

## NEW LECTURE XI

Most of the present lecture and all of the following one will be devoted to telling the story of the evolution of our understanding of superconductivity.

As I am sure you all know, the basic mechanism responsible for superconductivity remained a baffling mystery for nearly half a century after the first discovery, although there was expanding progress in the experimental knowledge of the behavior of superconductors and in the development of phenomenological theories.

And as we all know, a new age began in 1957, when Bardeen, Cooper, and Schrieffer proposed a theoretical mechanism that proved to be essentially correct for very many superconductors, and that led naturally into extensions and generalizations that gradually expanded our understanding of many phenomena and led to the prediction of new ones.

All parts of this history are fascinating, and there is so much to tell that I couldn't force myself to squeeze it all into one lecture.

Fortunately, there's a very natural way to divide my story into two separate though very unequal parts.

The first part, which I'll discuss today, covers the four and a half decades from 1911 to 1957, when more and more properties of superconductors were being discovered and measured, and even correlated phenomenologically, while all speculations about the atomic-scale mechanism of superconductivity kept turning out to be unsatisfactory.

The second part, to which I'll devote the next lecture, has to do with what may be called the "golden decade," the ten or twelve years initiated by the BCS paper when theorists and experimentalists everywhere published a rapid succession of papers extending the BCS work, making new predictions from it, and verifying the predictions.

Indeed, among all the laws and rules used today to understand the properties of superconductors, nearly all that are accepted as solidly

established by basic theory and also experimentally verified, date from the "golden decade."

My story will be divided into four time periods for each of which I've chosen a few words to indicate roughly what was uppermost in the minds of most research workers in this period.

The first three of these, which I'll discuss in this lecture, overlap each other somewhat, while the fourth, which forms the next lecture, of course, starts suddenly in 1957.

VG 1a So now, to get started, here's a list of major developments in the first period, which I've labeled with the words "Infinite Conductivity?" The entries are in my usual type of format with time increasing downward; theoretical references are on the right, and experimental on the left.

The initial discovery here was made in the low temperature laboratory of the University of Leiden which was under the direction of Heike Kamerlingh Onnes, and which at that time was leading the world in the achievement and application of low temperatures.

In the course of their explorations of the newly discovered strong dependence of the electrical conductivity of metals on temperature at low temperatures, they discovered that near 4.3 Kelvin the resistivity of mercury dropped suddenly by a factor of at least 300 to a value too low to measure.

This result they published at once, while pressing ahead with experiments on other metals, and with more accurate measuring techniques, and to lower temperatures.

I've listed here only a few of the more important of these early discoveries by the Leiden group.

A number of other metals were found to show the same sort of sudden drop in conductivity that mercury showed, but some metals, such as gold and platinum, did not show any such effect down to the lowest temperature the laboratory was then able to reach, which was about 1.2 Kelvin.

In the presence of a magnetic field, superconductivity was found to disappear above a certain field strength, of the order of hundreds of gauss, and the field due to the current passing through the superconducting sample itself had a similar effect, bad news for hopes about superconducting magnets.

And finally, when the ends of a superconducting coil bearing a current were joined and connection to the outside was broken, it was found that the current in the coil persisted unchanged for as long a time as it could conveniently be held below the transition temperature.

→ This required the resistivity of superconducting lead to be at least fifty billion times less than ~~of~~ the resistivity at room temperature.

Unfortunately, the Leiden work slowed down rapidly during the World War I years, but in the 1920's work resumed both at Leiden and in other countries such as the United States, Canada, and Germany.

While it had been known for some time that the properties of a superconductor depended not only on the fields present during a measurement, but also on the past history of the fields, it was only in 1925 that the Leiden group called attention to the striking analogy between the behavior of the magnetic moment of a superconducting specimen in response to changes in the external magnetic field and the hysteresis curves long known for ferromagnetic materials.

Throughout all these years, a lot of things were being learned about the behavior of superconducting metals, but all the understanding had been contributed by the experimentalists.

There were of course theoretical speculations, but no one could give a plausible reason why the scattering mechanisms responsible for electrical resistance should suddenly become ineffective.

There were two viewpoints, neither successful.

One was the idea that for certain materials, the state of lowest energy could be a current-carrying state.

The other viewpoint held that superconducting samples were never in thermodynamic equilibrium and that therefore thermodynamics could not be applied to them.

Our present-day view, namely, that laboratory-created states of superconductors, can sometimes be thermal equilibrium states to which thermodynamics can be applied, and at other times can be non-equilibrium but extremely metastable states, did not seem to be widely accepted for a number of years, although the Leiden hysteresis experiment should have suggested it strongly.

From the atomistic side, the leading quantum theorists after 1925 made various speculations, but in the great 1933 Sommerfeld-Bethe article in the Handbuch der Physik, Bethe discussed them, and found nothing that seemed to have any solid value.

It's amusing to note that what is probably the most memorable theoretical accomplishment of this period is a very simple argument by Bloch, whose conclusion was for a while quoted (somewhat inaccurately) as "superconductivity cannot exist."

The most citeable reference seems to be in the appendix to a paper by Brillouin in 1933, and the result seems not to have been universally appreciated for many years.

He assumed an electron system with any position-dependent interactions, moving in any potential field, but with no magnetic or spin-orbit interactions.

For such a system he showed that given any current-carrying eigenfunction, he could construct a zero-current wave function with lower energy.

The basis of Bloch's argument was to start out with an assumed ground-state wave function carrying a non-vanishing current, and then to show that one could always ~~construct a slightly different~~ <sup>make this</sup> wave function ~~with~~ <sup>in a way that</sup> lower <sup>it</sup> energy, making the original assumption self-contradictory.

The new wave function was obtained from the starting one by replacing the electronic part of the wave function by a wave function of identical



form but modified so as to impose a rigid motion with a velocity opposite that of the original electron flow.

Simple perturbation theory showed that the kinetic energy of the electrons would be decreased if the modification were carried out, while interaction energies among the electrons or between the electrons and the nuclei would remain unchanged.

However, this argument, quoted only second-hand, seemed, as I said, not to be widely appreciated.

Some continuing efforts to resurrect the idea of a current-carrying ground state—like these papers here—prompted David Bohm in 1949 to generalize Bloch's argument.

Bohm extended the zero-current theorem to apply to systems in thermal equilibrium at any finite temperature, and also to cover currents in a circular ring.

In a brief discussion of possible effects of magnetic interaction of electrons with each other, which had been neglected thus far in Bloch's work and his own, he was partially successful in showing that these would not affect the result.

Though this was still not air-tight for systems with spin-orbit coupling, it strengthened Bloch's position.

But unfortunately, it was largely wasted effort, because, as I shall explain, by the time of these papers here, the controversy over infinite conductivity had long been outdated.

VG 2a

In 1933, Walter Meissner, who had been working for a number of years in Berlin measuring superconductivity in many metals and alloys, and his colleague there, Robert Ochsenfeld, made a measurement of the magnetic field in the space between two single crystals of pure tin.

The crystals were cylindrical in shape, with their cylinder axes parallel.

They found that on gradually lowering the temperature  $T$  at constant applied field, the magnetic lines of force were suddenly totally expelled

from the cylinders when  $T$  passed through the transition temperature  $T_c$ , producing a more intense field between the cylinders.

This could not have been caused merely by a sudden development of infinite conductivity, because the constancy of the applied  $B$  field would forbid any  $E$  field from developing with time.

The phenomenon was reversible when  $T$  was raised.

So the superconductors must have been perfectly diamagnetic.

Realizing that this discovery could revolutionize the thinking about superconductors, and knowing that the Leiden group were doing closely related experiments, Meissner and Ochsenfeld published a brief paper as quickly as possible.

But awareness of the work and appreciation of its importance still spread rapidly.

Further experimentation completely confirmed the result, and a new set of conclusions, in harmony with the theorems of Bloch and Bohm, came to be widely, though not always wholeheartedly, accepted.

These conclusions were, first, that many, though not all of the measurements that had been made on superconductors could reliably be interpreted as measurements on systems in thermodynamic equilibrium, so that the laws of thermodynamics could be applied, and second, that superconductors often behaved like perfect diamagnets, expelling magnetic fields from their interiors by developing such distributions of currents in thin surface layers as to produce zero magnetic fields in the interior.

Adoption of this viewpoint led both to new types of experiments and to the formulation of phenomenological theories that could, with the aid of a few simple assumptions about the behavior of quasi-macroscopic fields in superconductors, give a very good quantitative account of a wide variety of experimental facts.

The most natural thing to do, at the outset, was to simply apply classical thermodynamics.

Some limited attempts to do this had already been made in earlier years, but now, after learning of the Meissner-Ochsenfeld results, Cornelius Gorter and Hendrik Casimir at Leiden developed a more intensive theory, using not only thermodynamics but also the assumption that the electrons of the superconductor could be divided into two classes, normal ones and superconducting ones.

It was now clear that the difference in free energy between the normal and superconducting phases at any temperature should be simply proportional to the square of the critical field at that temperature, and the transition between the two phases at zero field should have no latent heat but a specific heat anomaly proportional to the square of the temperature derivative of the critical field, etc.

The idea of distinguishing normal from superconducting electrons proved useful in stimulating two types of phenomenological theories.

I've continued to use green boxes for these and for some key experiments that tied in with fundamental concepts used in these theories.

The earliest of these theories, which had a long life and many successes, though it ultimately required some modifications, was proposed in 1935 by the London brothers Fritz and Heinz, who had just fled from Nazi Germany and taken up work at Oxford.

Not being a specialist in superconductivity, I made contact with the theory only a few years later.

I remember very well how impressed I was in the summer of 1940, when I had the opportunity, at the annual summer symposium on theoretical physics at the University of Michigan, to hear a series of lectures by Fritz London on the theory he and his brother had developed for superconductivity, and to take copious notes.

Although the equations were found to be inadequate in various cases later, and had to be modified or replaced, they were simple and provided insights that were very useful for many years.

To save time I'll have to limit my present discussion of their theory to a very brief statement of their key assumptions and equations.

VG 36  
Following earlier ideas, the Londons assumed that a superconducting metal contained two kinds of electronic fluids, normal, and superconducting, the quantities of each of these being conserved in the flow of currents at constant temperature.

The superconducting fluid was assumed to be frictionless and to respond locally to electric and magnetic fields at a rate inversely proportional to a single material-dependent constant  $\Lambda$  taking account of charge and mass densities.

These assumptions already required that in a certain easily describable gauge called the "London gauge,"  $\Lambda$  times the superconducting current density  $j$  should equal minus the magnetic vector potential  $A$  divided by  $c$ , a relation reminiscent of the theory of diamagnetism of atoms.

The behavior of the "normal" electrons was described by a conductivity constant, unimportant for steady-state situations because the  $E$  field would have to be zero to avoid accelerating the superconducting electrons.

With their new equations, plus of course Maxwell's, the Londons could predict the Meissner effect and calculate current distributions, and in particular, penetration depths, in terms of the  $\Lambda$  parameter of their theory.

With the Meissner effect now accepted and the London theory widely used, penetration depths started to get major attention.

So a number of different experimentalists devised several schemes for measuring penetration depths, and a large number of measurements were made, starting in the late 30's and continuing through the 1940's.

In 1953, Brian Pippard, at Cambridge, made an important discovery that forced the modification of the London equations.



Pippard was an expert at the measurement of the surface impedance of metals for high frequency electromagnetic waves, and you may remember, if you happened to hear Lecture VI of this series, how, a few years later, Pippard obtained the first map of the Fermi surface of copper from surface impedance data.

From his work with normal metals he had come to realize that because of the finite mean free path, an electric field acting only at one point could give rise to a current distribution extending an appreciable distance away from that point.

His measurements on superconductors, which sometimes departed significantly from the predictions of the London theory, might well, he supposed, have been affected by similar non-locality in the response of the super current to the electric field.

Specifically, he proposed replacing the London conclusion, that the supercurrent at any point should equal the vector potential  $A$  at that same point (in a certain special gauge) divided by  $c\Lambda$ , by a similar relation to an average of  $A$  over a region of diameter  $\xi$  centered on the given point, where  $\xi$  is a new "coherence length."

Well, so much for the London-Pippard type of theories, and the experiments by Pippard.

Now I want to switch to an entirely different area of development, which contributed great progress, although for many years it was confined to the Soviet Union.

The key step was a new type of phenomenological theory published by Ginzburg and Landau in 1950.

The basic ideas of the theory probably grew out of the thinking Landau had done over a number of years about order parameters in phase transitions and about the importance of a phase angle in the superfluid phase of liquid helium.

To save time, I'll skip mathematical details and just list their physical assumptions, describe qualitatively how they put them into a basic free

energy expression and then deduced from this a couple of equations useful for practical calculations.

The most basic of their assumptions was that the state of a superconductor can be described by a position-dependent order parameter  $\Psi$  that is a complex number.

They assumed the free energy per unit volume to be an analytic function of  $\Psi$ , with its minimum at  $\Psi = 0$  for  $T \geq T_c$ , and representable by the first few terms of a power series slightly beneath  $T_c$ .

All this is just for homogeneous material; inhomogeneities, if gradual, were assumed to increase the free energy density by a term proportional to the square of the absolute value of the gradient of  $\Psi$ .

Finally, the effect of a weak magnetic field was assumed to be of the same form as in a Schrödinger equation for particles of some effective mass  $m^*$  and some effective charge  $e^*$ .

With these assumptions, the final free energy density  $F$  looks like this equation here, where  $F_n$  is the free energy density of the normal state.

The only quantities on the right whose temperature variation is appreciable near  $T_c$  are  $\Psi$  and this coefficient  $a$ , which is taken to be proportional to  $(T - T_c)$ .

This makes the plot of the first three terms of  $F$  against  $\Psi$  look like the left diagram here if  $T > T_c$ , and like the right if  $T < T_c$ .

From this expression, many equilibrium properties of superconductors can be calculated by straightforward mathematics.

The first step is usually to employ one or both of the equations expressing the conditions on  $\Psi_{(r)}$  and the current density  $j(r)$  for which  $F$  is a minimum.

These equations, obtained by setting  $\delta F = 0$  for arbitrary  $\delta\Psi$  or  $\delta A$ , are written here and here respectively; the second has  $j$  on the left as a replacement for  $\text{curl } H$ .

So much, then, for what the Ginzburg-Landau equations are and how they got that way.

What's important is that they have really been extremely useful for several decades, despite their limitations to temperatures only modestly below  $T_c$  and to magnetic fields and inhomogeneities that are not too large.

Within this range of conditions, they can be used to calculate all sorts of macroscopic and mesoscopic equilibrium properties of structures made of a single superconducting material, in terms of the four material constants of the theory.

As you can see from our basic equation here, the constants are  $a$  (or rather, its slope with temperature),  $b$ ,  $m^*$ , and  $e^*$ , but as we now know and I'll explain later,  $e^*$  is always twice the electronic charge  $e$ , so there are only three that can vary from case to case.

Although there's not time for mathematical details, I can mention just a few of the simplest quantities that can be calculated in terms of these same three parameters.

One such is what is called the "thermodynamic critical field  $H_c$ " defined as the value of magnetic field strength at a given temperature at which the free energy of normal material plus a uniform magnetic field is the same as that of superconducting material with the magnetic field completely expelled from it.

Other general properties that can be calculated are the correlation length  $\xi$  of the London-Pippard theory, the distance over which fluctuations in  $\Psi$  produced by some local perturbation decay as one goes away from the perturbed region, and the familiar penetration depth  $\lambda$ , the distance over which the surface currents that screen the interior against an external magnetic field, decay as one goes in.

And of course there are all sorts of problems to calculate the distribution of magnetic field current and  $\Psi$ , for various geometries of superconductors and external sources.

Going beyond these routine applications was an important new discovery pointed out in a short paper by Alexei Abrikosov, a young theorist in Landau's group, in 1952.

Abrikosov called attention to some experiments that had been performed in 1936 by Schubnikov, one of the leading Russian experimentalists of his day, who unfortunately disappeared in the Stalin purges of 1937.

He had measured the magnetization of an alloy sample in various magnetic fields, and found unmistakable evidence that over a considerable range the superconducting material was not perfectly diamagnetic, but partially diamagnetic.

Western observers had found similar effects, and tried unsuccessfully to explain them as due to quasimacroscopic normal regions, as in the "intermediate state" of more familiar superconductors.

What Abrikosov noted was that the Ginzburg-Landau theory predicts that the partially diamagnetic behavior found by Schubnikov should occur if and only if the ratio of  $\lambda$  to  $\xi$ , a ratio commonly called  $\kappa$ , is greater or less than  $1/\sqrt{2}$ , these alternatives being called "Type II" and Type I," respectively.

Unfortunately, as I've noted before, Western scientists often ignored the Russian literature in these years. So Schubnikov's work and even Abrikosov's were for some years not followed up in the West, and it was only after Bruce Goodman in 1962 experimentally rediscovered some of the properties of Type II superconductors, that these properties and their explanation became widely appreciated.

Finally, in 2003, two of the three recipients who shared the Nobel prize in physics were Abrikosov, for his explanation of Type II behavior, and Ginzburg, for his work with Landau (an earlier Nobel laureate) on the Ginzburg-Landau theory.

So, let's take a look at what some of these properties are.

The simplest way to distinguish the two types unambiguously and measure the difference quantitatively is to measure the magnetization



of a long cylindrical sample with an external magnetic field imposed along its axis.

With this geometry, the magnetic field and magnetization are independent of position inside the sample and also outside of it, though the inside and outside values may be different.

For the Type I superconductors, which strongly predominated among the pure metals studied in the early years, the variation of magnetization with field is as shown in the green curve at the upper left.

The material behaves as a perfect diamagnet at low fields, with a magnetization opposite to the applied field and just sufficient to reduce the B field inside to zero.

Above the thermodynamic critical field  $H_c$ , the entire sample switches to the normal state, and its magnetic moment drops to the value corresponding to the normal typical para- or diamagnetism of a normal metal, which is too small to show on the scale of a graph of this sort.

For a cylinder of Type II superconductor, as shown on the right, the behavior is rather different.

Although the diamagnetism is again perfect at sufficiently low fields, when the external field rises above some characteristic value called  $H_{c1}$ , which is less than the thermodynamic critical field  $H_c$ , the negative magnetization suddenly lessens, and tails off gradually, past  $H_c$ , to a higher field  $H_{c2}$ , at which it finally becomes essentially zero, as shown by the red curve up here.

The distributions of the lines of magnetic force for the two types of superconductors are shown in the next pair of diagrams below.

For either Type, at low fields, there are no lines of force inside the specimen, except for the tiny penetration depth in the surface, and there is a uniform spacing outside, as shown in the left hand diagram by the purple lines.

And at high fields, the lines are uniformly spaced inside and outside.

For Type II, however, when  $H$  is between  $H_{c1}$  and  $H_{c2}$ , as shown here, there are lines of force everywhere, but the spacing is denser outside than it is inside, as shown by the orange lines in the right-hand diagram.

Actually, these patterns correspond only to a relatively macroscopic picture of the situation.

As Abrikosov showed in a 1957 paper, magnetic fields in the so-called mixed phase of Type II—the one pictured here—do not vary smoothly with position on a microscopic scale.

Rather, they penetrate in an orderly pattern of localized regions, which I have shown in the bottom diagram as they would look viewed along the lengthwise direction.

These regions, which are called "vortices" because each is surrounded by circulating currents in the superconductor, each contain a unit of magnetic flux, whose size, according to the Ginzburg-Landau theory, is  $ch/e^*$ .

We now know, though Abrikosov did not know at the time he wrote his paper, that because superconductivity is due to electron pairing, the proper value for  $e^*$  is  $2e$ .

Each vortex has a normal-metal core, where  $\Psi$  is zero, and the formation of separated vortices is a manifestation of a negative interfacial tension between the normal and superconducting phases.

Well now, having followed phenomenological theory and related experiments through some exciting times in mid-century, I should return to the continuing effort to understand the atomic-scale mechanism of superconductivity.

The years 1950-mid 1957 were in one sense a period of great discovery, in that the importance of electron-phonon coupling came to be realized, and some new experiments revealed important properties of electronic states of superconductors.

In another sense, however, these years continued to see a lot of misdirected effort by theorists.

YG 6a

In the year 1950, great attention was suddenly focused on electron-phonon interaction by several experimental papers on isotope effects and two theoretical papers, most of both initiated independently.

I've listed these and follow-up work in the orange boxes here.

The earliest papers to be published were two on the isotope effect in mercury, one by Emanuel Maxwell at the National Bureau of Standards, comparing ordinary mercury with almost pure mercury 198, and the other by Reynolds, Serin, Wright, and Nesbitt at Rutgers University, using samples with various degrees of isotopic separation.

The two groups were in touch, and intentionally had submitted their papers on the same day.

The first theoretical paper to be published, that of Herbert Fröhlich of the University of Liverpool, was submitted just a trifle too soon for him to have seen the experimental papers.

However, he learned about the experimental work while the paper was being processed, and was able to add a short paragraph in proof pointing out that the equations he had already written predicted a transition temperature inversely proportional to the square root of the isotopic mass, which was approximately the variation observed.

→ John Bardeen, the other theoretical author, <sup>working then at Bell Laboratories</sup> had actually begun to speculate about a possible role of electron-phonon interactions in superconductivity just as World War II was starting, but he published only a brief abstract on the subject before becoming involved in war work, and later, at Bell Laboratories, in semiconductor physics.

However, the idea remained in the back of his mind, and when he learned through personal contacts about the isotope effect experiments, he felt at once that he had been on the right track, and after some modification of his original ideas, he developed a theory by which it would be possible for electrons in a region very close to the Fermi surface to

lower the total energy of the system by coupling to small lattice distortions in such a way as to form states with wave functions extended over distances of hundreds of Angstroms and which had such small effective masses that in spite of their small numbers, they could yield a diamagnetism so large that it would be plausible for it to saturate at the perfect value  $\chi = -1/4\pi$ .

The transition temperature would be proportional to the inverse square root of the isotopic mass, in at least approximate agreement with the observations then available.

He published a letter-type paper as quickly as he could.

The details were explained in a full-length paper later in the same year.

Fröhlich's and Bardeen's papers both had similar expressions for the energy lowering due to the electron-phonon interaction, though the approximations made in the two calculations are quite different.

A more fundamental difference in the two approaches is that Bardeen concentrated on the perfect diamagnetism and did not discuss resistive currents, whereas Fröhlich ascribed superconductivity to finite-current states that were metastable.

Both found the ground state in the absence of a magnetic field to be current-free, in agreement with the Bloch theorem.

Soon after these papers, various people made criticisms, ostensibly fatal, of the calculational methods used, but most of these were eventually countered.

However, Schafroth, a Swiss scientist who moved to Australia, published an analysis of perturbation theory to all orders, and showed that the Fröhlich Hamiltonian would never yield the Meissner effect to any order in perturbation theory.

While this did not in itself prove the Fröhlich-Bardeen theory to be entirely wrong, it showed that straightforward perturbation theory would be inadequate.



A similar conclusion was suggested about the same time by some calculations of Fröhlich, but a safe way out was not obvious.

Suggestive though the work of both men was, no one succeeded in giving a completely logical argument for the construction of a state with superconducting properties—always, at one or more points, logic had to be abandoned in favor of pure intuition.

The ultimate disappointment of some of the best minds is typified by the discussion of the latest theories that Bardeen gave in his very scholarly review of superconductivity theory for the *Handbuch der Physik* in 1956.

He devoted surprisingly little time to his own theory, and concluded the entire article with the words "Some radically new ideas are required, particularly to get a really good physical picture of the superconducting state and the nature of the order parameter, if one exists."

Though their theories were very similar, the very thought of solving a problem that had been a mystery for many decades and baffled the best minds of the world was so exciting that the rivalry between Bardeen and Fröhlich was intense, though they were glad of any opportunity to talk to each other face to face.

I remember one day in the spring of 1950 when Bardeen had arranged for Fröhlich to visit him at his office at Bell Laboratories.

John had met Fröhlich at the railroad station and personally escorted him the remaining four miles to our building and into his office, which was adjacent to my own.

During the trip, he had started telling his guest about his own theory.

When they entered John's office, they saw, as John told me later, some newly delivered mail on his desk.

This included a large sealed envelope from the *Physical Review* offices, which John immediately opened, while Fröhlich looked on.

The contents turned out to be a copy of Fröhlich's paper, which the editors had just received and were sending to John with a request that he referee it.

John told me later that he was very relieved at the coincidence, since otherwise Fröhlich might have suspected that John had seen the paper earlier and was trying to steal some of the ideas and get them published quickly as a Letter.

At any rate, not much doubt remained regarding the importance of electron-phonon interactions for superconductivity.

So I have listed here one more paper that clarified this subject appreciably.

Bardeen had left Bell Laboratories for the University of Illinois in 1951, and among his first collaborations with his new colleagues there was a 1955 paper with David Pines taking proper account of electron screening, and showing that the interactions would indeed be such as to produce an effective attraction between electrons in states separated by only a small energy.

At about this time, theorists in other parts of the world were trying to construct alternative wave-mechanical models that would be more successful than those of Fröhlich and Bardeen in producing demonstrable superconductivity.

Stimulated by the similarity of superconductivity to the superfluidity of liquid  $^4\text{He}$ , which some Russians and others associated with Bose-Einstein condensation, Schafroth, Butler, and Blatt in 1957 proposed that a few electron pairs, forming spatially distinct bosons, could form a superconducting condensate.

(I'm sorry there wasn't room to list this on the transparency here.)

As I'll show in the next lecture, this sort of pairing would allow far too few of the electrons to participate.

Well, this is about all I need to say about the suggestive but not quite successful early efforts to construct a logically convincing theory of superconductivity produced by electron-phonon coupling.

But before I go on to the next and triumphal set of theoretical developments, I should mention briefly several experimental findings that gave important information about the nature of the superconducting state, though they were not crucial for the phonon-coupling model.

Theorists had speculated for some time that the ground state of a superconductor might be separated from the lowest-energy excited states by an energy gap of measurable magnitude and it had been argued, I think incorrectly, that the absence of a measurable Thomson effect for thermoelectric power would require such a gap.

But in the 50s there were several convincing experiments that I've listed in green boxes.

In 1953, the experimentalist Bruce Goodman in England published measurements of the thermal conductivity, whose rapid decrease at the lowest temperatures seemed to require activation of electron excitations across a gap.

In the same year, Brown, Zemansky, and Boorse, at Columbia University, published heat capacity measurements for niobium in the normal and superconducting states, and for the latter found the electronic contribution to be smaller at the lowest temperatures than expected from any of the available theories.

A quite different type of measurement was published in 1956 by Glover and Tinkham, working at Berkeley, who measured the optical transmission of films of superconducting lead and tin over a range of far infrared frequencies.

Though the normal and superconducting phases had very nearly the same transmission at quantum energies of the order of 15 or 20 times  $kT_c$ , the transmission of the superconducting phase became higher over

quite a range of lower frequencies and then suddenly lower at energies of just a few  $kT_c$ .

A rough analysis by Tinkham assuming an energy gap grafted on to a Ginzburg-Landau model suggested a gap of the order of  $3kT_c$ .

Various further energy-gap experiments were of course eventually conducted by various people with improved techniques and supplied a solid body of knowledge about the existence and magnitude of energy gaps.

But before I conclude this discussion of the pre-BCS years I'd like to say a few words about a few quite different experiments which, though less critical than the work on gaps, gave new information on the nature of superconductivity.

You may recall that in the history of magnetism, an important clue to the origin of ferromagnetism (though at first it was puzzling) was provided by measurements in 1915 and 1918 of the angular momentum associated with a given ferromagnetic moment.

Since the measured ratio seemed to correspond to a  $g$  factor of about 2, rather than to the value 1 that would be appropriate for an electron's motion in an orbit, this enabled physicists to conclude, after the discovery of electron spin, of course, that ferromagnetic moments consisted mainly of alignment of spins.

Since the diamagnetic currents at the surface of a superconducting specimen in a magnetic field give the specimen a net magnetic moment, one can test their nature by the same sort of measurement of the gyromagnetic ratio.

A measurement of the Einstein-de Haas effect—the change in angular momentum of a specimen when its magnetic moment is reversed—was made by Pry, Lathrop, and Houston at the Rice Institute, and published in 1952.



This confirmed the  $g$  value close to 1 that had been reported earlier by Russian workers, and in addition supplied the sign, which was that to be expected for the spin moment of negative electrons.

While this was of course what everyone expected, the feeling of ignorance about superconductivity that pervaded the physics community was at that time sufficiently strong that it was appreciably reassuring.

Another paper that I wanted to mention was an early example, and a frequently cited one, of a type of work that has proliferated greatly in more recent decades, namely, taking measurements of critical temperatures and fields and other properties of whole families of alloys or compounds, and trying to find significant trends with composition.

Bernd Matthias had come to Bell Laboratories a number of years earlier, applying his broad knowledge of a wide variety of materials, first to ferroelectrics, and later to superconductors.

In the work I've mentioned here, he found that there was a strong correlation of transition temperature, in alloys, with the average number of conduction electrons per atom.

There were peaks at about 5 and 7 electrons per atom, and very deep dips at about 2, 6, and 8.

General data collection on superconductors of course continued to grow in the fifties, and revealed a few further new properties and empirical correlations which I won't have time to discuss now.

But the great breakthrough that I mentioned at the start of the lecture was about to arrive.

The trigger for this breakthrough was the 1957 paper of Bardeen, Cooper and Schrieffer, work which was followed by what I called the "golden" decade in which theorists and experimentalists at many institutions clarified and extended this work and demonstrated that the new theoretical picture could not only account quantitatively for old observations but could also predict new effects.

The story of this decade is so rich that it can't be broken up and it will occupy my entire lecture XII, which follows this one.

## Reading times etc., Lecture XI (new)

pp 2.0-4.4" -- appreciated"  $28 \cdot 246 + 235 = 6 \frac{23}{60} \text{ m} = 6.38 \text{ m} / \text{w } 2.4 \text{ p} \rightarrow 2.66 \text{ m/p}$   
(possibly a little too fast, but not much)

$$\text{~~2.66~~ } 2.16 \times 29.6 = 78.7 \text{ m total written}$$

$$2.66 \times 21 = 55.9 \text{ m on manuscript.}$$

$$\left. \begin{array}{ll} \text{pp. 2.0-4.99} & 3.0 \text{ pp} \\ 11 \frac{1}{2} \text{ m} - 19.0 & 7.5 \text{ m} \end{array} \right\} 2.50 \text{ m/p}$$

$$2.50 \times 21 = 52.5 \text{ m for manuscript.}$$

pp 12-13, com. or names  
30+

Although I was not myself working in superconductivity, I got a rather early and sudden introduction to this work when Bardeen sent me a preprint of this paper, which was in press.

Even at first glance the idea of the paper seemed unquestionably new, and I felt one might ~~hastily look at it convinced me that it had a radically new idea, and when I combined this with my long-time respect for Bardeen's intuition and thoroughness, I felt the odds were pretty high that this would turn out to be the definitive explanation of superconductivity.~~

Now it was only about a year since Bell Laboratories had, for the first time, set up a department devoted specifically to theoretical physics, and it was a fairly strong one, with something like six or seven theorists in various areas of solid state theory, all or nearly all Fellows of the American Physical Society.

So I asked all of them if it wouldn't be a good idea to organize a little seminar, meeting perhaps once a week, to go through this paper bit by bit, with open discussion of each part as we went.

Although none of us had been working in superconductivity theory, we all were curious about such a long-lasting puzzle, and ~~with one exception~~, everybody supported the idea of a seminar, ~~though one said he~~

~~The one exception, though interested in the subject, was so fed up with previous unsuccessful theories that he feared it would be a waste of time to study one more. attempt that would probably be doomed to failure.~~

So we went ahead, and I think nearly everybody became finally convinced that despite one or two puzzling questions that remained, BCS was indeed a critical breakthrough.

The next few years confirmed this expectation spectacularly.

I won't try to reproduce their arguments in any detail now, for two reasons.

But in discussing the original BCS work,

One reason is that they are widely reproduced in most courses and textbooks dealing with superconductivity, and many of you will have been exposed to such already.

My other reason is that the real content of the theory can be made much more transparent by reformulating it along lines that were developed by others a few years later—lines that are both simpler and more general.

But my preference for explaining superconductivity in the language of these reformulations in no way implies any doubt about the credit that should be given to BCS for making the key breakthrough.

As I hope I can make clear in the course of my description, BCS for the first time proposed an explicit wave function for the superconducting state that could in principle be explicitly calculated from knowledge of the normal-state band

So naturally I have an obligation to say something at this point about the reasoning used by BCS and especially to present the equations that describe their principal results, which I'll have to use over and over again in discussing further progress of the field.



structure and phonon modes of any given metal, and which would give, when perturbed by an outside field, a full Meissner effect and other superconducting properties, such as a calculable penetration depth.

So let me begin by *stating a few key facts about the original BCS theory and some simple extensions of it.* ~~talking about several early reformulations of the mathematics of BCS theory, which I have put in the green boxes.~~

Actually, these are only a few of very many papers of this type, but think the ones I've chosen contain the main ideas, though they may have been influenced by a lot of contributions by others.

~~Please *omit* these.~~  
Of these few, the earliest in time were a pair of independent but similar papers by Nikolai Bogolyubov and by T. G. Valatin, respectively.

Bogolyubov, in Russia, led a group of theorists similar to the one that formed around Landau, though perhaps a little more mathematically oriented; Valatin in England, had a strong interest in the nuclear many-body problem.

*Q: Grackph?*  
What Bogolyubov and Valatin showed was that the ground-state wave function *I've called* ~~used~~ *by BCS* ~~which was a variational form with parameters to be chosen to optimize the energy, could be written in a form very analogous to that of a Hartree-Fock wave function that people had been using for years to get approximate solutions for problems with many interacting electrons.~~ *could be characterized as the vacuum state of a new set of fermion operators.*  
I have sketched the idea here.

*VG 108*  
*VG 75*  
We have to start, of course, by writing down the explicit form of the wave function proposed by BCS.

*The wave function proposed by BCS was*  
It is what had seemed to them to be a natural approximation to conform to two physical ideas.

One of these was that an appreciable number of electrons should occupy a pair state and the other was that it would be energetically advantageous for this *spin singlet* pair state to be a ~~singlet~~ in which the amplitudes of states with opposite wave vectors and near the Fermi surface would all be of the same sign.

*any two*  
The latter requirement grew out of the fact that such a  $\mathbf{k}$ ,  $-\mathbf{k}$  pair of electrons could always scatter off each other by absorbing and re-emitting a phonon of wave vector  $\mathbf{k}' - \mathbf{k}$ , if the energy difference between the  $\mathbf{k}$  and the  $\mathbf{k}'$  electrons was less than the phonon energy.

It's of course necessary, if one wants to get this beneficial effect, to start from a wave function that has the states  $\mathbf{k}$  and  $-\mathbf{k}$  occupied, and the states  $\mathbf{k}'$  and  $-\mathbf{k}'$  unoccupied.



I'll discuss the correction of this approximation in a few minutes, but while I'm on this transparency I want to point out that a variational wave function of essentially this same form would be appropriate for any theoretical model for which superconductivity is produced by any electron-electron interaction  $V(r_i - r_j)$ . Moreover, one can even consider the possibility of pairings other than  $k_F, -k_F$ .

So it was not unreasonable for BCS to assume, as a parameter-dependent wave function to be adjusted to achieve minimum energy, a wave function of the form I've shown here, with a linear combination of empty and paired states for each wave vector  $k$ .

In such cases one needs only to replace this product here of two creation operators by an arbitrary pair  $c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger$  and the coefficients  $u_k/v_k$  by an element  $c_{kk}$  of an antisymmetric matrix. Note that all spin states are covered: if we fix our attention on a particular wave vector  $k_0$ , the up-spin state with this wave vector will be covered when  $k = k_0$  in the summation, and the down-spin state at  $k_0$  will be covered when  $k = -k_0$ .

matrix, again to be chosen to optimize the energy.

The state labeled  $|0\rangle$  on which the creation operators act is of course simply the vacuum state with no electrons present.

The  $u_k$  and  $v_k$  here can be taken to be real numbers, and if the wave function is to be normalized, the sum of their squares should be 1. *in general complex though a suitable choice of phases of the Bloch functions can make them all real*

Subject to this constraint,  $u_k$  and  $v_k$  are determined by two further conditions, namely, that the expectation value of the total number of electrons be the appropriate number for the specimen under consideration, and, most importantly, that the total energy be minimized.

As regards the former of these conditions, you can easily see that the wave function is a linear combination of states with different numbers of electrons, from zero on up, since if one expands the product of operators given here, one will get a sum of terms with no  $c^\dagger$ 's, with two  $c^\dagger$ 's, with four  $c^\dagger$ 's, etc., etc.

If there is a range of  $k$ 's for which  $u_k$  is small and  $v_k$  nearly 1, practically all the Bloch states in this region will be occupied, just as is the case inside the Fermi surface of a normal metal, whereas if there is a range of  $k$ 's for which  $u_k$  is nearly 1 and  $v_k$  is small, these Bloch states will be nearly all unoccupied, just as is typical for states outside the Fermi surface of a normal metal.

It turns out that only for  $k$  vectors very close to the normal Fermi surface will there be sizable opportunities both for  $k$  up and  $-k$  down to be occupied and for neither to be occupied.

And only some of these pairs can be used in constructing a macroscopically occupied pair state, which I'll discuss in more detail in a minute.

Having thus described the BCS ground state wave function, I'd like to call attention to two mathematical properties of it that were pointed out by other workers within a year of the publication of BCS.

In each case, the discovery was made independently but nearly simultaneously by two or more independent workers or groups.

The Although the 1957 BCS paper considered only the case where the mutual attraction of paired electrons was produced by electron-phonon interaction, but to simplify the mathematics it replaced this interaction, which is actually time-delayed and non-local, by a simple position-dependent interaction  $V(r_i - r_j)$ .



There's a handy mathematical theorem, proved in these papers here, that says that any antisymmetric matrix  $c_{\alpha\beta}$  can be brought into block-diagonal form by a unitary transformation.

Small Greek  
alpha  
beta  
phi

In physicists language this means that with proper choice of the one-electron basis functions,  $c_{\alpha\beta}$  will be a diagonal set of  $2 \times 2$  matrices, as shown here.

Small Greek  
alpha  
beta  
phi

So state 1 is paired with state 2, state 3 with state 4, etc.

The many-electron state we've been talking about has the perhaps unfamiliar property of being a linear combination of states with all different values of the number  $N$  of electrons. While this property is useful in some situations that I'll mention later, it is sometimes convenient to work with a wavefunction limited to a single value of  $N$ , which can be simply the projection of  $\Phi_{BCS}$  onto the subspace with this  $N$ .

Cap Greek phi

Such a wavefunction, not normalized, is shown in the bottom equation here, and is sometimes called the Blatt wavefunction,  $\Phi_B$ .

So much for what one might call the "bare bones" of BCS. Its publication at once stimulated a rush by theorists ~~back~~ to develop new ideas about the mathematics of the theory or ~~and to~~ broaden its applicability to new physical conditions and phenomena.

publish a lot of independent but often overlapping papers, either

I've listed a few of the mathematical contributions in the green boxes over here.

Two of the earliest, and one might say "cutest," were made by

Enter material  
transferred from  
p.22



Any number of authors wrote papers from different viewpoints expanding different variations of the BCS ideas and equations, and the papers I have listed in the green boxes are only a selection, but I think they are sufficient to convey the main ideas. ~~None of these~~ ~~I'll take up later.~~

This is a striking testimonial to the excitement that the BCS work produced in the scientific community.

Insert  
sentences  
from p. 22

What Bogolyubov and Valatin did was to express the BCS wave function in terms of a new family of operators, which they defined in terms of the more familiar electron creation and destruction operators, which we've been using and representing by  $c^+$ 's and  $c$ 's.

The new operators still retained the label of a wave vector and a spin, but were defined as linear combinations of a creation and a destruction operator for electrons, as shown by this equation here.

For a given wave vector  $k$  and spin  $s$ , the typical new operator  $\gamma^+$  was defined as  $u_k$  times  $c_{ks}^+$  minus  $v_{ks} c_{-ks}$ .

Here  $u_k$  and  $v_k$  had essentially the same meaning as I have indicated above for the BCS wave function, but could simply be any two numbers whose squares added to 1. *small 5-10% fanning*

As one can easily verify, they and  $\gamma^-$  operators satisfy the standard fermion anticommutation relations, and every  $\gamma^-$  operator takes the BCS wave function into 0, as written here.

Another useful thing that was pointed out independently and almost simultaneously by Bruno Zumino in the United States and by Bloch and Messiah in France.

Any two-electron state can be represented as a linear combination of all possible products of one-electron states, suitably antisymmetrized or in other words, to the effect of an operator of the form I have written here on the vacuum state, where  $\alpha$  and  $\beta$  run over all states of an orthonormal set of one-electron states, and  $\phi_{\alpha\beta}$  is an antisymmetric matrix.

The theorem states that the choice of one-electron bases can always be made in such manner that the matrix  $\phi$  is zero everywhere except in a row of two by two squares along the diagonal, each square containing a two by two antisymmetric matrix with real components, as I have shown here.

Various other papers were published around this time on similar mathematical properties, especially on how to rectify the apparent lack of gauge invariance in the BCS mathematics.

This latter subject need not have been a worry, since, just as in the formulation of the Ginzburg-Landau theory, anything derived from wave mechanics has to be gauge invariant if changing the electromagnetic field variables to a new gauge is always accompanied by a corresponding change in the phase of the wave function.

But I do want to mention one paper for its value in dealing with a different subject, namely the one- and two-electron density matrices of a BCS-type system.

After above sentence ending " --- as written here", type the three sentences at the bottom of the next page (now numbered 24).

First draft pages 25, 26, and 27 were (correctly) omitted, and so after the last of the "p. 24" sentences, second draft continues with the sentence "All the post-BCS ..." which you already turned into "All the



This is a striking testimonial to the excitement that the BCS work produced in the scientific community.

What Bogolyubov and Valatin did was to express the BCS wave function in terms of a new family of operators, which they defined in terms of the more familiar electron creation and destruction operators, which we've been using and representing by  $c^+$ 's and  $c$ 's.

The new operators still retained the same form as linear combinations of a creation and annihilation operator as shown by this equation here.

For a given wave vector  $\mathbf{k}$  and spin  $s$ , the new operators are defined as  $u_{\mathbf{k}} c_{\mathbf{k}s}^+ + v_{\mathbf{k}} c_{-\mathbf{k},-s}$ .

Here  $u_{\mathbf{k}}$  and  $v_{\mathbf{k}}$  had essentially the same meaning as in the BCS wave function, but could satisfy a different equation.

Another useful thing that was pointed out by Bruno Zumino in the United States was that

Any two-electron state can be represented as a linear combination of all possible products of one-electron states, suitably antisymmetrized or in other words, to the effect of an operator of the form I have written here on the vacuum state, where  $\alpha$  and  $\beta$  run over all states of an orthonormal set of one-electron states, and  $\phi_{\alpha\beta}$  is an antisymmetric matrix.

The theorem states that the choice of one-electron basis can always be made in such manner that the matrix  $\phi$  is zero everywhere except in a row of two by two squares along the diagonal, each square containing a two by two antisymmetric matrix with real components, as I have shown here.

Various other papers were published around this time on ~~similar~~ <sup>other</sup> mathematical properties, especially on how to rectify the apparent lack of gauge invariance in their ~~formulation~~ <sup>of BCS wave functions</sup>. ~~BCS mathematics.~~

On this latter subject

Ginzburg-Landau theory, anything derived from wave mechanics has to be gauge invariant if changing the electromagnetic field variables to a new gauge is always accompanied by a corresponding change in the phase of the wave function.

So I'll skip the gauge-invariance literature and proceed to what I feel is the most important paper of the mathematically oriented group, namely the one and two electron density matrices of a BCS type system.

the most important paper of the mathematically oriented group.

Prof. Herring,

There were 2 page 24s, so I didn't know where to put this in. Laurie

defined  
ons, as

as  $u_{\mathbf{k}}$

for the  
ded to

sly by

see preceding  
pg 24

*Delete this page entirely*

As most of you probably know, density matrices are a very convenient way of describing the physically important aspects of a complicated many-body wave function or mixture of wave functions.

*VG:llr*

Let's just recall what density matrices are.

Suppose we have an  $N$ -electron system, in a quantum state described by some wave function  $\Psi$  depending on the coordinate and spin variables of all the different electrons, which I have for brevity called  $x_i$ .

Suppose we want to determine the expectation value of a one-electron operator, in other words, an operator  $V$  that is a sum of contributions from the individual electrons taken one at a time, as shown here.

The operator  $V$  is representable as a summation of all the matrix elements of the operator  $v$ , each multiplied by the corresponding product of a creation operator for the one state of the matrix and a destruction operator for the other.

Then the expectation value of  $V$  is, just as I have written here, the trace of the product of the one-electron matrix by the expectation value, in the state  $\Psi$ , of the corresponding product of a creation and a destruction operator, as I have shown here.

This latter expectation value is what is called the first-order density matrix of the system in this state.

Similarly, if one is interested in the expectation value of an operator given by a sum of identical operators acting on all the different pairs of electrons—the electrostatic interaction energy of the electrons would be an example—one can again describe the operator for a single pair of electrons by its matrix element between two quantum states of a pair, and if these are described by a pair of single-electron states, then the desired expectation value for the many-electron system can be written as the trace of the product of the one-pair matrix here and what is called a two-electron density matrix, defined by the equation on the bottom line.

One could go on defining higher and higher-order density matrices, but it turns out that nearly all the quantities one is interested in can usually be obtained from the  $\rho^{(1)}$  and  $\rho^{(2)}$  I have written here.

There is one more simple thing I should say.

Suppose, as sometimes occurs, we are interested not in a single quantum state of our system, but in an ensemble of quantum states that it may occupy with various probabilities but no phase relation among them, such as, for example, a thermal equilibrium ensemble.



Delete this  
page entirely

Obviously, one can just define density matrices for the ensemble by taking a suitably weighted sum of the density matrices for each of the various quantum states in the ensemble, and then use the density matrix in just the same way that we would for a pure state.

Well now, getting back to the subject of BCS type wave functions, I should mention a very useful 1963 paper by Michel Baranger, a French nuclear structure theorist who became interested in superconductivity theory as a possible sources of ideas for the nuclear many-body problem.

At about this time he emigrated to the United States.

In this paper he studied two types of ground-state wave functions.

One, which he called the "Hartree-Bogolyubov" form, was one I mentioned a few minutes ago, in connection with citation of Bogolyubov's 1958 introduction of Fermion operators that were linear combinations of electron creation and annihilation operators, where the superconducting ground state could be written as simply the vacuum of the family of Bogolyubov Fermions.

This ground state, you recall, was a superposition of states with all different numbers of total electrons.

The other type of ground state wave function considered by Baranger was simply the projection of this one onto the subspace with a particular number  $2N$  of electrons.

This is what he called the "Blatt" wave function, and it was already well known that it was given, in an unnormalized form, by applying this creation operator here  $N$  times to the vacuum state.

Notice that this is the same creation operator that we used, in a somewhat different manner, to create the Hartree-Bogolyubov ground state.

Now Baranger's important contribution was to derive simple formulas to express the expectation values of various products of electron creation and annihilation operators in either type of ground state in terms of the pairing matrix that I've called  $\phi$ .

I will quote some of his main results without proof, and even at risk of boring some of you with a lot of detail, but my main purpose is simply to give you a feel for the existence of a tool that will enable anyone who wants to propose any sort of model for a superconducting material and is willing to use a wave function of either of the types described here to compute ground-state averages of physical quantities once a choice has been made of which states are paired and how the strength of the pairing varies among these.

VG 128

Delete this  
page entirely

If one is using a Hartree-Bogolyubov model, it is convenient to define two types of matrices relative to any complete orthonormal 1-electron basis, the first, which he called  $\rho$ , being given by this equation, which you will recognize as the same as the definition of the 1-electron density matrix  $\rho^{(1)}$ .

The second type of matrix, for <sup>which</sup> he used the symbol  $\kappa$ , is defined somewhat similarly, but using two annihilation operators or two creation operators, instead of one of each, so that it is really a matrix element between portions of the wave function having different values of the electron number.

I've indicated some symmetries here for both of these.

He then showed that these would be given by the expressions I've written in the red box, in terms of the pairing matrix  $\phi$ .

He also showed that  $\rho$  and  $\kappa$  satisfy the equations in the purple box, and that any  $\rho$  and  $\kappa$  matrices with the proper symmetries that satisfy these two equations and have trace  $\rho = 2N$  determine the  $\phi$  matrix completely.

Especially important is the equation in the green box, which expresses the 2-electron density matrix in terms of the  $\rho$  and  $\kappa$  matrices.

All these could of course be expressed in terms of the  $\phi$  matrix, using the equations above.

This can be used to calculate the expectation value <sup>of</sup> ~~the~~ electron-electron interaction energy.

Incidentally, I've here corrected a typographical error in Baranger's paper.

Now all these formulas I've been talking about, especially those in the colored boxes, were derived for the case of the Hartree-Bogolyubov model.

For the Blatt model, the steps in the derivations had to be somewhat different, but the conclusions were for practical purposes the same.

While the same definition could be used for the  $\rho$  matrix as in the Hartree-Bogolyubov case, after suitable normalization of the wave function, the previous definition of the  $\kappa$  matrix would give identically zero, because the Blatt wave function contains only one value of the electron number.

Although Baranger's primary definition of this for the Blatt case involved a diagrammatic expression, for practical purposes one could just as well use the expression in the red box in terms of the  $\phi$  matrix.



With these definitions, all the equations in the colored boxes here turn out to be correct in the large- $n$  limit for the Blatt model.

Now I want to take up a very important paper.

<sup>post-BCS</sup> All the theoretical work I've discussed so far, on superconductivity, the material in the green boxes, has used the BCS model, or the minor generalizations of it used in this viewgraph over here, and nearly all the subsequent work that I'm going to discuss devoted to other physical conditions or novel effects, has done the same.

But this paper of C. N. Yang in 1962 undertook to do something more general.

As you may remember, Yang had recently shared, with his collaborator T. D. Lee, the 1957 Nobel Prize in Physics, for their work on non-conservation of parity in elementary particle physics.

Both of them were very versatile theorists, and had even earlier made historic contributions to the theory of phase transitions in condensed matter.

Although undoubtedly Yang, like all fundamental theorists, had been fascinated by the BCS breakthrough, his interest was undoubtedly further stimulated by a visit that he spent at Stanford in early 1961 when Bill Fairbank and Bascom Deaver were doing their history-making experiment on the quantization of flux in superconducting circuits, experiments which I'll discuss in a few minutes.

He had many discussions about this and other aspects of superconductivity with the experimentalists, with Felix Bloch, and with others.

<sup>I want to talk about</sup> The Yang's paper, which appeared in an issue of Reviews of Modern Physics dedicated to Eugene Wigner on his 60th birthday, started out with a description of a number of important properties of 1-particle, 2-particle, and higher order density matrices of general systems containing fermions, bosons, or both.

I'll concentrate on systems containing fermions only, presenting first, without proof, some simple algebraic limits on the bounds of the eigenvalues of the matrices, then showing, using the BCS type of theories as an example, a demonstration that some of these bounds can in practice be reached, and then show how in such cases systems can actually show a quantum type behavior on a macroscopic scale, which is what is needed to explain superconductivity.

So here goes.

<sup>some definitions</sup> Just as a reminder, I've repeated at the top, the definition of the 1-particle density matrix  $\rho^{(1)}$  <sup>For example,</sup> as the expectation value of the product of a creation operator and a destruction operator for single-particle states of the fermions or bosons being considered.

~~is already given quantum state or ensemble~~

A common use of density matrices ( $\rho^{(1)}$  and  $\rho^{(2)}$  especially) is to express the statistical expectation value of any operator that treats all particles alike, since any such operator can be expressed in terms of the single-particle creation and destruction operators.

The expectation value is that in a particular quantum state, perhaps the ground state, or in a thermal ensemble of states.

Similarly, as I showed you previously, one can define a 2-particle density matrix as an expectation value of a product of two creation and two destruction operators and so on for 3-particle and 4-particle density matrices, etc., with the general form I have shown at the right, here, and here.

Thus any one-particle  $V$ , definable by this equation here, has the expectation value  $\langle V \rangle$  in terms of  $\rho^{(1)}$  and any two-particle operator  $U$ , definable by this equation has this expectation value in terms of  $\rho^{(2)}$ .

Since the matrices are always positive semi-definite, these normalizations give upper bounds to the largest eigenvalues of density matrices of different orders, which I have designated by  $\lambda$ 's with the appropriate superscripts.

But since we have a special interest in the possibility of large eigenvalues, of the order of  $N$  for a macroscopic system, which will go with degrees of freedom corresponding to macroscopic behavior, we would like to know also, whether there are useful lower bounds to any of the largest eigenvalues.

Using elementary algebra, Yang derived a number of such lower bounds, some of which I've written down here using green for bosons and red for fermions.

You don't need to worry about all the details; I'll just point out a couple of noteworthy features.

One thing that is of course very obvious but that deserves mention anyway, is the fact that  $\lambda^{(1)}$  is not forbidden from being a large number for a many-boson system, but is limited to being no greater than 1 for a many-fermion system because of the Pauli exclusion principle.

So liquid  $^4\text{He}$  can have a macroscopic occupation for a single 1-particle state, but liquid  $^3\text{He}$  cannot, nor can a many-electron system.

Note here that  $\lambda^{(2)}$ , in contrast, is not forbidden to be a finite fraction of  $N$  for fermions.

Thus, macroscopic occupation of a pair state is allowed, and, as I will show in a minute, is what occurs for the BCS wave function.

It also occurs, though in a different manner, for superfluid  $^3\text{He}$ .



Here are some of the more important of these fields, listed in the boxes on the left hand side, with areas very crudely proportional to the volumes of research work being done in them.

Most conspicuous here is the area at the top in the orange box, and encompassing the properties and phenomena involving solid surfaces, interfaces between different solids, and thin solid films.

These can be structural, thermodynamic, electrical, or magnetic properties, and their mutual correlations.

This happens to be an area which has been of especial interest to me for many years, and I love to talk about it, so why did I leave it out?

For one thing, of course, the lecture series was getting too long.

But I didn't want to ignore any area whose development had an important effect on the development of the areas I did discuss.

And it seemed to me that very rarely had the development of understanding of bulk properties of solids been significantly influenced by prior advances on surfaces and interfaces.

So I omitted discussion of this field, although it has been a field of great importance and excitement, and its activity has grown greatly over the years because solid-state devices practically always involve surfaces and interfaces, especially with the current trend toward miniaturization.

And a succession of developments in experimental techniques for making reproducible clean surfaces and measuring atomic arrangements on them, has changed the field from a "dirty" science more and more toward a science of precise measurement.

In the few remarks I'll have time to make now on this field, I hope I can convince you that it's not dull, and sometimes reaches discoveries or insights that just make you say "gee whiz."

I've listed some examples in the column at the right.



One development, that I think I've already mentioned in these lectures, is the one known as STM, or scanning tunneling microscopy, a very powerful tool for studying the atomic surface structure of crystals with or without adsorbed atoms.

You've probably all seen lots of STM pictures and know the general physics of how they are produced, so I won't go into details describing them.

But there's one historical point I'd like to stress.

For many years experimenters had considered such a measurement essentially impossible, because they were unable to control the relative positions of the two electrodes to within a fraction of an angstrom, so vibrations from the outside world would cause uncontrollable fluctuations.

Finally, in 1982, Gerd Binnig and his colleagues at the IBM laboratory in Zurich succeeded in solving the problems of vibration and control by installing the vacuum chamber on a heavy stone bench floating on inflated rubber tubes and then isolating the electrode systems within it by static magnetic levitation inside a large superconducting lead bowl.

Relative motion of the experimental tip and the surface being studied was achieved piezoelectrically.

The first experiments simply verified the sensitivity and reproducibility of the variation of tunneling current with position, but further experiments soon aided by a simple theory due to Tersoff and Hamman at Bell Laboratories, opened up a dazzling world of new knowledge about atomic positions on metal and semiconductor surfaces.

→ *What's more,*

<sup>^</sup> But the formula also shows that in some cases useful information about the band structure and wave functions can be obtained.

But this isn't all.

A few years later, the existence of the STM gave rise to a second-generation technology that made possible the measurement of extremely small interatomic forces at surfaces, the technology called “atomic force microscopy.”

This was developed in 1986 by a collaboration of Binnig, Quate, and Gerber, the first and last authors being on leave from IBM Zurich.

Probably, many of you are familiar with the experimental procedure, but for others I’ve shown here a simplified picture of it.

The surface to be studied is placed here on the left and a moveable tip, very sharp, attached to a cantilever with a very soft spring constant, can be moved to any desired position at a small atomic distance from the surface, where it will feel attractive or repulsive forces from the surface atoms.

These forces will move the tip toward or away from the surface through a distance proportional to their strength, and the distance moved can be measured by a scanning tunneling microscope tip on the far side of the cantilever, and from this distance, with knowledge of the elastic constant of the cantilever, one can infer the strength of the force.

In practical use, it is usually convenient to introduce feedback controls and often to use a modification of the resonant vibrations of the cantilever by the force being measured to obtain greater accuracy.

Eventually, much useful information on van der Waals, ionic, and repulsive interactions has been obtained by force microscopy.

Now, just for variety, I’d like to mention a totally different type of surprise in the form of a new phenomenon that was predicted and then observed in Russia some years ago, the phenomenon of crystallization waves.

When a crystal is in static equilibrium with its melt, at constant temperature, the most stable configuration of the interface is simply a flat plane, at least locally since this is what minimizes the surface area and hence the interfacial free energy.

If some perturbing influence like inhomogeneous stress or temperature distorts the interface into some other shape and is then removed, the interface will relax back gradually to its flat configuration, normally by some combination of melting where convexities project into the melt and solidification where concavities project into the crystal.

These relaxation processes have to be accompanied by tangential motion of material within the liquid phase or possibly within the solid phase since in equilibrium both phases are uniform.

These processes are slow, because they involve things like diffusion and thermal conduction, which are dissipative.

However, in 1978, Andreev and Parshin, at the Institute of Physical Problems in Moscow, made the point that if the melt is liquid  $^4\text{He}$  in its superfluid phase, the  $^4\text{He}$  chemical potential must remain uniform and no entropy production by diffusion or viscosity can occur.

Because the boundary condition for melt-solid equilibrium across the interface is different in the convex and concave regions, a thermodynamic parameter of the solid must be different in those two regions, and this can lead to a dissipative transport of some kind in principle.

However, damping from such transport can be slow enough to allow a number of cycles of oscillation to take place before the up and down curvature of the interface is damped out.

The oscillations, like capillary waves in water, are of course due to the interplay of the kinetic energy of motion due to transfer of material between solid and liquid when the densities of the two are different, and the potential energy of the solid which, as I mentioned a minute ago, is varying as the interface moves, and to which must be added a gravitation term if the surface is horizontal.

When gravitation is absent or negligible, the dispersion law for propagation of crystallization waves turns out to be frequency proportional to the three halves power of the wave vector.

→ In the following year, experiments by Keshishev, P. Parshin, and Bobkin, also at the Institute for Physical Problems, verified the existence of crystallization waves and the correctness of the predicted dispersion law.

Well now let me leave surface and interface physics and go into the other subfields that I've listed on the left.

I'll treat all of these similarly, listing for each subfield one or more exciting developments on the right, skipping explanations of effects I think most of you are familiar with, and sketching quickly the physics of the others.

The brown box here has to do with what is today quite a major field, disordered media such as glasses, effects in crystals dominated by randomly distributed defects or impurities etc.

This area used to be what Pauli called a "dirty" field, namely one that was so complicated that one couldn't hope to describe much of it with simple or elegant theories.

But in recent decades, more and more elegant and general theorems are being proved.

One of the earliest was the phenomenon known as "Anderson localization."

In a 1958 paper, Phil Anderson undertook to formulate mathematically the problem of migration of an electron in the so-called "impurity band" of a semiconductor, a problem essentially identical with that of migration of a preferred spin polarization among dilute magnetic impurities.

→ He showed that if the variations in binding energy to different impurities were limited to a range not too large compared to the matrix elements for hopping to a near neighbor impurity, an electron could migrate an unlimited distance in the course of time but that for larger variations it could not.

delete { As an example for the electronic case I shown here a random positioning of impurity atoms, shown as black dots, and part of one of the many possible trajectories that an electron might follow, hopping successively from one to another of these atoms.

→ In this formulation of the problem the starting wave function was not a stationary state, but rather a superposition of many stationary states with energies in a narrow



range close to the energy of an isolated impurity level, the broadening being of course due to the ~~coupling term  $V$  in the Hamiltonian~~ between the states on different impurity atoms. **confinement.**

**Migration to infinity thus means that at least one of the constituent energy eigenstates has infinite extension.**

~~These states do not all have the same energy, because the electrostatic potential varies from one impurity site to another, producing a random spread of energies over a range whose width has some order of magnitude  $W$ .~~

**Randomness in the impurity energies and positions greatly simplifies the calculation of trajectory probabilities and the evaluation of averages, and**

**Now comes the all important tricky point, namely, that for some systems most of the imaginable hopping trajectories are of extremely low probability, makes the result essentially independent of the starting point.**

~~When  $n$  is large, the time  $t$  is also large, and the portion of the wave function remaining on this particular trajectory must consist mostly of eigenfunctions of the total system whose energies span a narrow range of order  $\hbar/t$ .~~

~~The hop to position  $(n+1)$  will be possible only if the atom at this position has an energy level in this narrow range, rather than somewhere else in the range  $W$ .~~

~~This probability will become very small as  $n$  increases, and the question is whether this can be compensated by the increase in the number of distinct paths as  $n$  increases.~~

~~To answer this question Anderson undertook to formulate the problem mathematically and solve the resultant equations.~~

~~It turned out that there is a critical value of the ratio of the mean hopping matrix element  $V$  to energy spread  $W$  below which diffusion to an infinite distance becomes impossible.~~

~~This critical value, which I've called  $f$  here, of course depends on the detailed properties of the system, such as the crystal structure.~~

~~This result has some important qualitative corollaries~~

**example,** One such, which is quite obvious, is that for a one-dimensional lattice, **randomness will always make diffusion to infinity will always be impossible**, since the number of

**Although Anderson's calculations were based on rather restrictive assumptions, the general idea that randomness can cause localization seems to be valid in a wide variety of situations.**



possible diffusion paths does not increase with the number of steps already taken.

Another corollary, one that is very important for semiconductors, is that as one moves away from the center of an electronic band toward the region of forbidden energies, there will always be a definite energy beyond which no mobile electronic states exist.

This energy is called the "mobility edge."

This is essentially because as the energy gets farther from the center of the band, the spacing of impurities with this energy gets larger and larger, and the tails of the impurity wave functions decay more and more sharply.

→ For both these reasons, the hopping matrix element  $\overline{H}_{ij}$  gets smaller and smaller, *adding further to the advantage of localization over migration.*

Now I should go on to some of the other fields.

The next box is for the various kinds of magnetic resonance, which I have touched on at several places in the previous lectures, notably the one on magnetism last month, but I left out a lot of interesting things in nuclear resonance.

A particularly cute phenomenon here is the <sup>production</sup> ~~phenomenon~~ of spin echoes, ~~where spins are~~ with which I think most of you are familiar.

The time evolution of the wave function of an electron initially at a particular site can be calculated by solving its time-dependent Schrödinger equation, which for each step has a term describing the ~~case of the hop~~ ~~and~~ ~~a term~~ energetic advantage of coupling the two sites and a term taking account of their energy difference.

What one has to do is to consider the <sup>spatial distribution of the</sup> ~~average~~ ~~the~~ ~~result of such~~ ~~calculation~~ ~~for a very long time, and average~~ ~~this distribution over the random distributions of~~ ~~the locations of the impurity sites, and~~ <sup>of</sup> ~~their~~ energies.

One can then see whether <sup>as time increases to infinity</sup> this average electron distribution grows indefinitely in width or whether there is a fixed volume within which nearly all of it remains.

We can call these the migrating and localized cases respectively.

Making the decision requires rather complicated mathematics, so about all I can do will be to list the important variables and show results of calculations for some simple cases.

I've listed here a minimal set of key parameters that obviously influence the competition between migration and localization.

The first one, called  $W$ , is the range of variation of the different site energies from each other. As I've indicated in green, ~~that~~ the wider this range the more difficult is migration.

The next parameter,  $V$ , is a typical magnitude of the <sup>coefficient</sup> ~~term in the Hamiltonian~~ ~~the~~ ~~product of the probability amplitudes on two~~ <sup>connecting</sup> neighboring sites — the quantity often called the "hopping energy", because it measures the rate at which an electron on one of the sites would hop to a neighbor of equal energy.

Obviously, the larger  $V$  is, the faster will be the migration.

A third key parameter, called  $K$ , is a measure of how rapidly the number of different paths<sup>?</sup> increases with the number of steps  $L$ , the asymptotic relation being  $P \propto K^L$ .

$K$  is usually one or two less than the number of nearest neighbors in the underlying crystal lattice.

Anderson's calculations showed that for a couple of types of physically plausible systems the transition from localization to migration took place across nearly the same surface in parameter space, as shown in the diagram here.

Several things in this diagram are striking.

Surprisingly large values of  $W/2V$  are required to produce localization for  $K$  values in the middle of the range shown, as <sup>are</sup> typical for 3-dimensional systems, and the values increase rapidly with  $K$ .

The curve should go to zero at  $K=1$



# Words Saved with Trial Revisions of Second Draft (on tape)

	Topic & pages 1st	2nd Draft	Words Saved	Cum.
1	Bohr-Bloch theorem 3,4	3,4	<del>209</del> 215	215
2	Messner effect <del>Loeffler effect</del>	4	<del>21</del> 107	322
3	Ginzburg-Landau	7-9	479	<del>694</del> 701
4	Intro. to BCS	16-17	218	919
5	Density matrix elements for BCS	22-24	$\approx$ 400	<del>1094</del> <del>1401</del> 1319
6	Ankersen's theory	26-28	$\approx$ <del>388</del> 363	<del>1457</del> <del>1564</del> 1782
7	Mag. rings.	28-29	<del>195</del> <del>241</del> 355	<del>1652</del> <del>1754</del> <del>1905</del> <del>1977</del> 2137
8	Graeber's tunneling	30-31	120	<del>1772</del> <del>1874</del> <del>2074</del> 2256
9	Josephson effect	32-33	399	<del>2185</del> <del>2254</del> 2273
10	Andreev refl. (tape + changes on 2nd draft)	38-39	<del>224</del> 196	<del>2851</del> <del>2854</del> 2672
11	Vortices pinning	42-43	461	<del>2273</del> <del>2340</del> <del>2801</del> 3312 <del>3360</del> 3447 <del>3557</del> 3901
Concluding Remarks			-180	3132
Corrections to typed pages, including purple			504	3636

# SIGNIFICANT ALTERATIONS IN 2ND DRAFT TEXT

page(s)	topic(s)	words out	words in	words saved	cum.
4	Meissner eff.	25	4	21	
5-6	London th.	231	56	175	196
12	Type II		31	-31	165
15-16	Gaps	52	12	40	205
20	Bogolyubov-Volatin	13	5	8	
38-39	Andreaf ref.	included water taped material			
40- <del>41</del> 41	Chaitin	81	50	31	<del>236</del> 244



# "Final" VG's, Lecture XI

Longhand copy	Computer version	VG no.		Title	P	Page, 2nd draft marked for final	Page found		Transp.
		a	b						
		1a		"Infinite Conductivity?"		1.6 ✓	✓	✓	
		2a		Perfect Diamagnetism; Phenomenology		4.3 ✓	✓	✓	
			3b	London Equations		6.05 ✓	✓	✓	
			4b	Ginzburg-Landau Theory Equation		7.9 ✓	✓	use paper	
			5b	Type I vs. Type II		10.9 ✓	✓	✓	
		6a		Electrons Pulled Together by Phonons		13.0 ✓	✓	✓	
		7a		See p. 11 <del>omitted or slighted</del>		17 ✓	✓	✓	
			8b	Atomic force spectroscopy, Crystalliz. waves		17, 20	✓	✓	



Lecture XI, VGs

Series a, final



# SUPERCONDUCTIVITY

## I. "INFINITE CONDUCTIVITY"?

Expt.

Theory

Kamerlingh  
Onnes 1911

Sudden drop of  
 $\rho(T)$  of Hg by  
factor at least  
300, at  $\sim 4.2\text{K}$

Kam. Onnes  
1913-14

Drop for Sn, not Au  
or Pt.

Superc. destroyed by  $H_c$

Persistent currents  
on a ring  $\rightarrow$   
 $\rho < 0.2 \times 10^{-10} \rho(0^\circ\text{C})$

de Haas, Sizoo,  
Kam. Onnes, 1925

Hysteresis

Argues ground  
state in  $H=0$   
has macroscopic  
 $J=0$

Bloch, ca.1929?  
1933

Bethe 1933

Survey: no  
substantial ideas

Idea current-carrying  
states can have  
lowest free energy

Heisenberg 1948

Born&Cheng 1948

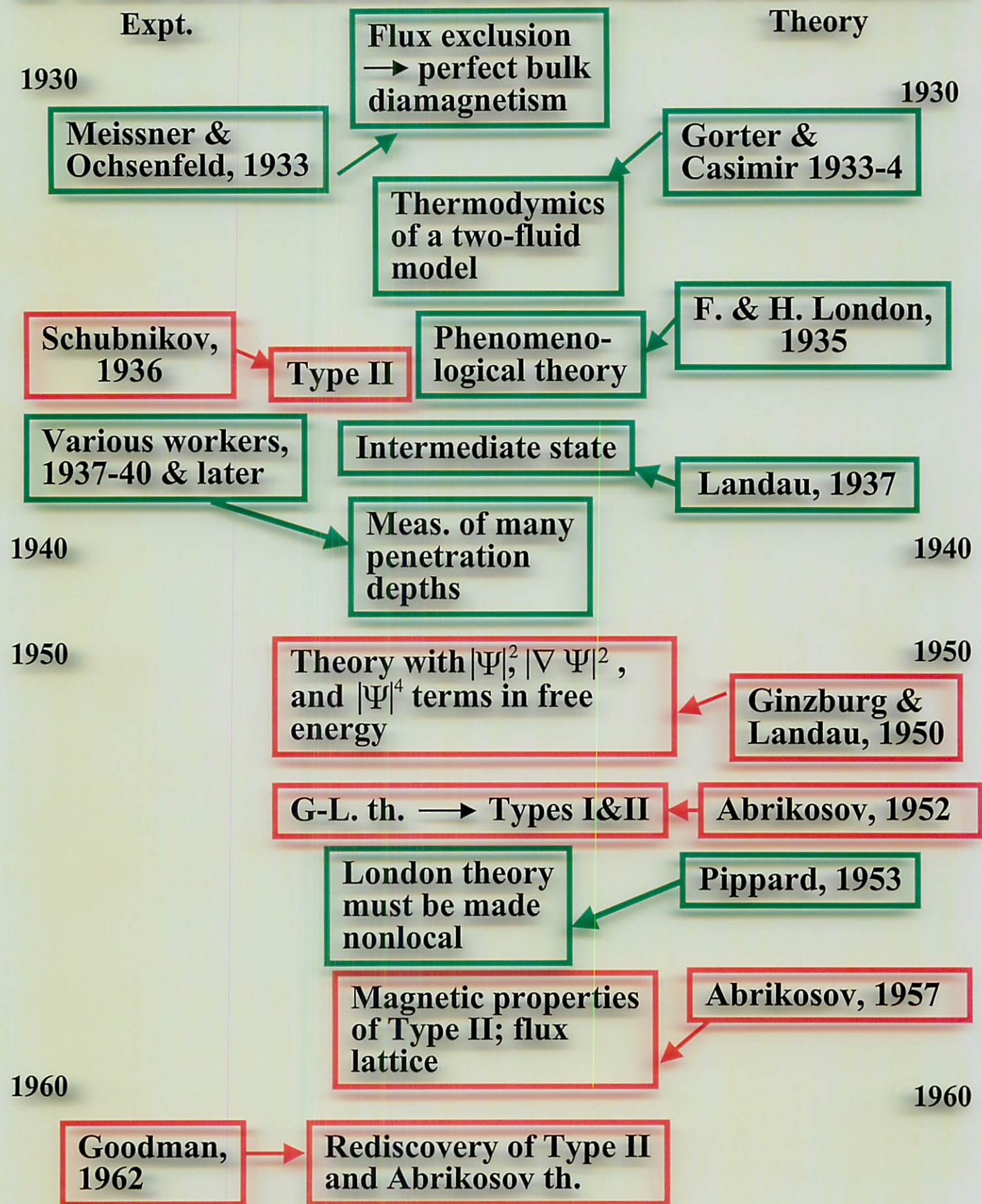
Gen. of Bloch  $J=0$  theorem,  
but not sure if spin-orbit  
int. spoils it

Bohm 1949



# SUPERCONDUCTIVITY

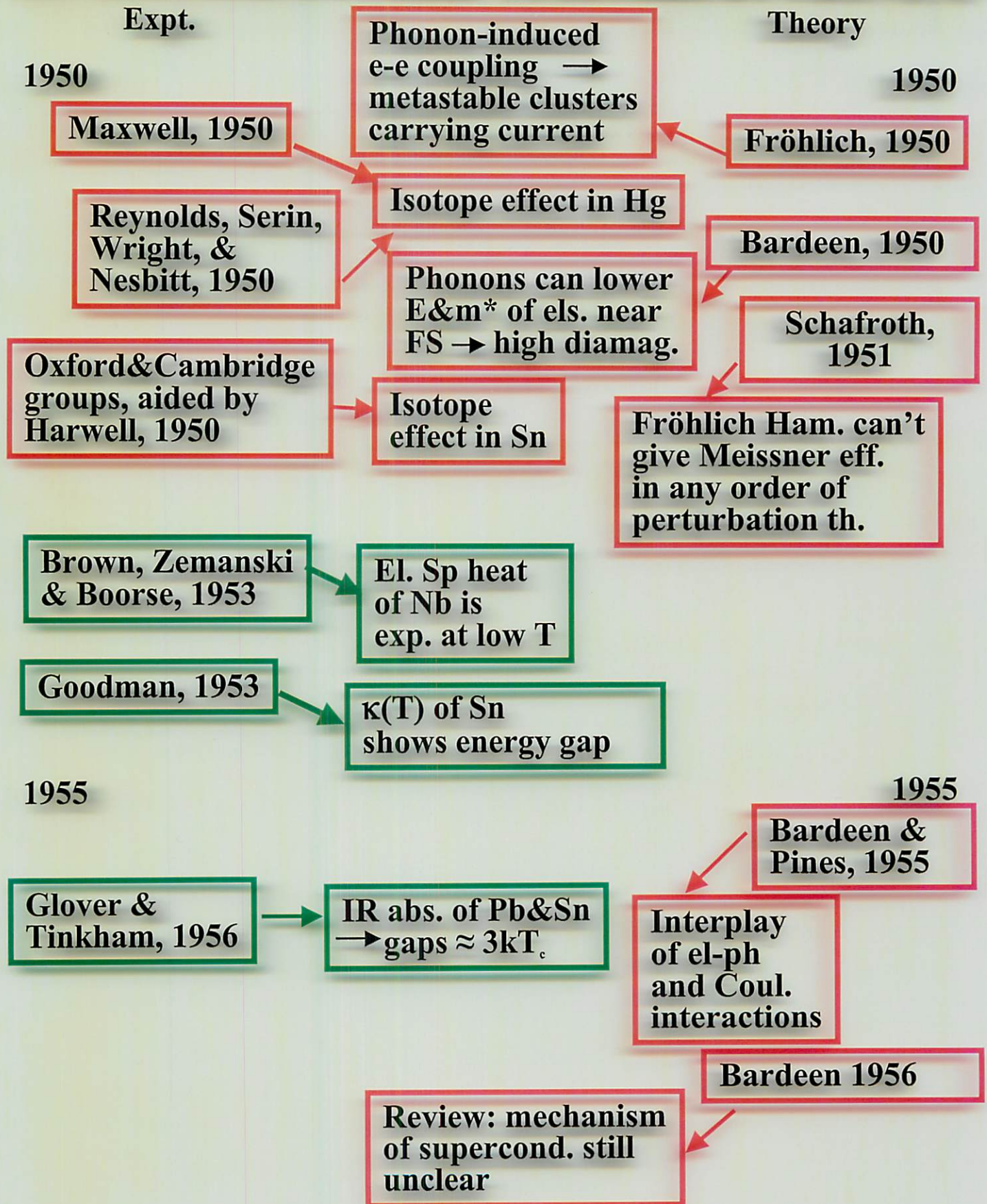
## II. PERFECT DIAMAGNETISM; PHENOMENOLOGY





# SUPERCONDUCTIVITY

## III. ELECTRONS PULLED TOGETHER BY PHONONS





Lecture XI, VG's

Series b, final

# LONDON EQUATIONS

## ASSUMPTIONS:

Two kinds of electrons, normal and superconducting, with densities  $\rho_n, \rho_s$  and separately conserved currents  $j_n, j_s$ .

Maxwell's equations

Current-field relations:  $j_n = \sigma E$ ,  $\partial(\Lambda j_s)/\partial t = E$ ,  
( $\rho_s$  is frictionless),  $\Lambda$  a material constant.

## SOME CONCLUSIONS:

In the "London gauge"  $A(r)$ ,  $\Lambda j_s = -A/c$

In a homogeneous steady state

$$\nabla^2 j_s = j_s / \lambda^2, \quad \lambda^2 = \Lambda c^2 / 4\pi$$

( $\lambda$  = penetration depth)



# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$  .

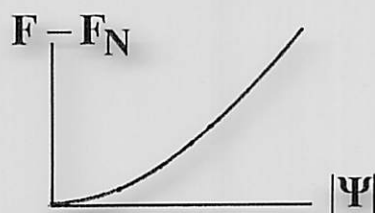
Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$  , hence can let terms in  $|\Psi^0|, |\Psi^2|, |\Psi^4|$  suffice.

Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

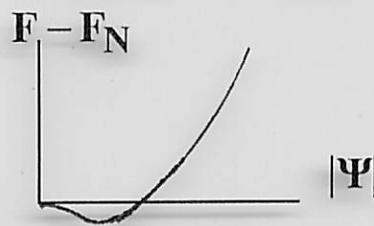
In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A\Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*} \left| \nabla\Psi - \frac{ie^* A\Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$



$T > T_c, a > 0$



$T < T_c, a < 0$

## MINIMIZATION ON $\Psi$ GIVES WAVE EQUATION:

$$\frac{\hbar^2}{m^*} \left( \nabla + \frac{e^*}{\hbar c} A \right)^2 \Psi + a\Psi + b|\Psi|^2 \Psi = 0$$

## AND DITTO ON $A$ GIVES CURRENT DENSITY

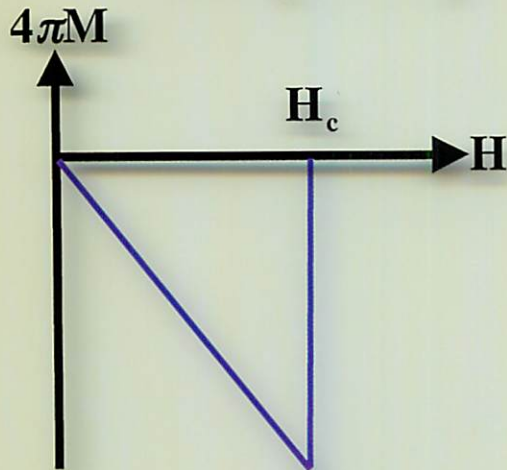
$$\mathbf{j}(\mathbf{r}) = \frac{ie^* \hbar}{m^*} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) - \frac{e^{*2}}{m^* c} A |\Psi|^2$$



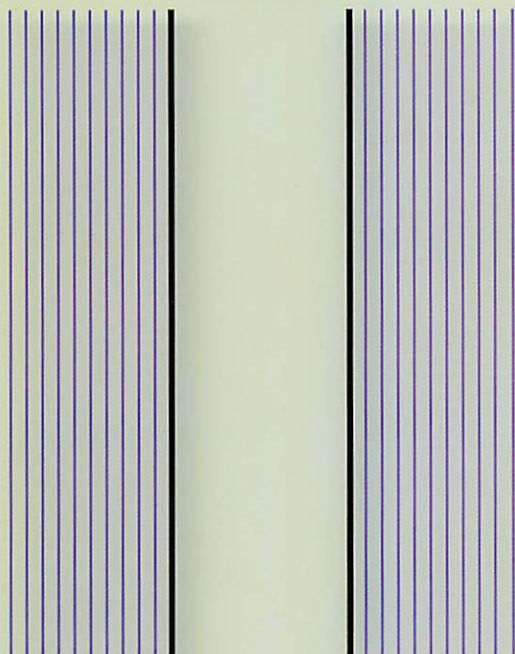
## TYPE I VS. TYPE II

For a long cylinder  $\parallel H$  (field independent of  $r$  over most of length):

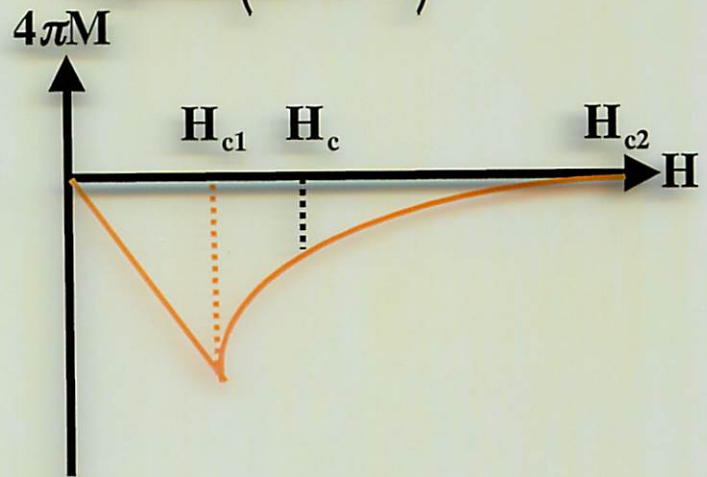
Type I ( $\kappa < 2^{-1/2}$ )



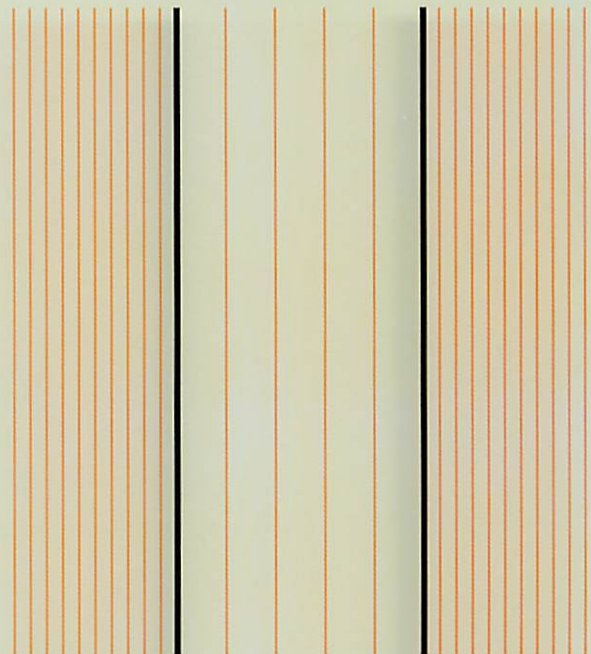
$H < H_c$



Type II ( $\kappa > 2^{-1/2}$ )



$H_{c1} < H < H_{c2}$



Vortex structure viewed along field direction:

```

o o o o o o o
o o o o o o o
o o o o o o o
o o o o o o o
o o o o o o o

```

Each vortex carries a flux  $ch/e^*$



Lecture XI, VG's

Series b, paper finals

# **LONDON EQUATIONS**

## **ASSUMPTIONS:**

**Two kinds of electrons, normal and superconducting,  
with densities  $\rho_n, \rho_s$  and separately conserved  
currents  $j_n, j_s$  .**

**Maxwell's equations**

**Current-field relations:  $j_n = \sigma E$ ,  $\partial(\Lambda j_s)/\partial t = E$ ,  
( $\rho_s$  is frictionless),  $\Lambda$  a material constant.**

## **SOME CONCLUSIONS:**

**In the “London gauge”  $A(r)$ ,  $\Lambda j_s = -A/c$**

**In a homogeneous steady state**

$$\nabla^2 j_s = j_s / \lambda^2, \quad \lambda^2 = \Lambda c^2 / 4\pi$$

**( $\lambda$  = penetration depth)**



# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$  .

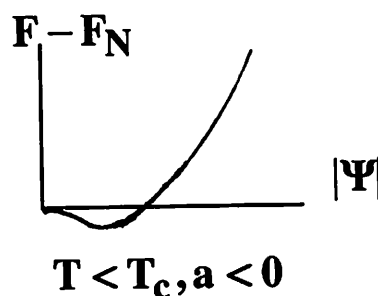
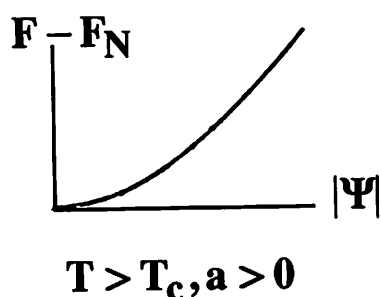
Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$  , hence can let terms in  $|\Psi^0|, |\Psi^2|, |\Psi^4|$  suffice.

Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A \Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*} \left| \nabla\Psi - \frac{ie^* A \Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$



MINIMIZATION ON  $\Psi$  GIVES WAVE EQUATION:

$$\frac{\hbar^2}{m^*} \left( \nabla + \frac{e^*}{\hbar c} A \right)^2 \Psi + a\Psi + b|\Psi|^2 \Psi = 0$$

AND DITTO ON  $A$  GIVES CURRENT DENSITY

$$j(r) = \frac{ie^* \hbar}{m^*} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) - \frac{e^{*2}}{m^* c} A |\Psi|^2$$

# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$  .

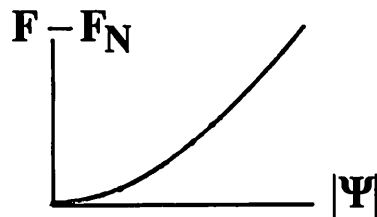
Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$  , hence can let terms in  $|\Psi|^0, |\Psi|^2, |\Psi|^4$  suffice.

Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

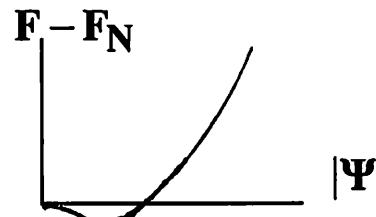
In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A \Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*} \left| \nabla\Psi - \frac{ie^* A \Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$



$T > T_c, a > 0$



$T < T_c, a < 0$

## MINIMIZATION ON $\Psi$ GIVES WAVE EQUATION:

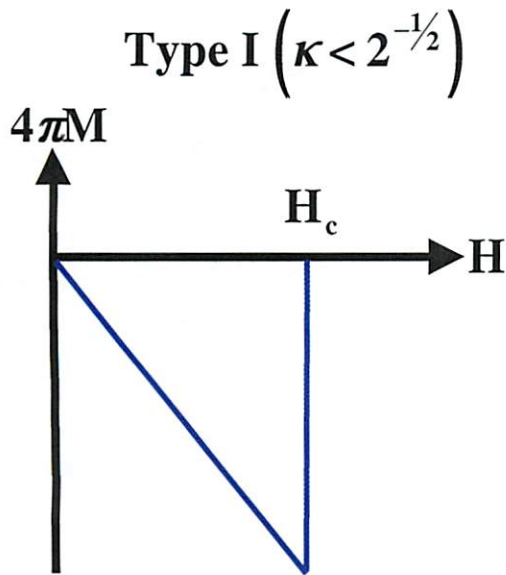
$$\frac{\hbar^2}{m^*} \left( \nabla + \frac{e^*}{\hbar c} A \right)^2 \Psi + a\Psi + b|\Psi|^2 \Psi = 0$$

## AND DITTO ON $A$ GIVES CURRENT DENSITY

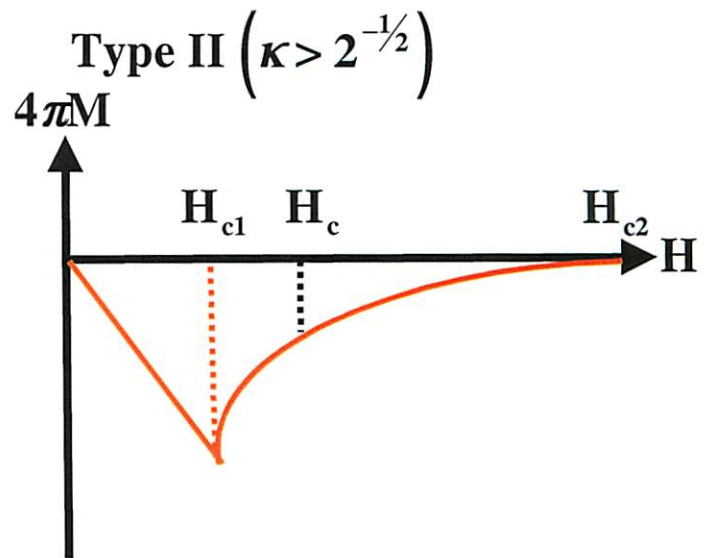
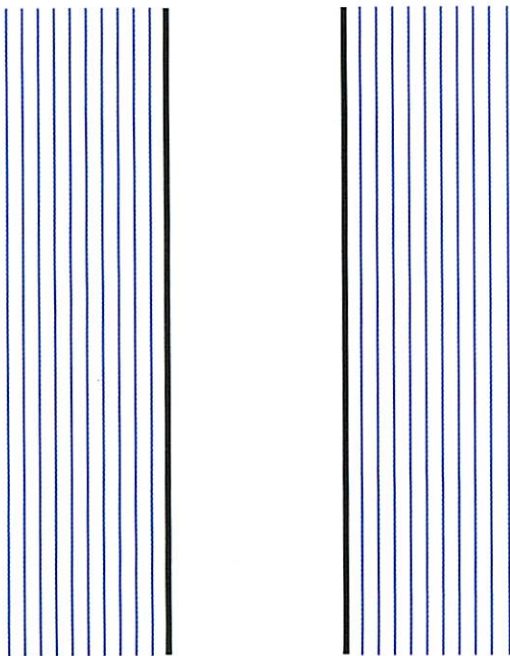
$$\mathbf{j}(\mathbf{r}) = \frac{ie^* \hbar}{m^*} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) - \frac{e^{*2}}{m^* c} A |\Psi|^2$$

# TYPE I VS. TYPE II

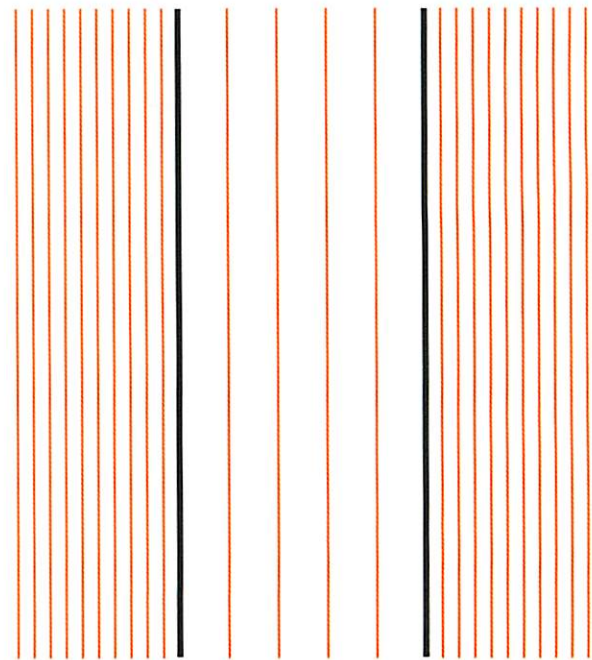
For a long cylinder  $\parallel H$  (field independent of  $r$  over most of length):



$$H < H_c$$



$$H_{c1} < H < H_{c2}$$



Vortex structure viewed along field direction:

```

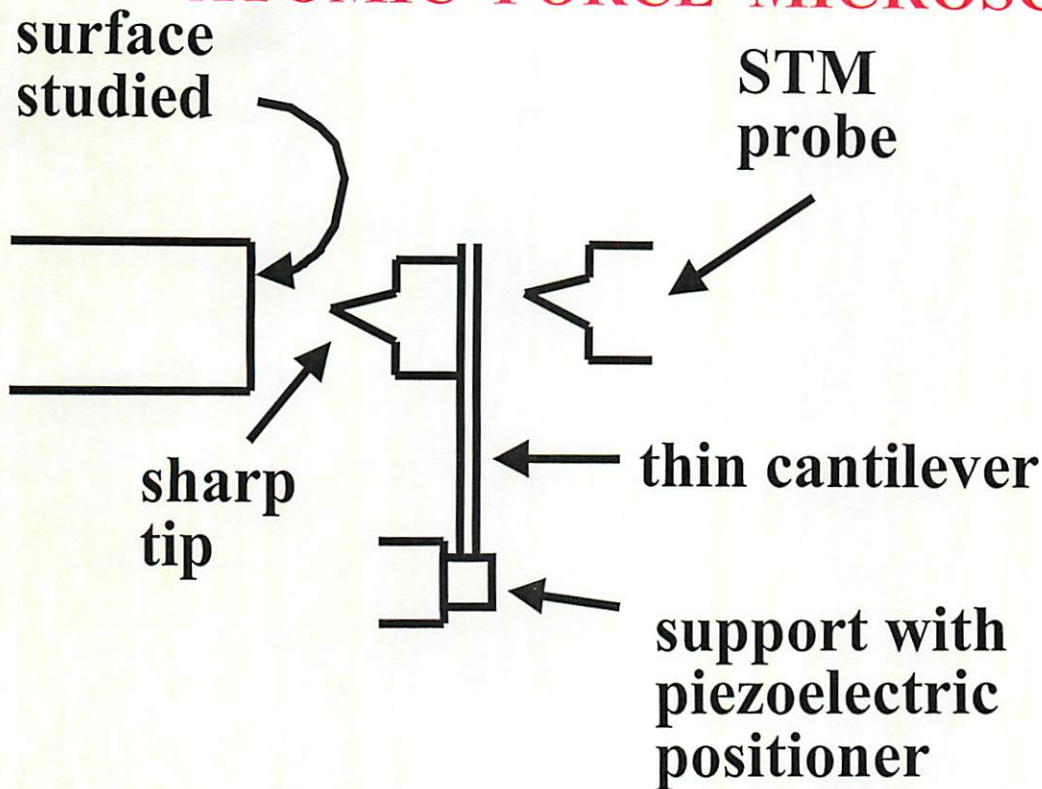
o o o o o o o
o o o o o o
o o o o o o o
o o o o o o
o o o o o o o

```

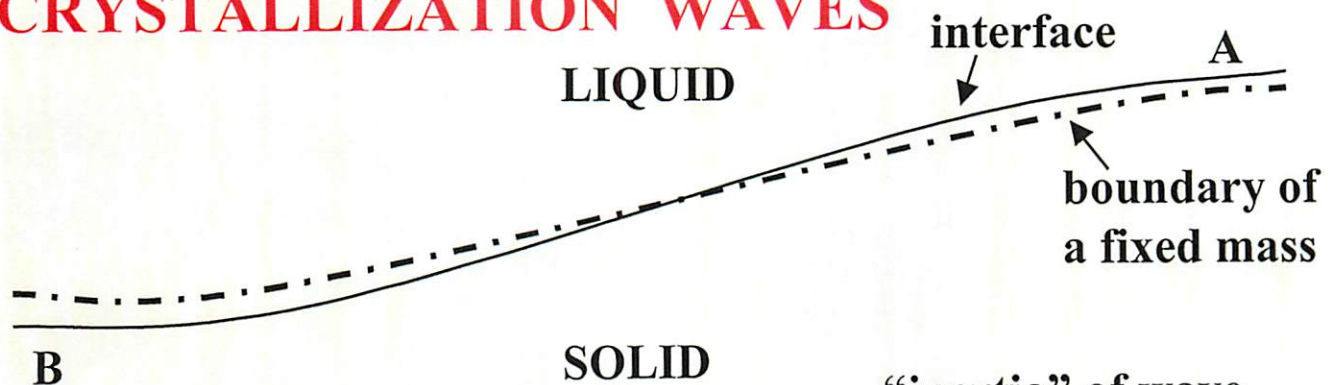
Each vortex carries a flux  $ch/e^*$



## ATOMIC FORCE MICROSCOPY



## CRYSTALLIZATION WAVES



“inertia” of wave

$$\propto |\rho_{\text{sol.}} - \rho_{\text{liq.}}|$$

$$[\mu_{\text{sol.}} - \mu_{\text{liq.}}]_{\text{interface}} \propto \gamma \text{ (curvature)}$$

Main dissip., due to transport in liquid,

$$\propto |\mu_{\text{liq.}}^{(A)} - \mu_{\text{liq.}}^{(B)}|$$

(non-superfluid waves very overdamped.)

Dispersion law in absence of gravity:  $\omega \propto q^{3/2}$



# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$ .

Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$ , hence can let terms in  $|\Psi^0|, |\Psi^2|, |\Psi^4|$  suffice. Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A \Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2M^*} \left| \nabla\Psi - \frac{ie^* A \Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$

$F - F_N$



$T > T_c, a > 0$

$F - F_N$



$T < T_c, a < 0$

## MINIMIZATION ON $\Psi$ GIVES WAVE EQUATION:

## RESULTS:



LECTURE  $\boxtimes$  VG's

Series a

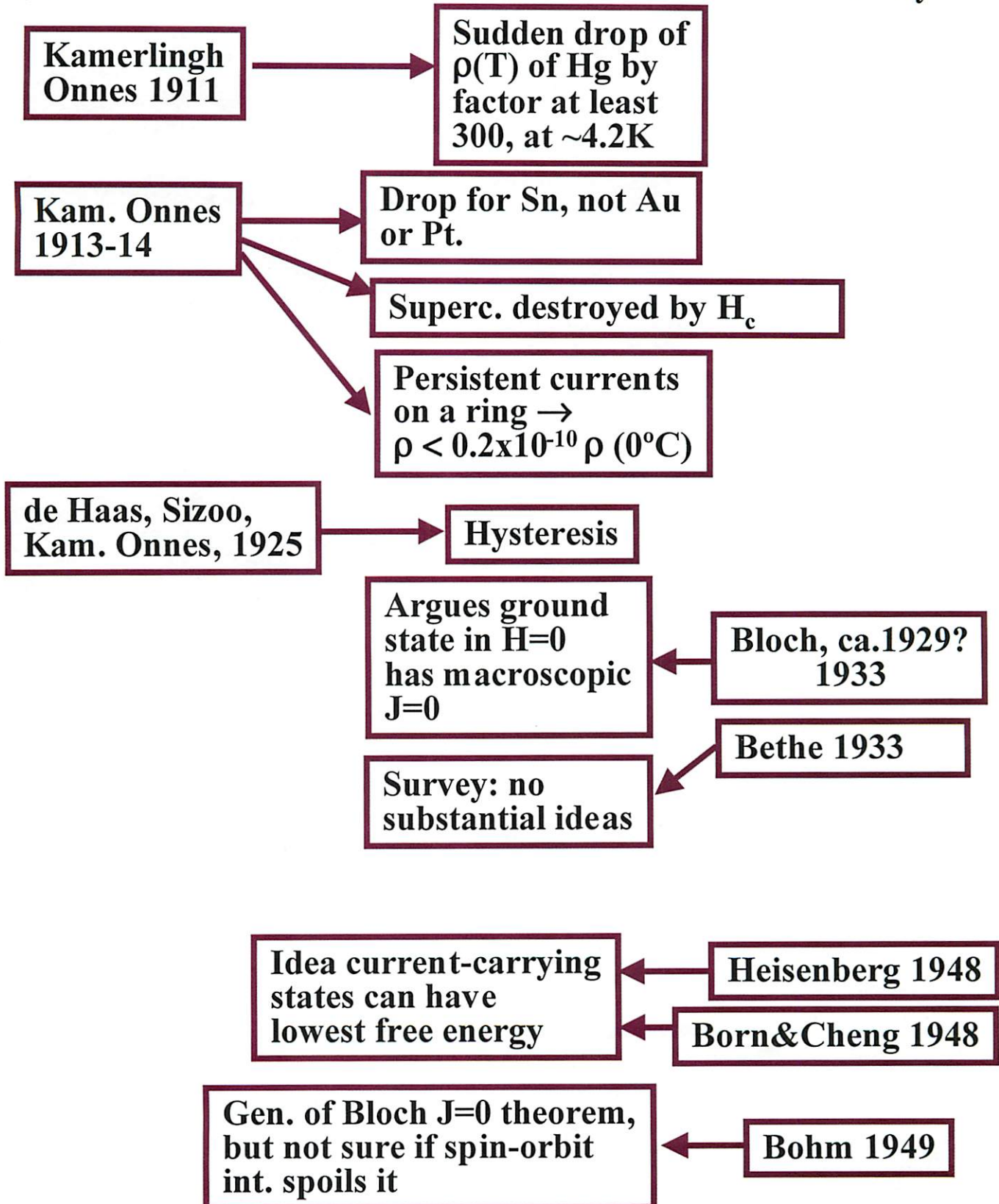
Paper final

# SUPERCONDUCTIVITY

## I. "INFINITE CONDUCTIVITY"?

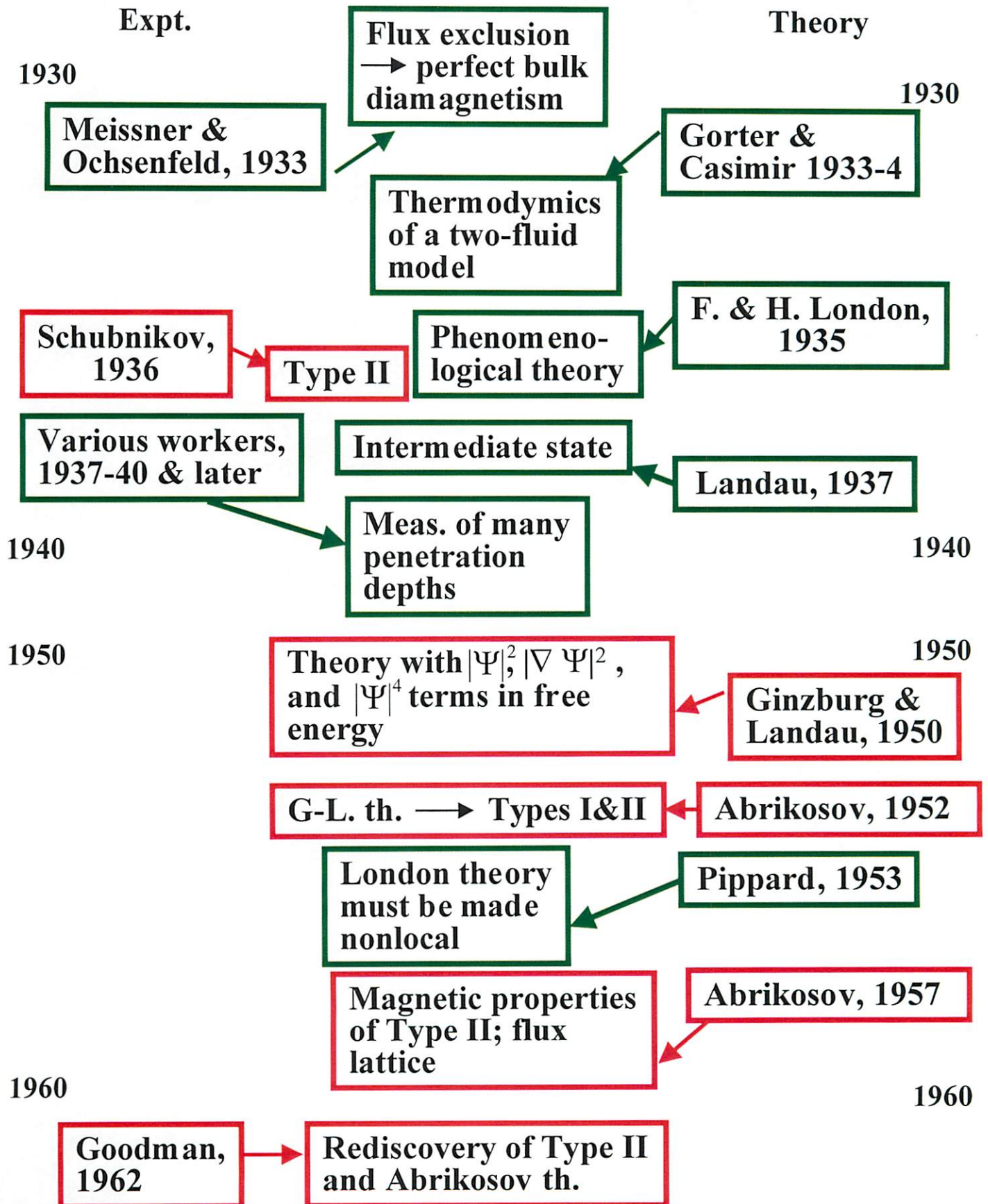
Expt.

Theory



# SUPERCONDUCTIVITY

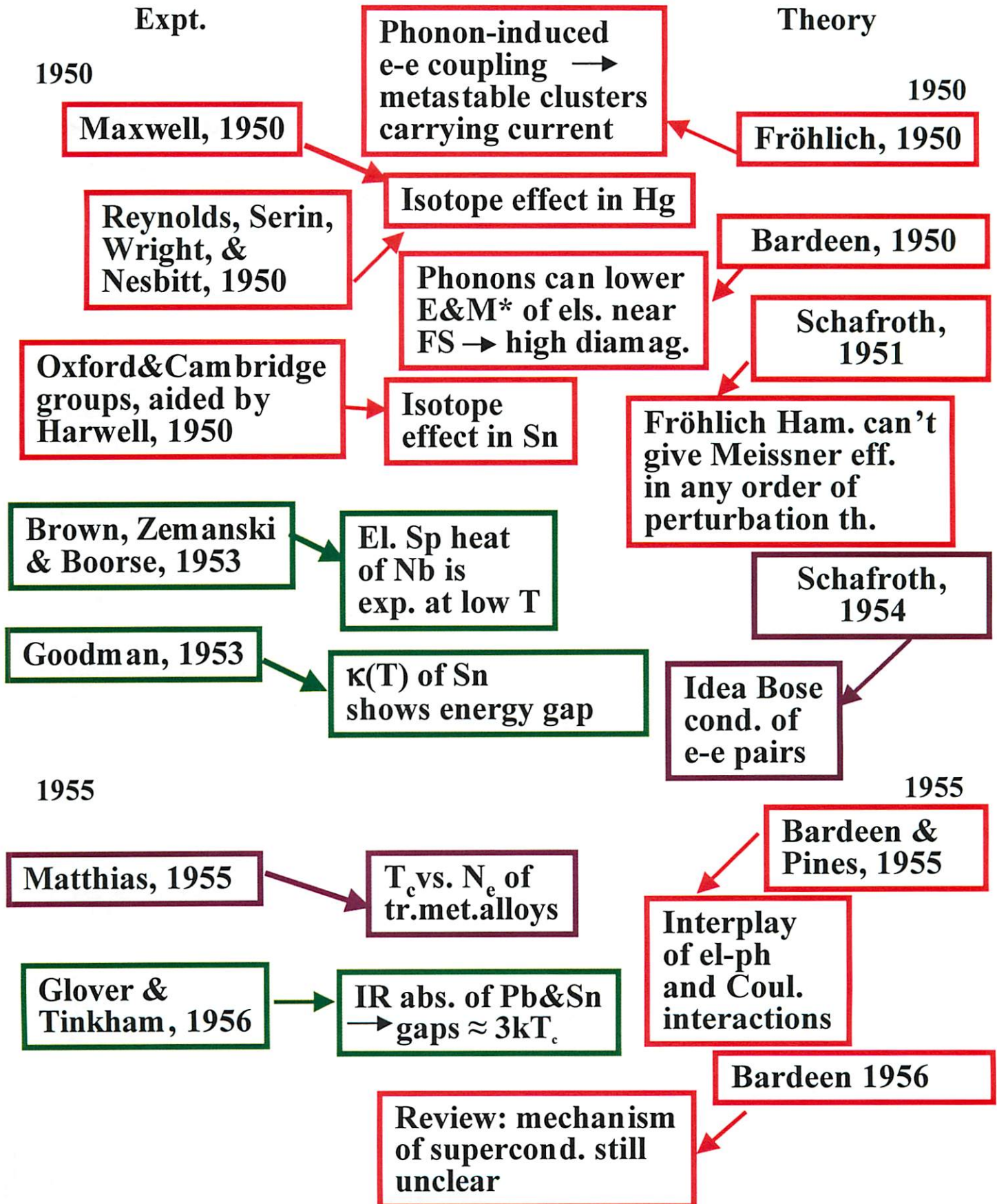
## II. PERFECT DIAMAGNETISM; PHENOMENOLOGY





# SUPERCONDUCTIVITY

## III. ELECTRONS PULLED TOGETHER BY PHONONS



# SOME FIELDS OMITTED OR SLIGHTED

## Field

## Samples of striking discoveries

Surfaces, thin films, and interfaces

(Structure, thermodynamics, electronic properties, etc.)

STM & force microscopy

Crystallization waves

“Wigner crystal”  
in 2D electron gas

Disordered materials

Mobility edges  
2-level systems

Mag. Res.  
(EPR, FMR, NMR)

Spin echoes

Optics & laser phys.

Doppler-free spectroscopy  
Self-focusing

Fast-particle bombardment

Channeling  
Anisotropic radiation growth

# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$ .

Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$ , hence can let terms in  $|\Psi|^0, |\Psi|^2, |\Psi|^4$  suffice.

Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A\Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*} \left| \nabla\Psi - \frac{ie^* A\Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$



$T > T_c, a > 0$



$T < T_c, a < 0$

## MINIMIZATION ON $\Psi$ GIVES WAVE EQUATION:

$$\frac{\hbar^2}{m^*} \left( \nabla + \frac{e^*}{\hbar c} A \right)^2 \Psi + a\Psi + b|\Psi|^2 \Psi = 0$$

## AND DITTO ON $A$ GIVES CURRENT DENSITY

$$\mathbf{j}(\mathbf{r}) = \frac{ie^* \hbar}{m^*} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) - \frac{e^{*2}}{m^* c} A |\Psi|^2$$



# GINZBURG-LANDAU EQUATION

## ASSUMPTIONS:

Complex order parameter  $\Psi$ , finite below  $T_c$  .

Free energy density  $F$  of a homogeneous state is an analytic function of  $|\Psi|$  near  $T_c$  , hence can let terms in  $|\Psi^0|, |\Psi^2|, |\Psi^4|$  suffice.

Gradual inhomogeneity of  $|\Psi|$  increases  $F$  by a term  $\propto |\nabla\Psi|^2$

In a weak magnetic field of vector-potential  $A$ , replace  $\nabla\Psi$  by  $\nabla\Psi - \frac{ie^* A\Psi}{\hbar c}$

## EQUATION:

$$F = F_N + a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*} \left| \nabla\Psi - \frac{ie^* A\Psi}{\hbar c} \right|^2 + \frac{H^2}{8\pi}$$



$T > T_c, a > 0$



$T < T_c, a < 0$

MINIMIZATION ON  $\Psi$  GIVES WAVE EQUATION:

$$\frac{\hbar^2}{m^*} \left( \nabla + \frac{e^*}{\hbar c} A \right)^2 \Psi + a\Psi + b|\Psi|^2 \Psi = 0$$

AND DITTO ON  $A$  GIVES CURRENT DENSITY

$$\mathbf{j}(\mathbf{r}) = \frac{ie^* \hbar}{m^*} (\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) - \frac{e^{*2}}{m^* c} A |\Psi|^2$$

# APPLICATIONS OF GINZBURG-LANDAU THEORY

~~Calculate~~ Distributions of  $H$  and  $\Psi$  for various geometries (especially near surfaces)

~~Calculate~~ Surface and interface free energies

~~Calculate~~  $\xi$  (correlation length for  $\Psi$  in absence of  $H$ )  
and  $\lambda$  (penetration depth of  $H$ )

In terms of the four independent constants of the theory ( $a$ ,  $b$ ,  $c^*$ , and  $m^*$ ) or the equations as written above, or any other set of four independent ones obtainable by replacing one or more of these by some of the measurable quantities listed below) one can calculate:

Various kinds of critical fields (i.e.,  $H_c$  for thermodynamic equilibrium of  $n \geq s$  phase, and  $H_{c1}$ ,  $H_{c2}$ ,  $H_{c3}$ )

# SOME FIELDS OMITTED OR SLIGHTED

## Field

## Samples of striking discoveries

Surfaces, thin films, and interfaces

(Structure, thermodynamics, electronic properties, etc.)

STM & force microscopy

Crystallization waves

“Wigner crystal” in 2D electron gas

Disordered materials

Mobility edges  
2-level systems

Mag. Res.  
(EPR, FMR, NMR)

Spin echoes

Optics & laser  
phys.

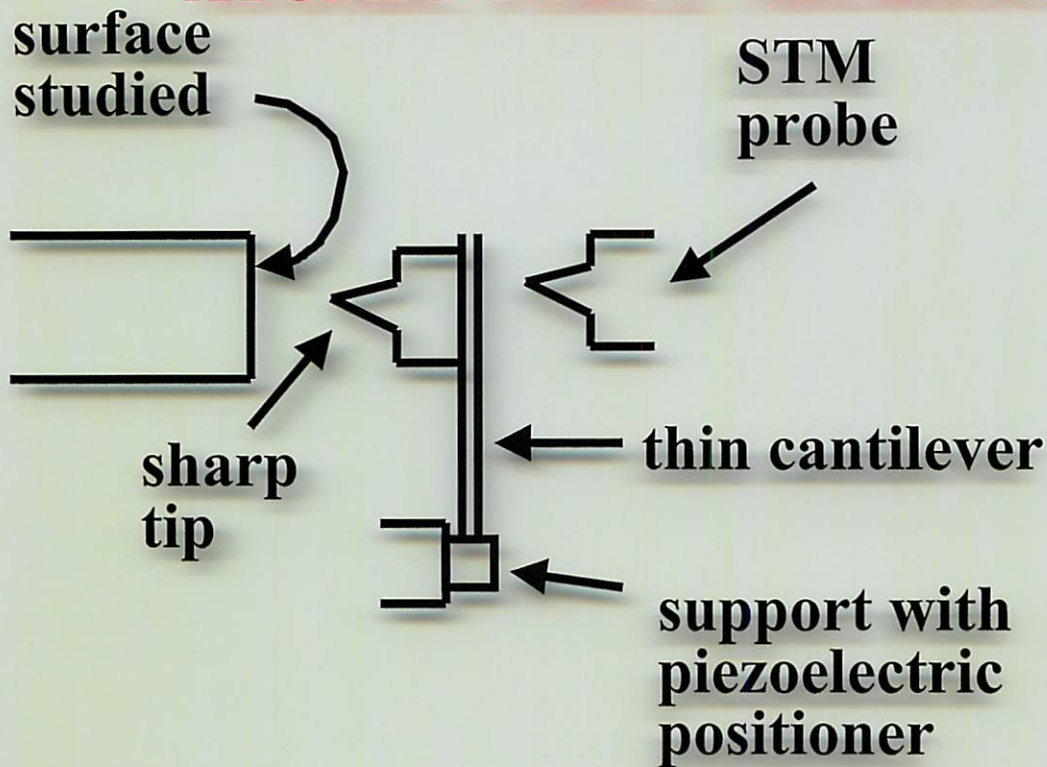
Doppler-free spectroscopy  
Self-focusing

Fast-particle bombardment

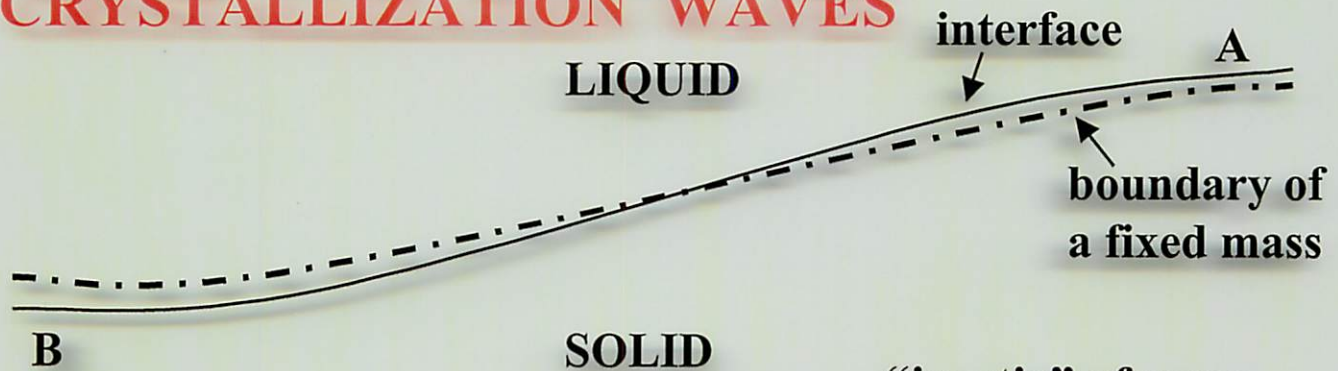
Channeling  
Anisotropic radiation growth



## ATOMIC FORCE MICROSCOPY



## CRYSTALLIZATION WAVES



“inertia” of wave  
 $\propto |\rho_{\text{sol.}} - \rho_{\text{liq.}}|$

$[\mu_{\text{sol.}} - \mu_{\text{liq.}}]_{\text{interface}} \propto \gamma \text{ (curvature)}$

Main dissip., due to transport in liquid,

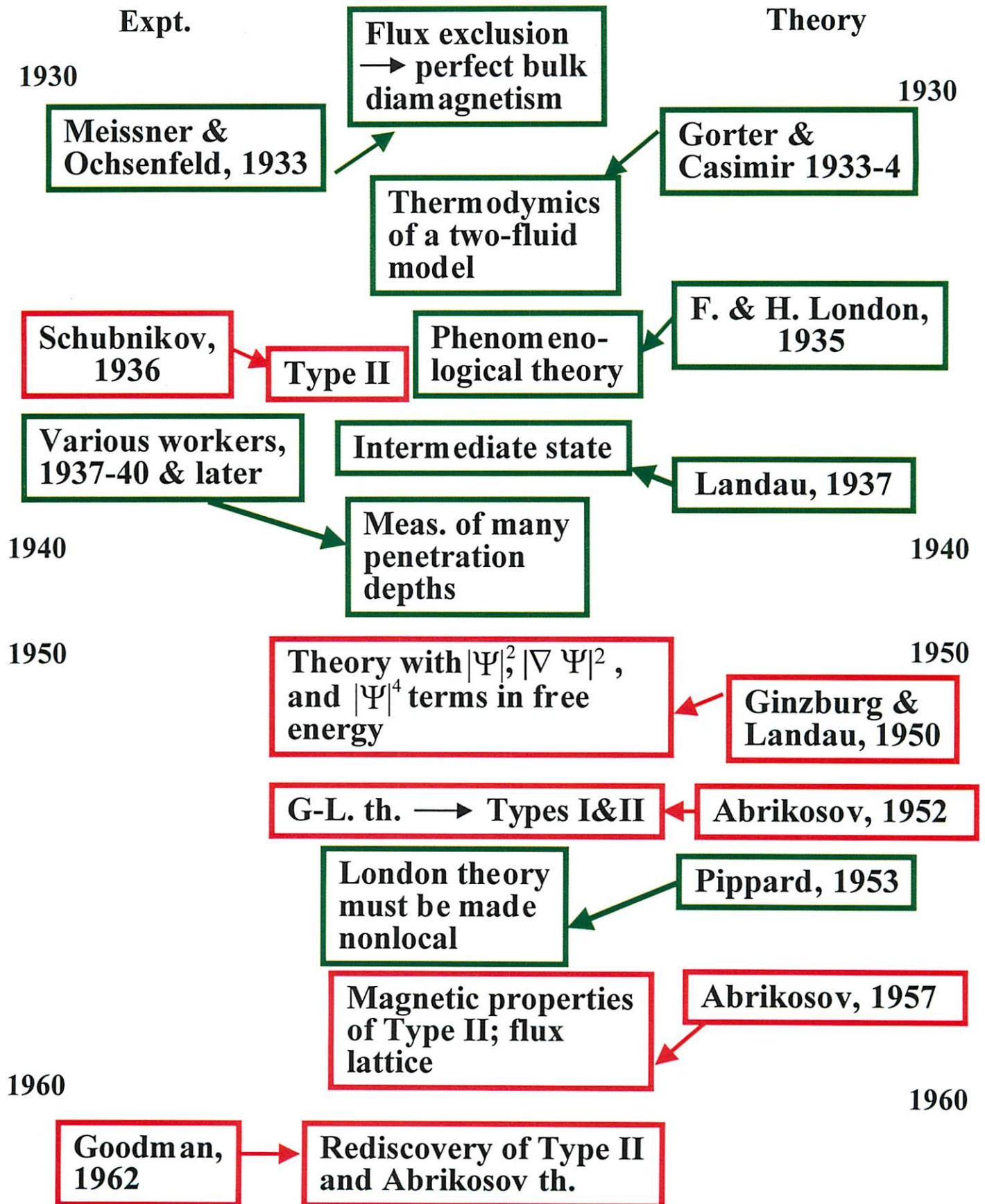
$\propto |\mu_{\text{liq.}}^{(A)} - \mu_{\text{liq.}}^{(B)}|$

(non-superfluid waves very overdamped.)

Disperson law in absence of gravity:  $\omega \propto q^{3/2}$

# SUPERCONDUCTIVITY

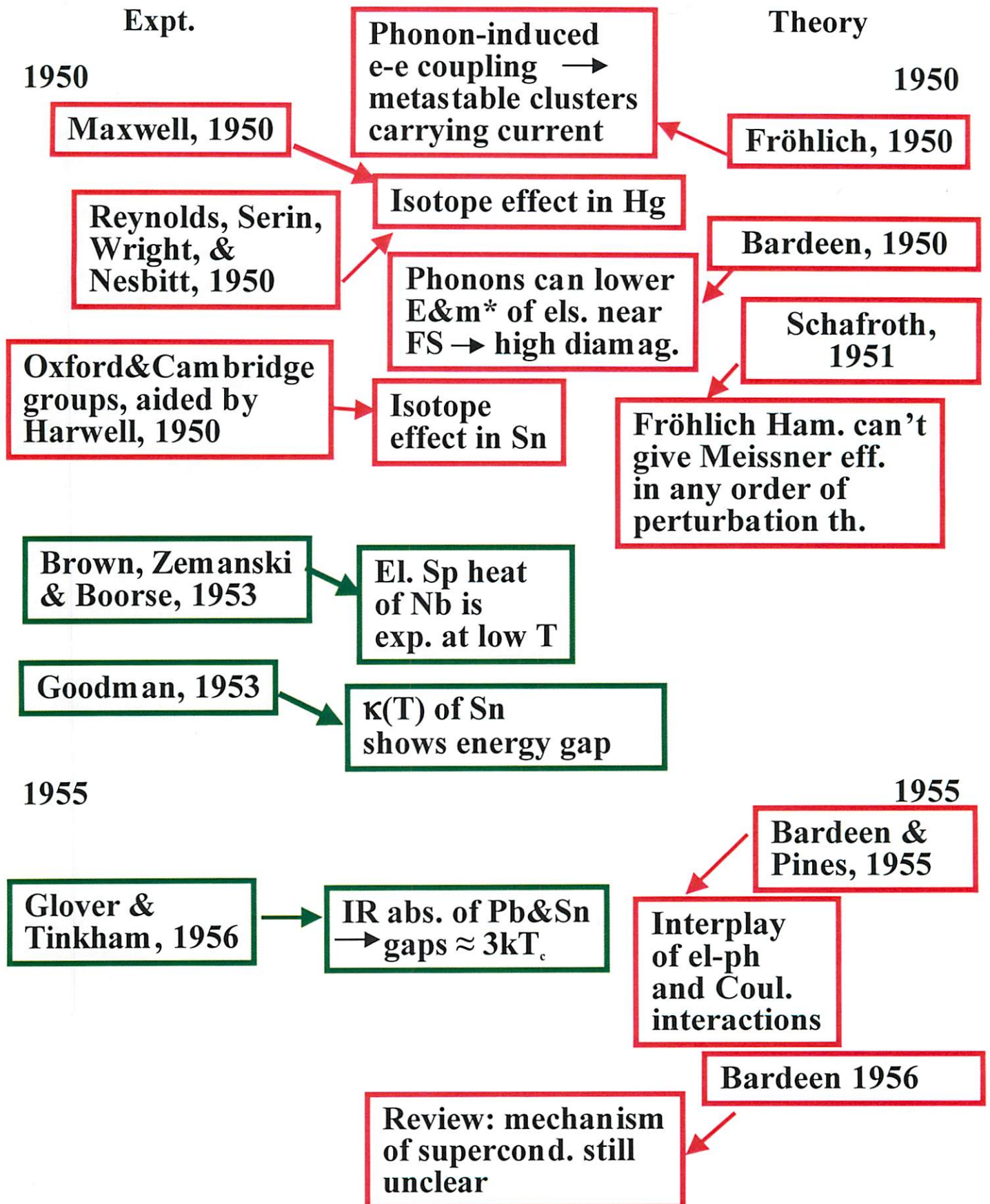
## II. PERFECT DIAMAGNETISM; PHENOMENOLOGY





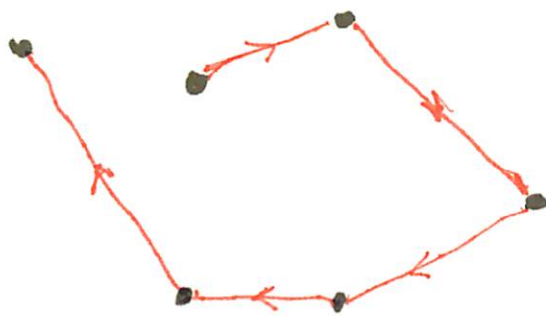
# SUPERCONDUCTIVITY

## III. ELECTRONS PULLED TOGETHER BY PHONONS





# ANDERSON LOCALIZATION



Randomly located  
trapping sites with  
random energies

Orange: part of a  
migration path.

Key parameters for a rough description:

Encourages  
localization

$W$  : width of energy distribution  
of site energies

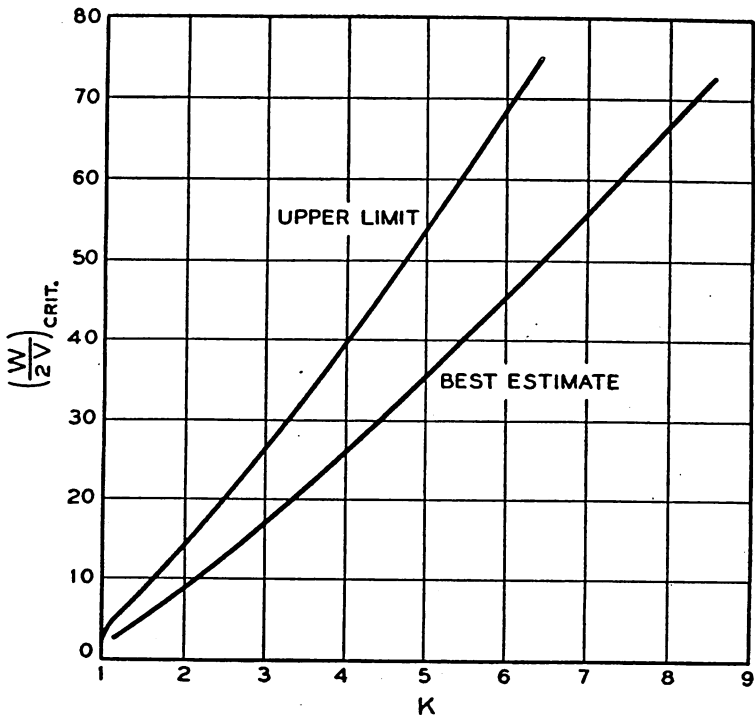
Encourages  
migration

$V$  : mean near-neighbor value  
of hopping energy  
(or  $\hbar/\text{hop rate}$  if energies equal)

Encourages  
migration

$K$  : the "connectivity" of the lattice,  
describing how the number of different  
paths increases with the number of steps.

Anderson's result:



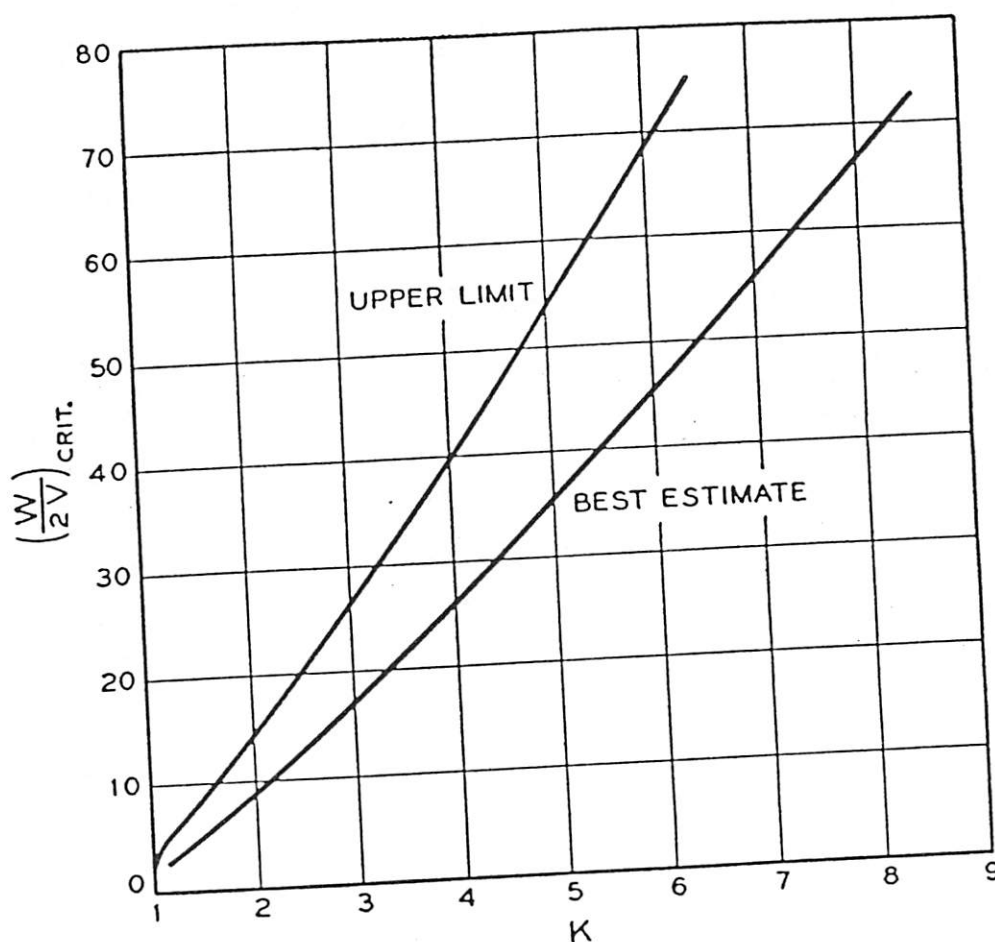


FIG. 3. Numerical estimates for the critical  $W/2V$ , the ratio of line width to interaction, for transport, plotted against connectivity  $K$ . The upper curve is a quasi-exact upper limit; the lower one is our best estimate.

solution is the lower curve of Fig. 3. It is very unlikely that (85) is accurate for  $K \sim 1$ , so no plot has been made in this region. This concludes our estimates of the critical ratio for transport.

final a  
scriptio

where  
j of t  
atom /  
square  
eigene  
usual

[This  
Th  
repla  
only

Then  
the

It is  
part  
Let  
so t  
Th



Spin pol.  
in static  $H_0$



ditto just after  
start of RF pulse



ditto after  
 $\pi/2$  pulse



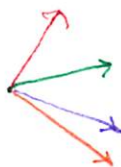
Spin echoes

viewed in rotating  
coordinate system

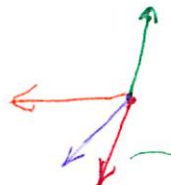
Several spins  
viewed along  $H_0$   
just after pulse



ditto: after a  
short wait



ditto after a  
long wait  $\tau$



preceding after a  
 $\pi$  pulse along  $\downarrow$



after a further  
wait  $\tau$



Macroscopically occupied pair state:

Max. Eigenstate of  $\rho^{(2)}$  is  $\sum_{\alpha} \frac{\phi_{\alpha}}{1+|\phi_{\alpha}|^2} [\psi_{\alpha}(1)\psi_{\alpha}(2) - \psi_{\alpha}(1)\psi_{\alpha}(2)]$   
(not normalized)

and occupation  $\sum_{\alpha} \frac{|\phi_{\alpha}|^2}{[1+|\phi_{\alpha}|^2]^2}$  pairs

# ANDERSON LOCALIZATION

B. L. Altshuler & A. G. Aronov *Sov Comm.* 39, 115 (79); *JETP* 50, 968 (79) e-a int. + disorder  
 → singularities at  $E_F$

P. W. Anderson, *Phys Rev* 103, 1492 (58) Based on Laplace transform of the propagator.

P. A. Lee & T. V. Ramakrishnan *RMP* 57, 287 (85) Scaling th. in 3, 2+ $\epsilon$ , 2,  
 & 1D, including magnetic & JT effects, weak loc., etc.

N. F. Mott & E. A. Davis, Electronic Processes in Non-Crystalline Materials  
 (2nd Oxford 1973)

D. J. Thouless in IV-Condensed Matter (G. Toulouse & R. Balian, Eds, NH 1979) p. 1

F. J. Wegner *ZPB* 25, 327 (76) Early appl. of scaling th.



# ASK KAM

Spin echoes	yes
Anderson loc.	less yes
Mob. edges	no
2-level systems	prob. yes
Channeling	maybe not
Mössbauer eff.	yes



Key point = difference between  $s$  and  $t$  by fixed path  $c$  by

imp. weights each  $\rightarrow$  shortest path  $\rightarrow$  shortest path

Simple algorithm for  $f$  from  $t =$

$I_1 \dots t$

~~Then~~

What if instead

where  $V$  is  $\dots$   $X$  is  $\dots$   $S_i$   $35$

Can't make a general algorithm

Part 4th = looking for <sup>like</sup> golden rule

where  $I$  is  $\dots$   $F$  is  $\dots$

$I$  is  $\dots$   $2F$  is  $\dots$

Min  $I$  is  $\dots$  plus 2  $I$  is  $\dots$

2nd order (maybe not function)  $I$  to  $F$  via various

'broken' states  $B$  which give  $E_B = E_I$  is

and if  $E_B = E_I$  is  $\dots$   $I$

where  $f$  is permitted  $\dots$  and  $d^B B$  is  $\dots$  and  $d^B B$

How Korte's object was to find a consistent  $d$  that is  $\dots$

Will need at least  $n$   $d$  and one  $f$

And count only ~~from~~ broken states  $B$  that are reachable from  $I$

Since  $B$  is reachable  $\dots$  need  $f$  path

a little messy to keep track of  $f$ 's and  $f$

but <sup>main</sup> ~~not~~ conditions are

In  $n$  set of  $n$  states, basically true to  $\dots$

But this is not the end of the story