) that *L*-amino acids (which may be adsorbed in the surface of *L*-quartz) may serve as a reservoir of chirally-pure samples. Some amplification mechanism may have acted on, so as to enhance the small chiral bias that the QCCs suggest in favour of *L*-amino acids.

The analogous *D*-amino acids (that may be similarly adsorbed by the surface of *D*-quartz), presumably may not have benefitted from the small advantage due to the weak interactions in favour of the *L*-amino acids. Hence, it is forced upon us to discuss possible physical mechanisms that while acting on both *L*- and *D*-amino acid crystals may, nevertheless, act as amplification mechanisms on chirally-pure samples.

4.2. *The Possible Relevance of Quartz In Chemical Evolution*

The abundance of quartz and its presence in a variety of conditions typical of the Archean eon, militate in favour of the possibility that quartz may have provided early chirally-pure environments for amino acids.

We shall consider a few arguments that favour a physical mechanism in which *L*-quartz is the first step in the pathway that leads to the observed homochirality

of protein amino acids; the environment in which quartz is found is ubiquitous. Although quartz is one of the thousand silicate minerals that make up the bulk of the Earth's outer crust, it is however one of its commonest minerals (12 % by volume). Furthermore, all terrestrial planets have a crust similar to the silicate crust of the Earth. In the case of Mars, for example, samples (fines) have been analyzed by the Viking missions. It was demonstrated that quartz is a prominent mineral in the fines that were retrieved from both the Chryse and the Utopia Planitiae (cf., [54] and the articles that follow his summary). Quartz is known to crystallize directly from igneous magma (i.e., from molten rock material). It occurs in deep-seated coarse-grained (plutonic) rocks such as granites, as well as in volcanic rocks such as rhyolites, which are igneous rocks containing megascopic crystals of quartz.

An additional reason to focus our attention on quartz is that it is stable in sedimentary conditions; it may occur in marine and desert sands, but also as cement in compacted rocks such as sandstone, in which quartz appears as rounded grains between the diameters of 0.06 and 2 mm, with a variable content of other mineral grains. What seems even more pertinent is that quartz is also stable under low- and high-grade metamorphic conditions. In fact, a high-pressure, high-temperature form (coesite) is found in meteorite impact rocks. Another form (stishovite) is found to occur naturally in meteorite craters, such as Meteor Crater, Arizona.

Hence the probable presence of quartz in favourable environments during the heavy-meteorite impact-period (the Hadean) may have been a factor influencing the origin of life in the selection homochirality, which has persevered as a distinctive feature of the earth's biota.

5. On the Breaking of Chiral Symmetry

5.1. Amplification Mechanisms

One of the principal difficulties in understanding the asymmetry of biomolecules is the question of the amplification mechanism that would boost a primordial small physical effect [26]. New suggestions of amplification mechanisms should be considered, in addition to the earlier possibilities such as those considered in the past:

- 5.1.1. Amplification of the Vester-Ulbricht processes, namely amplification mechanisms that may apply to the interaction of polarized particles with biomolecules.

- 5.1.2. Amplification of the Yamagata processes, namely those processes (such as those discussed in this work) in which the breakdown of the discrete P symmetry is considered as a possible source of biochirality.
- 5.1.3. Amplification known as the Kondopoudi-Nelson catastrophic [55]. According to this proposal the small electroweak energy difference between the enantiomers is sufficient to determine which of the two single-enantiomer reaction sequences was adopted at the metastable stage in a flow reactor that is off thermodynamic equilibrium.

The suggestion of Salam that Bose-Einstein condensation may act as a novel amplification mechanism still suffers from a difficulty: the underlying theory requires that large activation energy barriers be overcome in the process of turning a racemic mixture into optically pure amino acids. This requires that the phase transition may induce molecular changes that lead to the breaking of chemical bonds. Amongst various options that the phase transition hypothesis may be faced with is that the origin of life may be extraterrestrial, provided that the critical temperature is too small for the phase transition to have been supported by the environment of the early Earth.

5.2. Different Mechanisms for Implementing Parity Violation

The possibility of an alternative model incorporating P violation of a third kind has been suggested in the past [56], in which the phase transition acts on a racemic mixture of amino acids inducing spontaneous separation of the chiral phases due to their environment. The ground states of the two optical pure phases are taken to differ in energy (the L-amino acid having the lower ground-state energy), as discussed in Sec. 2.3.

In fact, it has been found that a small electroweak energy increment adds to the binding energy of a given state in one enantiomer and subtracts from that of the corresponding state of the other, giving an electroweak binding energy difference between the two optical isomers.

This rationalizes the observed bias of protein amino acids for the left-handed chirality, a phenomenon that has been preserved by biological (i.e., neodarwinian) evolution. The interpretation of the postulated phase transition provided in this note does not suffer from the difficulty of implying large activation energy barriers for the production of

optically pure amino acid concentrations from an initial primordial racemic mixture.

If, on the other hand, extraterrestrial origin of homochirality is envisaged (cf., Sec. 2.2), a more compelling argument in favour of the present proposal is that, as pointed out above, molecules behave rather differently from macroscopic systems in the sense that there are no sharp transitions such as those considered in the original Salam proposal) between symmetric and asymmetric states in free molecules.

The BCS-like phase transition in the amino acids may occur at a certain critical temperature T_c . Preliminary experiments reporting negative results (cf., Sec. 3.3) have attempted to find the value of T_c for the original theory. This situation motivates the search of further insights into the sources of homochirality. We suggested that one possible insight may be found in the connection between chiral symmetry breaking and pattern formation.

It has been observed that two-dimensional liquids composed of achiral units can spontaneously separate into right- and left-handed regions. This induces a breakdown of natural mirror symmetry, an effect which is related to ferroelectricity at the [57].

However, one of the important aspects of these experiments is that a new example has been provided, in which structure and symmetry at the molecular level have implications at the macroscopic level. This phenomenon has been observed at molecular length scales in some experiments (Eckhardt et al. 1993). The molecular lattice of a racemic organic monolayer has been imaged and was observed to spontaneously undertake separate chiral regions.

5.3. Novel Amplification Proposals

We assume that the connection between chiral symmetry breaking and pattern formation may occur in bulk three-dimensional systems such as amino acids. A temperature gradient would induce a racemic mixture of amino acids, through the Bose-Einstein condensation into a regime of spontaneously broken mirror symmetry, in which the chiral phases may be separated. This, we conjecture, should manifest itself physically through pattern formation.

The question of the amplification of the small effect of the electroweak interaction which gives the preferential stability to the L-amino acid, becomes a relevant problem due to the smallness of the coupling constant of the electroweak interaction. We shall refer to the corresponding parity-violating energy-difference, which constitutes a basic concept in the postulated nonlinear mechanism for amplification.

Salam made two different proposals, a point that has not been widely [56].

5.3.1. He proposed the existence of a phase transition in a racemic mixture of amino acids in which large activation energies need to be overcome. This proposal does not refer to the environment in which the racemic mixture was inserted. This is the aspect of Salam's conjecture that was tested in two experiments (cf., Sec. 4.1).

5.3.2. Salam went further in a separate proposal of a new mechanism for the amplification of the small effect of the neutral electroweak interactions on the ground state energy of the amino acids. This possibility was suggested on the bases of the QCCs (cf., Sec. 2.3). The macroscopic quantum mechanical amplification mechanism is analogous to Bose-Einstein condensation, currently assumed to occur in other forms of condensed matter, such as in liquid helium II and superconductors. It is this aspect of Salam's conjectures that has been preliminarily tested in the most recent experiment, which clearly requires independent confirmation [51].

The proposal (5.3.1) has the difficulty that large activation energies have to be overcome, so that chemical bonds are broken for a given right-handed amino acid to be converted to its left-handed form. The second proposal (3) will be discussed below.

5.4. On Some Experiments Testing the Question of Homochirality

Unlike Salam's first suggestion which referred to a racemic [58,15,59,60,61], we advocate the second part of his proposal (5.3.2). The main reason is the evident considerable difficulty in explaining the means of overcoming the large activation energies which would inhibit the phase transition in the racemic mixture of amino acids.

At present, in order to test the theory, one needs to address the question of the possible occurrence of a phase transition in a chirally-pure sample of L-amino acids. For instance, experiments could address the question of chirally-pure samples of amino acids that have been adsorbed preferentially on the surface of L-quartz crystals, as explained in the above illustration (cf., Sec. 4).

In spite of the difficulties in the original phase-transition theory of 1991, non-linear mechanisms of

amplification of the small parity-violating energy-difference may still be relevant, but one should search those theories that are free from the considerable difficulty implied by the underlying large activation energies needed in the transition from the racemic mixture to the chirally-pure samples. One possibility of an acceptable phase transition theory, free from the above-mentioned difficulties, may be found in the generation of chirally-pure domains by the action of L-quartz surfaces, a process that was already discussed in Sec. 4.2.

5.5 Chiral Amino-Acid Crystals and Superconductivity

Evidence for the phase transition in chirally-pure samples of L-amino acids should be searched for with similar experiments to those preliminary experiments which tested the possible existence of the phase transition, in which a range in temperature was scanned for the signature of the putative phase transition (cf., paragraph 5.3.1).

On the other hand, some evidence that should be kept in mind is that Salam and the present author [15.1] were already aware that in the special case of melanin, a derivative of the amino acid tyrosine, a phase transition may already have been detected experimentally (cf., Sec. 3.1). A similar experiment directly on a sample of the amino acid L-tyrosine would serve as a test of the conjectured unusual behaviour of amino acids. Further, the importance of testing for high-temperature superconductivity, in the present case of biological relics of the earliest steps in chemical evolution (homochirality in protein amino acids), was pointed out in the same above-mentioned section of our 1991 paper.

Having raised the question of spontaneous onset of homochirality, experimental attention finally seems justified at present to search for signs of a phase transition in single chirally-pure crystals of amino acids. As stated in Sec. 5.2, this mode of symmetry breaking should be distinguished from either Quack's *de facto* symmetry breaking (the ground state does not show the same symmetry as the hamiltonian), or from *de lege* symmetry breaking (parity violation occurs in the hamiltonian, as in the case Salam discussed in his 1991 paper). For more details of the first two types of parity violation we refer to the original Paer [62].

6. Conclusions

The postulated parity violation of a third kind (in which the homochiral domains may form spontaneously due to their environment) may be

illustrated in the case of the chiral quartz crystals discussed in Sec. 4, or in the case of phenomena that is known to occur in the liquid crystal state (cf., Sec. 5.1). From what we have said above we feel that preliminary experiments testing parity violation of the third kind (such as the Wang et al. experiments) are finally justified (i.e., tests of phase transitions in single amino acids). In this manner we have been led naturally to suggest testing a form of condensed matter that has so far, from the present point of view, escaped the attention of experimentalists although considerable information already exists on the crystal structures of amino acids). In this context it may be worth recalling the lesson learnt when ceramics surprised the scientific community by showing two aspects that normally complement the phenomenon: superconducting currents (with the associated signature in the specific heat curves, as well as the Meissner effect).

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