# SOCCERBALLS AND SUPERFLUIDS

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### ABSTRACT

The 1996 Nobel Prizes in both Chemistry and Physics were awarded for wonderful discoveries in the form and characteristics of condensed matter. Both discoveries were ultimately about the behavior of atoms on a microscopic scale and involve nature's strongest atomic bonds in one case and the weakest in the other. Specifically, the discoveries relate to the amazing structure and characteristics of clusters of carbon atoms formed in such common activities as the burning of candles and to the astounding superfluid properties of one of the simplest of atoms in the most esoteric of environments.

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## I. The Fullerenes

### Natures solution to combining sixty atoms in three dimensions, each with three nearest neighbor covalent bonds.

**Carbon atoms, each with six protons and six electrons, interact with other carbon atoms by forming covalent bonds in an attempt to occupy all the electrons in completing the 2s and 2p orbitals. When the conditions of formation are such that all four of the electrons in the second shell can participate in covalent bonds - called sp3 bonding - the single 2s and three 2p electrons covalently share the orbitals with the same electrons from each of its nearest neighbors. That can happen in one of two ways - either each carbon atom forms one covalent bond with each of four nearest neighbors or it forms a single covalent bond with two neighbors and a double bond with a third. The only way that a single atom can have four nearest neighbors in three dimensions, of course, is to be located at the center of a tetrahedron**

formed by the four neighboring atoms. When car-bon bonds with only three nearest neighbors, it forms "sheets" of open hexagons - like chicken wire - with each atom at the apex of three bonds (one of which is a double bond).

When carbon atoms crystallize in tetrahedral arrangements, of course, they ulimately form the diamond crystal structure when the neighbors of each atom is accounted for. That is, when each atom is the center of a tetrahedron of its closest neighbors, and each of those is the center of a tetrahedron of its neighbors, etc., the result is the diamond crystal structure - with its related hardness and other properties.

In graphite, each atom shares its electrons covalently with only three neighbors - but one of the bonds is a double bond (and alternates among the neighbors). This arrangement leaves each atom with three nearest neighbors with strong covalent bonds - the geometry of which is a planar structure with each atom at the corner of a hexagon. Graphite, then forms as layers of these open hexagons of carbon atoms - the layers being loosely bound to each other by the van der Waals bond due to the fluctuating electric dipoles associated with the remaining electron from each atom which participates in the double bonds.

An interesting question, then, asks what form carbon atoms will arrange themselves in when they form small clusters - for example in the smoke of a burning candle? The answer turns out to be one of the most interesting structures in nature. Each atom is covalently bound to three nearest neighbors with two single bonds and one double bond - similar to graphite. This would seem to imply that planes would form - except that the atoms at the boundary would only have two nearest neighbors and could further minimize their energy by completing the third covalent bond. That, of course, suggests that the otherwise planar structures would somehow have to close on themselves. Euler, in the early 1800s, showed that closed figures of regular polygons can be constructed if there are both hexagons and pentagons - as long as there are exactly twelve pentagons. In those closed structures, each edge of each polygon can be of equal length, and each apex shares three edges. That is exactly the condition that is necessary for each carbon atom to covalently share its electrons with three nearest neighbors in three dimensions.

## The $C_{60}$ Molecule

The most symmetric of those structures has twenty hexagons and twelve pentagons which creates sixty apexes - and the "envelope" of the structure would be a sphere. The figure is an icosohedron. This soccer ball-like figure is the basis of the geodesic domes designed by architect Buckminster Fuller - hence the name "fullerenes".

The 1996 Nobel Prize in chemistry was awarded to Robert Curl and Richard Smalley for the discovery and verification (in 1988) that one of the allotropic forms of carbon is the formation of icosohedral clusters of sixty atoms in a single molecule (and more generally for the discovery of the class of fullerenes which includes $C_{70}$ and many others). The diameter of these large molecules is about one nanometer (or ten Angstroms) . The fullerenes - as they have come to be called - represent natures solution to the problem of a three dimensional structure formed of carbon atoms each with exactly equivalent roles and each with three nearest neighbors of identical atoms.

## Solid $C_{60}$ - van der Waals bonding and the FCC structure

The $C_{60}$ molecules are essentially spherically symmetric. Each atom shares three of its four valence electrons with its neighbors in covalent bonds. That leaves, of course, sixty electrons per molecule (one for each atom) that are covalently shared with its neighbors but alternate among them. So a useful conceptual picture of a single $C_{60}$ molecule is a soccerball shaped structure of carbon atoms with sixty additional electrons in effect on the surface. The molecule, of course, is electrically neutral, since there are as many electrons as protons in the sixty carbon atoms.

Due to the very large number of electrons surrounding the "cage" of carbon ions - those electrons forming fluctuating double bonds, large electric dipole moments can be created due to any distortion in the spherical symmetry of the outer electron distribution. But this is very similar to the dipole moments that form when noble element atoms are in close proximity. The Van der Waals interaction between noble element atoms allows the noble gases to first liquify and then solidify. The equilibrium crystal structure for Van der Waals bonded solids is face-centered cubic. Solid $C_{60}$ is also an fcc crystal which exists at room temperature (rather than the very low temperatures required for the noble elements) due to the large number of outer electrons. The lattice para-meter of the fcc crystal structure for solid $C_{60}$ is about 14 A

**(which is just �2 times the diameter of the molecule - just as it would be for an fcc stacking of ping-pong balls).**

### Doped $C_{60}$ and Superconductivity

**When solid $C_{60}$ is doped with the metal atoms potassium, cesium and/or rubidium (three metal atoms per carbon molecule to form $M_3C_{60}$), the dopants find the voids between the large molecules and form a very stable structure which is superconducting as high as 33 K (in $CsRb_2C_{60}$)! The discovery was made in 1989 and would have become the most significant discovery in superconductivity in decades if it had preceded the discovery of the cuprate superconductors with transition temperatures above liquid nitrogen temperature rather than followed it.**

## II. The Superfluids

### Electrons, Helium 4, Helium 3 - Quantum liquids that represent the grand discoveries of low temperature physics.

**The story of the 1996 Nobel Prize in Physics began in 1702 with the prediction by Guilliume Amontons that the proportionality of pressure and temperature of a gas when it is held in a constant volume leads to the notion of an absolute zero of temperature. The subsequent quest to attain absolute zero led to liquefaction of the gases and created the entire field of low temperature physics. One of the early stars of the field was Kamerlingh Onnes who first liquified helium (1908) at atmospheric pressure and 4.2 K and showed that the temperature can be taken to within a degree of absolute zero by evacuating the helium vapor pressure. (The dewar which contained the liquid became the only place in the universe known to have a temperature below 2.7 K!).**

### Superconductivity - Zero Resistance

**The first of the great discoveries in liquid helium was made by Onnes three years after his successful liquifaction of helium. Although most metals - in particular the good conductors like gold, silver, and platinum - can only achieve a minimum resistivity at very low temperatures (the contribu-tions to the resistivity due to impurities, crystal dislocations, and grain boundaries -**

the combined effect called the residual resistivity), the resistivity of mercury drops to zero at four degrees above 0 K. That result was especially significant since the impurity resistance (or residual resistance) would have been measurable. That is, the measured resistance dropped to below what the impurity and lattice disloca-tions would have caused even at absolute zero! About a third of the elemental metals and literally thousands of alloys and compounds have since been shown to exhibit the effect.

This new state was called superconductivity and has been a central theme in the study of solid state physics since 1911 - and has accounted for more Nobel Prizes (5) than any other field of inquiry.

A consequence of zero resistance, of course, is that an electric current can be carried in a superconductor without a potential difference across the superconducting sample. This implies that the superconductor does not support an electric field even when the sample carries a current. And an important feature of the zero resistance associated with superconductivity is that once initiated, a current induced in a closed loop of superconducting material will circulate forever as long as the sample is maintained below its superconducting transistion temperature. The effect is often referred to as persistent current.

Although all of the superconducting elements and most alloys have critical transition temperatures below 10 K, the last decade has shown the possibility of high temperature superconductors with the discovery of the cuprates - which have raised the "record" critical temperature to above 135 K at atmospheric pressure and nearly 160 K under high pressure.

## The Meissner effect - the exclusion of magnetic flux

A discovery as significant as the zero resistance (or the persistent current effect) was made by Meissner and Ochsenfeld in 1932. When a superconductor is placed in the presence of magnetic field, as long as the field strength is less than some critical field and the temperature is below Tc, the interior of the superconductor is shielded from magnetic flux by induced currents on the surface of the super-conductor. That is the mechanism that is responsible for the levitation of magnets that has become the icon for high-temperature superconductivity, since it is so easily demonstrated. This effect, which is also described in terms of the magnetic susceptibility of the solid, is common to all superconductors - and is hence a property of the superconducting state.

## Theory of Superconductivity

A successful theory of superconductivity was not developed until 1957 when Bardeen, Cooper, and Schrieffer proposed that pairs of electrons were responsible for the flow of current which cannot be diminished by the normal collision process. The electron pairing is an essential feature, since that makes the pair a boson - a particle that obeys Bose-Einstein quantum statistics - rather than a fermion - a particle that obeys Fermi-Dirac quantum statistics which describes the behavior of a normal single electron. The distinction between the Bose and Fermi descriptions of the quantum behavior of particles depends on the spin of the particle. All electrons are spin 1/2 (meaning they have spin angular momenta of h/2, where h is Planck's constant). The essential feature of the theory is that at and below the critical temperature, some electrons form pairs - and consequently become bosons - and fall into the Bose condensation ground state. The electron pairs that are in that ground state cannot have their state changed by individual particle collisions, unless the interaction with the lattice imparts more energy to the pair than the binding energy of the pair. So a normal electron collision with the vibrating lattice does not change the motion of the electron pair - hence cannot diminish the current being carried by the pair. Even though not all the electrons form pairs, the normal electrons do not contribute to current flow since their contribution is quickly diminished by electron-lattice collisions in the absence of an applied voltage. Hence the zero resistance - or persistent current - associated with the superconducting state is a consequence of the electrons which pair and form bosons in their ground state.

It should be added, of course, that the theory of superconductivity is by no means complete. It does not predict what materials will become superconducting, nor does the BCS theory explain the high temperature superconductors. What is common to all models for superconductivity - even those that are being explored to explain the effect in the exotic superconductors - is that it must be pairs of electrons acting as bosons in their ground state that are responsible for all the effects associated with superconductivity.

## Superfluidity in $^4$He

When helium is liquified (at 4.2 K) it behaves just as any other liquid which is surrounded by surfaces higher that its boiling temperature. It boils. And when a vacuum system evacuates the air space above the liquid, thus reducing the helium vapor pressure, its temperature drops. As the temperature drops toward 2 K, the boiling becomes more and more violent. Then the boiling suddenly disappears at 2.17 K - and the liquid surface becomes perfectly calm as the liquid continues to evaporate from the surface further dropping the temperature. Although the pheno-menon must have been seen before its formal discovery, the significance of the observations were not made until 1938 - three decades after the original liquifaction of helium.

Boiling in a liquid occurs when the temperature of parts of the liquid below the surface is greater than the temperature at the surface when the surface liquid is in equilibrium with its vapor pressure. (For example, when you boil water on the stove, the surface -and most of the liquid- is at 100 C, while the bottom surface of the liquid is in contact with the pan which is trying to come to equilibrium with the stove at a higher temperature. The bubbles form at the hot surfaces and rise through the liquid bursting at the surface.) Liquid helium is in equilibrium with its vapor pressure at 4.2 K and one atmosphere. But the dewar that contains the helium is trying to warm to the temperature of its surroundings - hence the boiling. As the pressure is reduced, the most energetic helium atoms are removed, which further cools the surface and the boiling becomes more rapid. For the boiling to stop even though the helium is still being cooled by reducing the vapor pressure, the entire helium bath must be at the same temperature. And that can only occur if the thermal conductivity of the helium suddenly becomes extraordinarily large. At 2.18 K,the thermal conductivity of liquid helium suddenly jumps by many orders of magnitude! This phase transition is reflec-ted in the temperature de-pendence of the heat ca-pacity, which exhibits a discontinuity at the tran-sition (called the lambda point ).

At that same temperature, other equally dramatic changes also occur. The viscosity of the superfluid phase goes to zero (rather, drops by twelve orders of magnitude) - hence the liquid can exhibit non-decaying circulation once initiated, analogous to the persistent current in superconductors, and can flow through micro-scopic orifaces without a pressure gradiant - as if inviscid.

The superfluid can also climb the walls of a container, in apparent defiance of gravity, in a system whose temperature is below the lambda point. This phenomenon is called "creep" as the liquid forms a thin layer that climbs the walls of the container and ultimately siphons the superfluid helium out of the inner container. And an attempt to create a thermal gradient in the liquid can create a dramatic fountain effect where liquid can be ejected to considerable heights. The heat capacity exhibits the characteristics common to phase transitions even though there is no obvious change in the helium itself (that is, no change in density or structure, for example).

All are manifestations of helium being a quantum liquid - a superfluid. The transition temperature to the superfluid state is referred to as the lambda point because of the similarity of the Greek letter to the graph of heat capacity vs temperature at the transition.

The cause of all of these intuition violating phenomena bear close resemblance to the superconductivity that was observed decades earlier. Helium is a spherically symmetric closed shell atom with two protons, two neutrons, and two electrons. Its electrons fill the 1s shell - and hence have a total orbital and spin angular momentum of zero. The four nucleons also have a total angular momentum of zero. Helium atoms (at least He4) are necessarily bosons (at all temperatures). The theory of superfluid helium concludes that at 2.17 K, some helium atoms collapse into a state called a Bose condensate - and hence are in their ground state with zero energy and entropy. As the temperature of the bath is further lowered, more of the helium atoms collapse into that ground state. Those atoms are no longer behaving as individual helium atoms but rather act cooperatively as a single entity. This quantum ground state has been invoked (by Richard Feynman in 1959) to explain all of the peculiar characteristics and phenomena exhibited by liquid helium.

It is interesting that although there seem to be great similarities between the states of superconductivity and superfluidity, they are not identical. Electrons, of course, carry negative electrical charge and are themselves fermions - hence could not individually fall into a state of Bose condensation in the absence of a mechanism for pairing. The success of the theory of Bardeen, Cooper, and Schrieffer in explaining superconductivity came in demonstrating that there was a mechanism by which electrons could form singlet pairs - hence become bosons which would allow the Bose

**condensation to occur. That mechanism, of course, requires an interaction with another system - the lattice - which means that it is not just the properties of the electrons that lead to the "superfluidity" of the electron gas. Additionally, as soon as the bosons are formed by pairing electrons, they are in the superconducting ground state. In helium 4, on the other hand, the atoms themselves are bosons. It is only when the temperature drops below the critical lambda point temperture that the condensate forms and the superfluid properties are exhibited.**

## Superfluidity in $^3$He

**The theory that explains superfluidity in helium 4 would not seem to apply to the isotope of helium that has only three nucleons in the nucleus. That is, Bose condensation can only occur when the system is made up of bosons - atoms with integral values of the angular momentum quantum number. But $^3$He has two protons and only one neutron in the nucleus along with its two orbiting electrons. Hence it cannot be a boson. But the success of the BCS theory in explaining the phenomenon of superconductivity among electrons has been invoked to suggest that $^3$He atoms could also pair to form bosons just as electrons do in superconductors. If they do, then Bose condensation is a possibility and $^3$He could also have a superfluid state. That possibility led many research teams to look for the superfluid state in the rare helium isotope. Of course, for it to be possible to pair and for pairing to actually occur are two different things. For one thing, there has to be a mechanism for pairing - that is, pairs will only form if they can lower their energy by doing so. Among conduction electrons in superconductors, the pairing mechanism (according to the BCS theory) is through interactions with the vibrating lattice. That is, with the correct set of conditions, two electrons with opposite momenta and opposite spins can interact through electron-phonon coupling to reduce the energy of the pair. This reduction in energy is called the energy gap for superconductors, since it would require an input of the binding energy of the pairs (per pair) to cause each electron to again behave as an individual electron acting alone. It is more difficult to think of an interaction mechanism for $^3$He atoms since they are electrically neutral. Neutrons do, however, have a weak magnetic moment. That allows for a very weak interaction between neighboring helium atoms. That weak binding energy might be just enough for the two helium atoms to have a weak binding energy. And according to the BCS theory (which is sufficiently**

general to apply to atoms as well as electrons), if pairing is possible, then there will be a temperature at which pairing will occur. That is, if there is a mechanism to do so, there will be a temperature below which $^3$He will exhibit superfluidity.

The discovery that led to the Nobel prize was made in 1972 by Robert Richardson, Douglas Oscheroff and David Lee at Cornell. They were looking at the "melting" curve, where the liquid and solid are in equilibrium as the temperature and pressure are varied, in the millikelvin temperature range and high pressure (where as the pressure increases, the temperature decreases). The pressure was cycled over time so that the temperature was first decreased then increased between 1 mK and 5 mK. Very close inspection of that curve showed some structure which occurred at the same temperature and pressure both on heating and cooling - evidence of a phase transition of some sort. The initial interpretation was that the phase had changed from liquid to solid - and that phase transition was reflected in the melting curve. Further analysis showed the transition to be between two different liquid states. And the discovery of superfluid $^3$He had been made.

The transition in $^3$He occurred at a temperature nearly a thousand times lower than the superfluid transition in He4! - at 2.7 mK! In the quarter century since the discovery, two distinct phases of superfluid $^3$He have been detected - and the two phase transitions were evident in the original discovery.

1. R. Curl and R. Smalley, "Fullerenes", Scientific American, Oct. 1991.

2. D. Huffman, "Solid C60", Physics Today, Nov. 1991.

3. R.F. Brown, *Solid State Physics - An Introduction for Scientists and Engineers*, El Corral, 1998.

4. R. Cava, "Superconductors beyond 1-2-3", Scientific American, Aug. 1990.

5. F. Adrian and D. Cowan, "The New Superconductors", Chemical and Engineering News, Dec. 1992.

6. R.J. Donnelly,"The Discovery of Superfluidity", Physics Today, July, 1995.

7. O. Lounasmaa and G. Pickett, "The $^3$He Superfluids", Scientific American,

June, 1990.

8. N. D. Mermin and D. Lee, "Superfluid Helium 3", Scientific American, Dec., 1976.

9. "He3 and He4", Physics Today, Special Issue, Feb. 1987.

10. D. Goodstein, *States of Matter*, Prentice-Hall, 1975.

11. The 1996 Nobel Prize in Physics, http://www.nobel.se/announcement-96/physics96.html