

## 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 (Oró 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  $3 \times 10^{-19}$  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 km<sup>2</sup> 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  $1.5 \times 10^4$  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 ( $\varphi$ ) that can arise for some theories (provided the potential for  $\varphi$  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

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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 primordial 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

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

(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 ( $\nu_e, e$ ) left-handed doublets (of weak isospin), i.e.,  $T_{3L} = \bar{\psi} \gamma_\mu \left( \frac{1 + \gamma^5}{2} \right) \tau_3 \psi$  where  $\tau_3 = 1/2(1, -1)$  where  $\psi$  stands either for the doublet of protons ( $p$ ) and neutrons ( $n$ ), or for the doublet of neutrinos ( $\nu_e$ ) 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  $\phi$ , 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  $b \geq \%$ . Some physicists, like Y. Nambu, take this as the defining property of the field  $\phi$ , i.e.,  $\phi$  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

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

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  $C_\alpha$  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  $\nu$  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  $V_\mu \times A_\mu + A_\mu \times V_\mu \approx \bar{\psi} \gamma_\mu \psi \bar{\psi} \gamma_\mu \psi + \dots$ . 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  $(1 - 4 \sin^2 \theta)[(e^+ e^- \times \frac{\sigma \cdot p}{m_e}) + (e^+ e^- \times n^+ \frac{\sigma \cdot p}{m_n})] + n^+ n \times e^+ \frac{\sigma \cdot p}{m_e}$ . 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  $\omega_D$  is the Debye cutoff  $\approx 10^3 K$  for most metals,  $p_F$  stands for the Fermi momentum,  $\omega_F$  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  $T_c = 10^3 K$  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  $\Delta(T) \approx \pi \left( \frac{8}{7\zeta(3)} \right)^{1/2} [T_c(T_c - T)]^{1/2} = 3.06 [T_c(T_c - T)]^{1/2}$

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)  $C_v(T_c) = C_v(T_c) + \frac{4}{7\zeta(3)} \frac{p_F m}{\hbar^2} T_c$ . 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,  $f_+ \times e^{-\gamma}$  for  $T > T_c$ , provided the susceptibility for  $T < T_c$  has the form  $f_-(-e)^{-\gamma}$ , 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.  $\omega_D$  could be as high as  $\approx 10^3 K$ ; and (2) an attempt to find a transmitting system of electrons with high polarizability: molecular organic crystals, polymers, for example  $C_{60}$  (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  $T_c = \Delta E \exp(-1/\lambda)$ . " $\Delta E$  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)."  $\lambda$  depends on the interaction of electrons for the case of superconductivity, and  $\Delta E$  is related to  $\omega_D$ , 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  $10^{12}$ 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  $\bar{\psi}\gamma_\mu n \times \partial_\mu \psi \gamma_\nu e$ . 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  $\bar{e}-\bar{n}$  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  $\bar{n}e \cdot \partial_\mu \psi \gamma_\mu n$ . Both factors contained here are scalars and a field  $\psi$  can be invented that could have the effective coupling  $[\psi \times (\bar{n}e + \partial_\mu \psi \gamma_\mu n)]$ . 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  $g'v' \approx 1$ ,  $\omega_D$  can be taken as  $3 \times 10^{-18}$  eV.

What field does  $\psi$  correspond to? Clearly an  $\bar{e}-\bar{n}$  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  $\approx 10^{14}-10^{15}$  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  $\langle \phi \rangle = 250$  GeV? In other words is  $\langle \phi \rangle = \langle \psi \rangle$ ? 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  $\langle \psi' \rangle \neq 0$  of spin-0 particle, which has interactions with  $\bar{n}e$  and  $e\gamma_\mu n$ . 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  $250^\circ\text{K}$  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

$$T_c \approx \frac{\langle \phi \rangle}{10^3} \exp[-2/gv(1 - 4 \sin^2 \theta)] \approx 2.5 \times 10^{20} \text{K} \quad (\text{C.1})$$

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

Because the only quantity that has the right transformation character (for such parity-violating interactions) is  $Z_\mu^0$ , or its longitudinal part where  $\partial Z_\mu^0 / \partial x_\mu \approx M\phi$ , 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  $T_c = \omega_D \exp - 2/(1 - 4 \sin^2 \theta) = 5^\circ\text{K}$  if one takes  $\omega_D \approx m_e \approx 2 \times \frac{\langle \phi \rangle}{10^6}$ .

## 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  $m_t^2$ , which is of the order of  $m_t^2$ .



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, Ponnampetuma, and others have confirmed Miller's findings. The Miller–Orgel–Ponnampetuma "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!" (Orò 1961; Ponnampetuma and Molten 1973; Mitten 1977; Hanel et al. 1979a; Orò and Mills 1989; Orò 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" (Orò 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- $\alpha$ -aminobutyrate  $Cu(OOC-C_2H_4NH_2)_2$  (Wyckoff 1966).