Is There a Sea of Free Electrons in Metals?

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Keywords: Sea of Free Electrons, Metallic Bond, Compression Bond, Electrical Resistance, BCS Theory

Abstract

Challenges regarding the widely accepted BCS superconductivity theory may arise from misconceptions about the sea of free-moving electrons and metallic bonds. Based on these concepts, electrical resistance is assumed to be caused by electron vibrations and collisions in conductors. Implicitly granted by this model, the BCS theory suggests that coupled electrons in Cooper pairs can minimize their vibrations and resistance, leading to the phenomenon of superconductivity. However, if delocalized electrons were responsible for holding molecules together in metallic bonds, how could metal structures remain stable when electrons move in a current? The primary challenge to these models is the negative impact of pressure on resistivity and superconductivity. Abandoning these models, an alternative theory introduces the concept of isopotential electron tunnels within conductors. Formed between closely spaced molecules, these tunnels allow electrons to move across molecules at the same energy level, resulting in currents. Electrons in conductors, rather than being free-moving, are typically confined to orbitals within their respective molecules, below the energy level of these conducting tunnels. Raising electrons into the tunnels requires energy, which manifests as electrical resistance. The resistance of a conductor can be reduced by compressing the molecular spacing, which minimizes the gap between the tunnels and valence orbitals. This gap can be further reduced to zero with additional pressure, resulting in the tunnels overlapping with valence orbitals. Consequently, electrons reside naturally within the tunnels without a need for the lifting energy to the tunnels, resulting in zero resistance—superconductivity. This theory comprehensively explains observed superconducting phenomena, including the Meissner effect, critical current density, critical magnetic field, the inverse relationship between resistivity and pressure, and why many high-temperature superconductors are achieved under high pressures. According to this theory, compressing molecular distances is the key to synthesizing room-temperature superconductors. An optimal approach involves engineering molecular structures to leverage attraction between specific molecules, thereby minimizing the gap.

Introduction

Certain fundamental misconceptions have been so integral to many aspects of science that they may have skewed our perspective and understanding of observations, thereby limiting or hindering advancements in theory, technology, and civilization. For instance, energy shortages have been a key factor restricting economic growth and are closely linked to environmental problems, as green alternatives are currently insufficient. Ultimately, energy constraints affect the development of civilizations across the universe.

Fusion reactions offer a promising solution for a clean energy supply. One of the primary tasks in designing a tokamak fusion reactor is using magnetic fields to confine the charged particles within the reactor. However, generating these intense magnetic fields with normal conductor coils consumes enormous energy. Superconductors that can operate at less

restrictive pressures and temperatures are crucial for designing a tokamak fusion reactor capable of achieving breakeven energy production.

The misconception surrounding electrical resistance may have been a key factor delaying the development of practically useful superconductors for over a century since their discovery. Both the concept of electron resistance and metallic bonding are rooted in the idea of free electrons within conductors. It is widely believed that electrons in conductors can detach from their host atoms to form a “sea of free-moving electrons”. These free electrons are also thought to act as the binding “glue” holding together the lattice of positive metal ions, forming metallic bonds. Electrical resistance is then explained as resulting from collisions between the flowing electrons and these ions. However, despite the broad acceptance of these ideas, they have yet to be conclusively verified by experimental data or definitive evidence.

In this article, we will investigate a series of misconceptions, ranging from the sea of electrons to metallic bonds, the electrical resistance model, and the BCS (Bardeen-Cooper-Schrieffer) theory for superconductivity. With these insights, a unified theory is proposed to address the misconceptions while providing comprehensive explanations for superconducting phenomena and integrating the behaviors of insulators, conductors, and superconductors under a unified mechanism. Importantly, the new theory offers crucial strategies for synthesizing practical room-temperature superconductors.

Additionally, building on discoveries from studies of superfluids, a compression bond—proposed as an alternative to the metallic bond—is predicted to be responsible for holding molecules together in metals. This bond explains various common physical properties observed in metals, including opacity, luster, ductility, high density, tensile and shear resistance, as well as electrical and thermal conductivity.

No Such Sea of Free Electrons or Metallic Bonds

According to the traditional model of conductors, valence electrons detach from their host atoms, creating a sea of free-moving electrons. Each atom loses at least one electron, becoming a positively charged ion (cation). These free electrons serve as a cohesive medium between cations, forming metallic bonds. It is commonly believed that the cations form the stable lattice structure of conductors, while the electrons move freely to create electric currents.

This model presents two conflicting ideas: firstly, the electrons act as the cohesive glue between the cations to form metallic bonds and stabilize the structure of conductors; secondly, the electrons need to move in conductors to generate currents. These electrons thus play dual roles that seem contradictory. In the first scenario, electrons must be localized to maintain the stable structure of conductors. In the second scenario, they must be mobile to create currents.

Furthermore, the electrons and cations should be mutually free and mobile in this model. There is no mechanism to prevent the cations from moving. Why then can’t cations move in conductors? Additionally, if this model were accurate, removing free electrons from conductors would cause the cations, which constitute the lattice, to repel each other and lead to the disintegration of the conductor's structure. This raises doubts about how the structure of conductors can remain stable with such an unstable form of "glue", especially when the electrons flow through the conductors as currents.

In reality, however, conductors, mostly metals, have a very stable structure and can withstand high shearing and tension forces, indicating that their molecules must be attracted together through strong and stable interactions. So, the widely

accepted concepts of free-moving electrons and metallic bonds do not align with these observations and warrant further investigation and reconsideration.

Challenges to the Electrical Resistance Model and BCS Theory

Based on the concept of free-moving electrons, a further misconception about electrical resistance was proposed in the Drude model.[1] According to this model, free electrons flow through conductors to generate currents. Electrical resistance arises from collisions between these electrons and the lattice of conductors, as illustrated in Figure 1. Each collision scatters the electrons and dissipates some energy, resulting in electrical resistance. This model explains the correlation between electrical resistance and temperature: higher temperatures increase molecular vibrations. The intense vibration, in turn, elevates the likelihood of collisions.

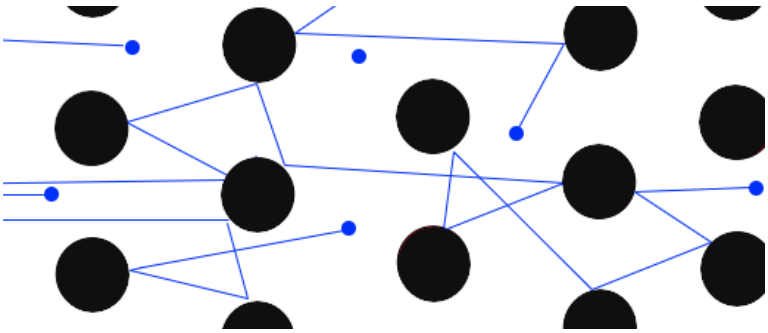

Figure 1: The Drude model for electrical resistance.

However, if the Drude model were accurate, one would expect high-density materials to exhibit higher resistance. As the confining pressure increases, molecules are packed more densely, resulting in more frequent collisions and, consequently, higher resistance. However, observations indicate the opposite: resistance negatively correlates with pressure.[2-4]

This resistance model encounters a further challenge in an intuitive argument. Setting aside the stability concerns related to free-moving electrons, let's assume the presence of metallic bonds that potentially bind molecules together in metals. The existence of bonds between molecules implies electrostatic interactions or forces between them, indicating that the space between molecules is not empty but contains electric fields. An electron, carrying a negative charge, would interact with these fields and consequently cannot move freely between molecules as depicted in Figure 1.

To collide with the crystal lattice, an electron must be accelerated to a very high energy to traverse across the electric fields in a straight trajectory. Generating such high-energy electron streams requires extremely high voltage, similar to the levels used in J.J. Thomson’s cathode ray experiments[5] or Rutherford’s scattering experiments[6]. Electrons in conductors under normal voltage do not possess sufficient energy to move at such high speeds. In other words, electrons are unlikely to collide with the lattice of conductors. Instead, without the influence of external electrical or magnetic fields, electrons typically remain confined within their orbitals in their respective molecules and cannot move freely.

The widely accepted BCS theory of superconductivity is implicitly grounded in the traditional model of electrical resistance. According to this theory, superconductivity emerges when electrons form Cooper pairs, bound together through electron-phonon interactions that stabilize the electrons and reduce collisions, thereby lowering electrical resistance.

However, a fundamental challenge to this model lies in the assumption that a free electron attracts nearby nuclei, creating a high-density region of positive charge. In reality, each nucleus is surrounded by electron clouds that repel other electrons at short distances. Consequently, rather than attracting neighboring nuclei, a free electron would push them away, resulting in a low-density region of positive charge. This contradiction raises serious questions about the physical validity of the electron-phonon interactions that are central to Cooper pair formation.

Another challenge to the BCS theory is that electron-phonon interactions are generally thought to be significant only at low temperatures. As the temperature increases, the vibrations of the electrons and crystal lattice reduce the strength of these interactions. However, since 1986, superconductors have been discovered that operate at increasingly higher temperatures, far surpassing the theoretical maximum predicted by the BCS theory.[8-12] At elevated temperatures, Cooper pairs become unstable and tend to break apart. Additionally, most high-temperature superconductors are synthesized under high pressure, a factor that the BCS theory fails to explain in terms of its positive effect on superconductivity.

Coincidentally, the traditional model of electrical resistance encounters similar challenges under high pressure, where resistance decreases as pressure increases. This suggests that the failure of superconductivity under these conditions may stem from analogous, yet flawed, assumptions within the conventional model of electrical resistance.

These misconceptions may have misled scientists and impeded their accurate understanding of electrical resistivity and superconductivity. Consequently, these erroneous concepts and theories could have delayed the discovery and synthesis of room-temperature superconductors.

The Unified Theory of Resistivity and Superconductivity

The failures of these theories in both resistivity and superconductivity at high pressures may not be coincidental but rather a consequence of incorrect assumptions in the collision model for electrical resistance and misconceptions of the free-moving electrons. By abandoning the traditional model of electrical resistance, an alternative theory has been proposed in the "Unified Theory of Low and High-Temperature Superconductivity".[13] Rather than employing separate models for resistivity and superconductivity, the theory suggests that both phenomena share a common underlying physical mechanism. The new theory introduces the concept of isopotential electron tunnels, depicted in Figure 2, which form between closely spaced molecules. Within these tunnels, electrons can move between molecules at the same energy level, resulting in currents.

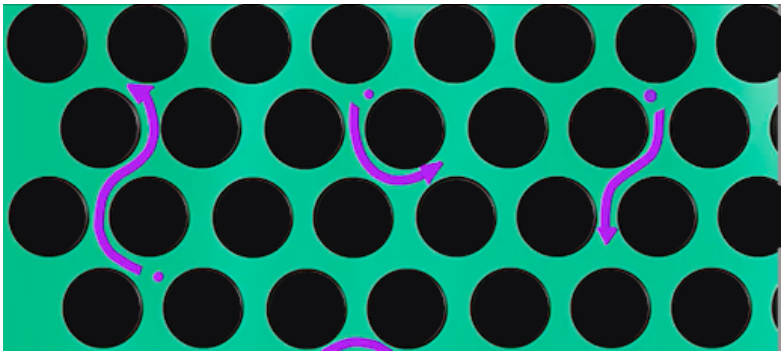

Figure 2: Electron tunnels between molecules.

Here is an intuitive thought experiment to understand superconductivity. Consider two separated hydrogen atoms. At a distance without interactions, their electron clouds are evenly distributed around the protons. When they are placed next to each other, their clouds interfere with each other and deform, inducing attraction between them. At a distance close enough, the cloud of one atom can overlap with the other proton, and vice versa, forming a covalent bond, as observed in normal hydrogen gas molecules. A covalent bond can be considered the shortest segment of an electron tunnel between these two atoms. However, electrons are still restricted only to these two atoms.

Now, let's place two such hydrogen molecules next to each other perpendicularly. To force them together, pressure is required. Under enough pressure, the four atoms are arranged in a tetrahedron, with each atom equidistant from the others. Their electrons can move in a four-way covalent bond from one atom to any other. This four-way covalent bond becomes an electron tunnel among all four atoms. When all hydrogen atoms are arranged in this manner in a piece of solid hydrogen, an electron can travel from one atom to any adjacent atom without any resistance, resulting in a superconductor.

Unlike superconductors, there are usually no free-moving electrons or currents in normal conductors. Electrons are typically confined within their molecules, as illustrated by the black cells in Figure 2. The electron tunnels between the molecules do not overlap with their valence orbitals, as depicted by the purple paths in the figure. To generate currents, energy is required to lift electrons into these conducting tunnels, representing the electrical resistance of the conductors. When an electron retreats to an electron-hole in a molecule cell, its stored lifting energy dissipates in the form of electromagnetic waves, released as resistive heat. Electrical resistance represents the energy spent to elevate electrons from valence orbitals to the tunnels to create currents.

The resistance of a conductor can be reduced by compressing molecular spacing, which minimizes the gap between valence orbitals and electron tunnels, thereby lowering the lifting energy required to access the tunnels. Increasing the pressure even further can close this gap completely, causing valence orbitals to overlap with electron tunnels. Consequently, electrons naturally reside in these tunnels, eliminating the requirement for lifting energy to access the tunnels, leading to zero resistance—superconductivity. This explains the inverse relationship between resistivity and pressure and clarifies why many high-temperature superconductors are achieved under high pressures.

As temperature decreases, electrons transition to lower energy orbitals, which reduces repulsive forces between molecules and leads to a contraction of molecular spacing. Under these conditions, ambient pressure becomes more influential, creating a compressive effect similar to that of increased pressure, thereby lowering electrical resistance. At sufficiently low temperatures, many materials undergo a transition into the superconducting state. This behavior explains the correlation between resistivity and temperature and why conventional superconductors are typically observed only at low temperatures.

In insulators, electron tunnels are disjointed due to the large distances between certain molecules. Applying pressure can reduce these distances, thereby creating new electron tunnels that connect existing ones. This explains why some ceramics may transition to superconductors under high pressure. Electron tunnels can be envisioned as shared paths between molecules at high-energy orbitals. In insulators, these paths are segmented. In conductors, they are connected but at an energy level above the typical valence orbitals. In superconductors, they overlap with the valence orbitals. The key difference between these states lies in the distances between molecules.

This distance is a dynamic factor determined by pressure and temperature. Consequently, the electrical resistance of materials correlates with both pressure and temperature, collectively defining the electrical states of matter. According to

this mechanism, the tunnel theory predicts insulators, conductors, and superconductors as different resistance states of matter under varying pressures and temperatures, as illustrated in Figure 3. Phase transitions between these states are determined by molecular spacing, which in turn dictates the presence, connectivity, and distance of valence orbitals relative to electron tunnels. These factors themselves are influenced by pressure and temperature.

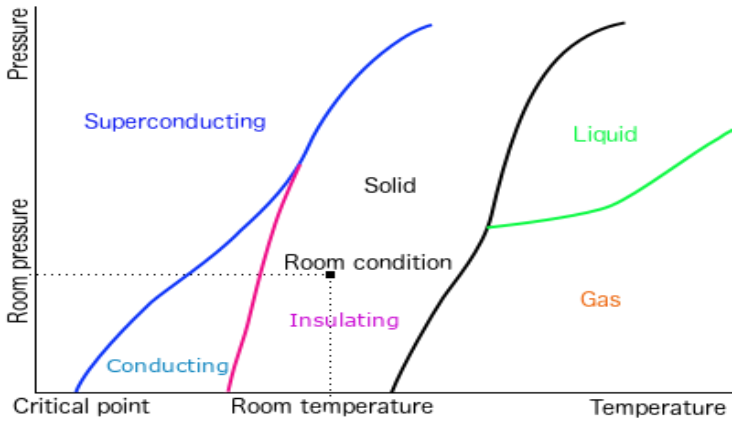

Figure 3: Electrical resistance phase diagram depicting superconducting, conducting, and insulating transition boundaries, along with the transition boundaries of conventional states.

Moreover, the new theory provides comprehensive explanations for various superconducting phenomena, including the cause of the Meissner effect, the limit on critical current density, and the temperature dependence of critical magnetic fields. The concept of electron tunnels also clarifies why superconductivity may appear along specific dimensions or crystal planes in certain materials. According to this theory, superconductivity represents an ordinary state of matter typically observed under high pressures. Consequently, the theory predicts that superconducting substances are common inside large planets and may be responsible for their magnetic fields—a hypothesis that not only explains the origin of Earth's magnetic field but also those of other planets.[14]

A crucial insight of this theory for synthesizing room-temperature superconductors is the necessity to compress molecular distances. However, a significant obstacle lies in the repulsion between molecules. Overcoming this repulsion through external pressures, as commonly practiced to achieve most high-temperature superconductors, proves impractical for many applications. An optimal approach could involve engineering molecular structures to leverage attractive forces between specific molecules, thereby overcoming the repulsion.

The Prediction of Compression Bond

Without a sea of free electrons for metallic bonds, what is the attractive force that binds molecules in stable structures in metals? This role may be fulfilled by a newly discovered bond, termed a compression bond, predicted in a study on superfluidity.[15]

In liquids, viscosity is inevitable due to the ubiquitous presence of intermolecular attraction. However, in superfluids, viscosity disappears because of the absence of such attractions, a rare condition typically unattainable in most substances. Helium-4, with its simple and symmetric atomic structure, is largely immune to most intermolecular interactions except for the London dispersion force, the weakest form of intermolecular forces. At low temperatures, electrons tightly pack into

lower orbitals, reducing their dispersion, and eventually, at 2.17 K, the weak attraction of the London dispersion force vanishes, as illustrated in Figure 4B. Without any attraction, helium in its superfluid phase experiences no viscosity. Essentially, superfluids are not traditional fluids but a collection of individual particles.

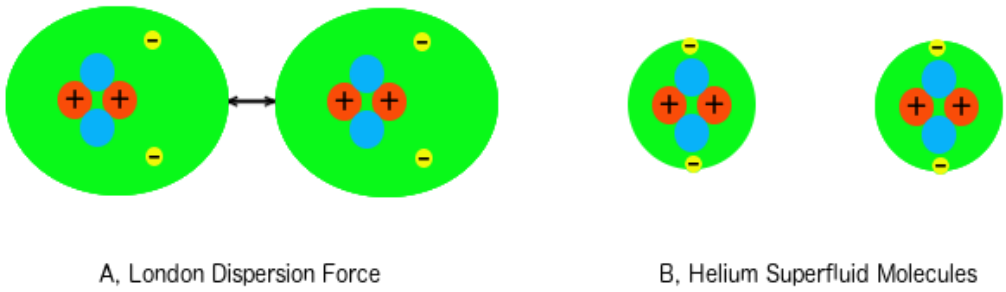

Figure 4: The vanishing of intermolecular attraction and viscosity in superfluids. A) Due to the single fully occupied valence orbital in helium atoms, there are no other interactions between helium molecules except for London dispersion forces, contributing to the viscosity of helium liquids. B) At low temperatures, electrons retreat to lower orbitals, reducing their dispersion and eventually leading to the disappearance of intermolecular attractions.

Understanding the absence of intermolecular attraction in superfluids explains many observed phenomena. This lack of cohesion also clarifies why a solid cannot form simply by lowering the temperature of a superfluid without additional pressure. However, under high pressure (>2.5 MPa), solid helium-4 has been obtained at temperatures between 1-1.5 K.[16-17] Under normal pressure below 2.17 K, helium-4 is typically in the superfluid phase and experiences no attraction between molecules. The solidification of helium under high pressure indicates that the pressure induces intermolecular attraction. Additionally, helium can solidify at room temperature, but this requires much higher pressures (>113 GPa).[18] Under normal pressure at room temperature, London dispersion forces govern the interactions between molecules. However, the formation of a solid under such high pressure suggests that a different type of bonding force predominates over the London dispersion force.

Thus, the formation of helium solids at high pressures suggests that the applied pressure induces a novel type of attraction between molecules, distinct from the London dispersion forces observed at low pressures. This new bonding mechanism, termed a "compression bond", was proposed in the article “Superfluids Are Not Fluids”. Under high pressure, helium molecules experience compression, causing the electron cloud to contract along the axis defined by the two protons in response to repulsive forces from neighboring molecules' electric fields, as illustrated in Figure 5A. This cloud deformation leads to an uneven distribution of electron density in various directions, generating local fields that are positive towards the ends of the proton-defined axis and negative towards the periphery of the plane perpendicular to that axis. This disparity induces an attractive force between these fields. Driven by this force, molecules reorient themselves to minimize their potential energy, eventually stabilizing in a low-potential-energy arrangement between molecules, as depicted in Figure 5B.

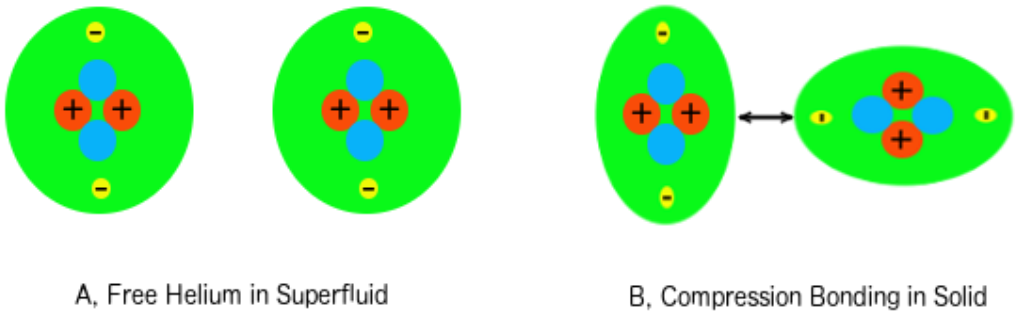

Figure 5: Helium solids form due to the formation of compression bonds. A) Under standard pressures, superfluids can be obtained from helium liquids by lowering the temperature. However, further decreasing the temperature does not lead to the production of helium solids because there are no attractive forces to hold the molecules together. B) Under high pressures, the electron cloud of helium molecules deforms and contracts along the axis defined by the two protons. The resulting uneven distribution of electron density in various directions generates local electric fields, leading to an attraction between molecules.

These compression bonds may be responsible for the formation of helium solids at high pressures and could also be present in solids composed of other elements. For instance, when subjected to high pressures of approximately 400 GPa, hydrogen transitions into a metallic state.[19-20] Under such extreme pressures, traditional covalent bonds between hydrogen atoms may be replaced by compression bonds, transforming hydrogen from a diatomic to a metallic form.

Additionally, molecules in metals may also be predominantly formed by this type of bond. Unlike helium atoms, metal atoms are typically much larger and involve p, d, and even f orbitals. This makes their electron clouds more susceptible to deformation and more likely to form compression bonds without the need for extremely high pressures. Helium's symmetric electron structure requires high pressure to deform its cloud. In contrast, the larger electron clouds of metals are naturally asymmetric and deformed, making compression bonds native interactions between the molecules.

Both compression bonds and London dispersions involve deformation in electron clouds, but they exhibit notable differences. Firstly, London dispersions occur at low pressures with electron clouds stretching out, whereas electron clouds are tightly packed in compression bonds, where high pressures may be required for small atoms. Secondly, London dispersion forces are the weakest of all intermolecular forces, while compression bonds are significantly stronger. Lastly, substances exhibiting London dispersion forces are typically low-density nonmetals, whereas materials with compression bonds are high-density metals.

Characteristics of Compression Bond

Several characteristics can be predicted for substances with compression bonds. Firstly, ductility and malleability are distinct features of materials formed by compression bonds. Unlike covalent and ionic bonds, which can fracture and render materials brittle, compression bonds result from the deformation of electron clouds. When subjected to forces, their clouds can naturally deform further to accommodate and withstand substantial stress without breaking. Molecules within a

compression bond can even slide relative to each other and form bonds anew with adjacent molecules. This flexibility contributes to the malleable and ductile properties commonly observed in metals. However, these properties diminish in steel, where iron is mixed with a small amount of carbon. Carbon atoms form covalent bonds with adjacent iron atoms, resisting deformation and reducing ductility. Indeed, these are the intended properties of many alloys.

Secondly, molecules involved in compression bonds are typically densely packed. The gap between electron tunnels and valence orbitals is relatively small, requiring less energy to access these tunnels and resulting in low resistance. This characteristic might imply that materials featuring compression bonds would be ideal candidates for superconductors under pressure. However, this is not necessarily the case. Under pressure, valence electron clouds can deform substantially before overlapping with electron tunnels. This is why ceramics can more readily transform into superconductors under pressure compared to metals.

Additionally, due to the densely packed molecules, substances with compression bonds exhibit high density and luster, often appearing opaque. The compact arrangement of molecules facilitates efficient thermal energy propagation, leading to high thermal conductivity. These are typical characteristics observed in metals.

Conclusions

A series of misunderstandings and misconceptions, ranging from the idea of a free-moving electron sea and the glue model of metallic bonds to the collision model of electrical resistance and the concept of Cooper pairs explaining superconductivity, may have led us astray. These misunderstandings could have impeded theoretical progress and practical discoveries, delaying the development of highly valuable superconductors for over a century since their initial discovery. Hopefully, the new models and theories put forth in recent studies will steer us more effectively toward engineering room-temperature superconductors.

Revision History

- 06/25/2024: Initial Post on Stanford Site
- 11/01/2025: Published on Zenodo
- 12/17/2025: Adding Links to Summaries of Related Articles

Links to Summaries of Related Articles

- https://cs.stanford.edu/people/zjl/abstract.html, PDF
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- https://xenon.stanford.edu/~zjl/abstract.html, PDF
- https://doi.org/10.5281/zenodo.17967154, PDF

Further Literature

- Misconceptions in Thermodynamics (PDF: DOI) (中文: DOI)
- The Mechanism Driving Crookes Radiometers (PDF: DOI) (中文: DOI)
- The Cause of Brownian Motion (PDF: DOI) (中文: DOI)
- Can Temperature Represent Average Kinetic Energy? (PDF: DOI) (中文: DOI)
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- Is There a Sea of Free Electrons in Metals? (PDF: DOI) (中文: DOI)
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