Conductivity Equations Based on Rate Process Theory and Free Volume Concept for Addressing Low Temperature Conductive Behaviors like Superconductivity

Tian Hao

Chino Hills, CA 91709, USA

(Dated: September 15, 2014)

Abstract

New conduction equations are derived on the basis of Eyring's rate process theory and free volume concept. The basic assumptions are that electrons traveling from one equilibrium position to the other may obey Eyring's rate process theory; the traveling distance is governed by the free volume available to each electron by assuming that electrons may have a spherical physical shape with an imaginative effective radius. The obtained equations predict that the superconductivity happens only when electrons form certain structures of a relative small coordinate number like Cooper pair at low temperatures; If each electron has a large coordinate number such as 8 when electrons form the body-centered-cubic (bcc) lattice structure like Wigner crystal, the predicted conductivity decreases instead increases when temperatures approach to zero. The electron condensation structures have a big impact on the conductivity. A sharp conductivity decrease at low temperatures, probably due to an Anderson transition, is predicted even when the Cooper pair is formed and the electrons can only travel short distances; While the Mott transition appears when crystalline structures like Wigner crystal form. On the other hand, the electron pairing or called the strong spin-spin coupling is predicted to induce Kondo effect when electrons are assumed to travel a very short distance. The Anderson localization seems to have a lot of similarities as Kondo effect such as electron pairing and low traveling distances of electrons at low temperatures. The Cooper pair that is the essence of BCS theory for superconductivity and the spin-spin coupling that is the cause for Kondo effect seem to contradict each other, but are seamlessly united in our current conductivity equations. The topological insulators become the natural occurrences of our equations, as both Kondo insulator and superconductivity share a same physical origin–the electron pairs, but the electrons just travel different distances at these two cases. A material containing an element of a high electro-negativity (or high ionization energy) and an element of a low electro-negativity(or low ionization energy) may form a good topological insulator and superconductor. Any magnetic element, like Iron, Nickel, and Cobalt, that has unpaired electrons and can induce Kondo effect as a dopant, could be a very good superconductor candidate once it is synthesized together with other proper elements of low electro-negativity (for example forming pnictide superconductors). The numbers of both conduction and valence electrons and the volume of a material under investigation have positive impacts on the conductivity. Any method that may increase the numbers of both conduction and valence electrons may move the superconductivity transition temperatures to higher regions. Any method that may reduce the volume of the material like external pressure seems to lower transition temperatures,

unless that the applied pressure is so high that the electron density between the chemical bonds increases. The derived equations are in good agreement with the currently observed experimental phenomena. The current work may shed light on the mechanisms of superconductivity, presenting clues on how to move the superconductivity transition temperatures to higher regions.

I. INTRODUCTION

Conductivities of materials have been extensively addressed for many decades. The rich and distinctive conductive phenomena have generated many different theories and/or models with the attempts of better understanding the underlying physical mechanisms. From pure crystalline materials like metals to semi-conductive metal oxides, amorphous solids, and to superconductors, each class of materials gives remarkable different conductive behaviors, encouraging researchers to patch the models with more complications added in. However, what we don't know grows proportionally with what we have already known so far, especially after the discoveries of Kondo effect, Mott insulators, Anderson insulator, high temperature superconductors, ferropnictides superconductors, topological insulators, and so on. As scientific history has shown repeatedly, we always start with simple and idealized models, enjoy the success of those achievements for some periods of time, be surprised and puzzled with new experimental discoveries that cannot be explained with the current mechanisms/models, be excited with new theories that seem to work perfectly for everything we have observed, and then start a new cycle again...

Back to the knowledge we have accumulated in conductive behaviors of a wide variety of materials, the following facts may be true in the event that we still have many unknowns. 1) The conductivity is resulted from the movements of charge carriers like electrons and ions; 2) The inter-electron interactions cannot be overlooked even in metallic materials; the resistivity comes from not only electron-lattice interactions, but also electron-electron interactions; 3) At low temperatures close to zero Kelvin, electrons may tend to condensate, forming pairs as suggested in BCS theory [1] and even crystal lattice structures predicted by Wigner [2]. Recent experimental evidences may confirm the existence of cooper pairs [3] and the body-centered cubic (bcc) structure in 3D [4] and triangular lattice structure in 2D [5]. An improved precise measurement indicates that the shape of electron is a perfect sphere [6]. All those facts listed above may drive us believe that electrons may be reasonably considered as a spherical particle with a "physical" radius, carrying a negative charge and behaving like a colloidal particle in a liquid phase, since colloidal particles usually carry charges, interact repulsively each other, and can form a perfect bcc crystal lattice in a liquid under certain conditions, mainly due to the lowest energy of bcc lattice structure [7] [8] [9] among all crystal lattice structures.

Similar to electron systems containing a huge amount of fast-moving electrons, colloidal suspensions contain thousands of thousands particles that are non-stop moving due to the Brownian motion. Both systems have complicated many-body problems, and the exact solution to the total interaction energy between particles (electrons) are hard to be estimated. In colloidal suspensions, we know that the inter-particle forces are important to physical properties of whole systems. For example, the viscosity and the micro-structures of colloidal suspensions are strongly dependent on how strong the inter-particle forces are [10]. If an external electric or a magnetic field is applied to a colloidal suspension, the particles are polarized, generating additional amount of charges on particle surfaces and dramatically altering the inter-particle forces. Several orders of magnitudes of viscosity increase are observed under such situations, and those suspensions are called electrorheological fluids [11] or magnetorheological fluids [12] and have been explored extensively within last two decades. The dramatic increases of rheological properties are attributed to the crystallized bcc lattice structure formed by polarized particles and induced by the applied external field. The conductive mechanism of electrorheological fluids obey the variable ranges hopping model [13]. The particle volume fractions that scale how crowded the particles are in a suspension can induce a very similar viscosity increase, due to a percolation type phase transition [14]. Analogous to charged colloidal particles, the electrons, if have a physical shape, can be easily polarized under either an electric or magnetic field and might easily form a crystallized structure, which may strongly control the conductivity, even superconductivity properties of materials.

The Eyring's rate process theory is based on quantum mechanics, and has been widely used in many fields since it was first incepted in 1935 [15][16] [17]. Although his simple and elegant treatment approaches have been fiercely criticized from day one, the success in resolving many fundamental problems like chemical reaction rate, viscosity and diffusion, electrochemical process, and biophysics, etc.., has demonstrated again that the truth is alway simple and his approaches are powerful and accurate, indeed. Together with the free volume concept that has been employed in chemistry and physics fields with great success, Eyring's rate process theory is successfully utilized to describe the viscosity of colloidal suspensions with and without an electric field [18]. The idea is very simple: The free volume unoccupied by the particles in suspensions determine the free "walking" distance of particles, and the process of particles traveling from one equilibrium position to another

is considered to obey Eyring's rate process theory [19]; The viscosity of whole systems is inversely proportional to the available free volume and the rate of particle motion. Instead of trying to calculate the exact multiple-particle interaction forces, we group the impact of surrounding particles into the average "free volume " available to each particle. If many random, disordered, and multi-body systems can be well treated with Eyring's theory, why not electron systems? Such an attempt is made in this article with the aid of the free volume concept. The obtained conductivity equations seem able to describe many distinctive conductive behaviors, especially the superconductivity, at low temperatures.

II. THEORY

As we know, the conductivity, σ, can be expressed as [20]:

$$\sigma = eN_c\frac{v_d}{E} \tag{1}$$

where e is the charge of an electron, N_c is the number of conduction electrons, v_d is the drift velocity of electrons, and E is the applied electric field. For calculating conductivity, one may need to determine the drift velocity, v_d. Assume that an electron moving from one equilibrium position to another obeys Eyring's rate process theory, then according to Eyring [19], a reactant molecule(an electron in this article) should cross a potential barrier (the activation energy) in order to react with another molecules and produce the final product. As illustrated in Fig.1, when an external electric field is applied, this activation energy is reduced by an amount of αw, making the reaction much easier in the forward direction. However, the potential barrier will be raised by an amount of $(1-\alpha)w$ in the backward (reverse) direction, where w is the amount of work done in moving an electron from one equilibrium position to the next, and α is a fraction operative between the initial and activated states. In his late article published in 1958 [21], Eyring pointed out that in condensed systems, α is directly related to the coordinate number (c_n) of a molecule in the system with the relationship, $\alpha = 1/c_n$. The number of electrons crossing the energy barrier in unit time in the electric field direction should be given:

$$\text{Rate in the forward direction} = K^+\lambda[\exp\frac{\alpha w}{k_BT}] \tag{2}$$

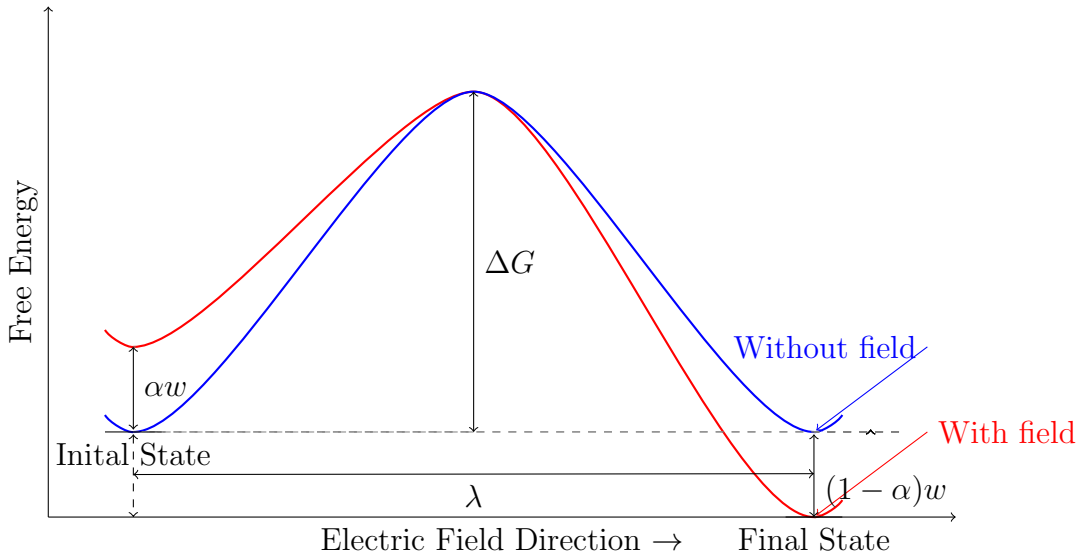

FIG. 1: Illustrative diagram for activation potential energy with and without an electric field

Where $K^+ = \frac{k_B T}{h} \exp(-\Delta G/RT)$, is the specific velocity rate in any direction for the undisturbed system, k_B is the Boltzmann constant, ΔG is the standard Gibbs free energy of the activation process, R is the gas constant, h is the Planck constant, and λ is the distance between the initial equilibrium position to the final position. In analogy, the number of electrons crossing the energy barrier in unit time in the reverse direction should be given:

$$\text{Rate in the backward direction} = K^+ \lambda [\exp \frac{-(1-\alpha)w}{k_B T}] \tag{3}$$

The net rate, the velocity of an electron in the direction of an applied electric field, is thus written as:

$$\text{Net Rate } = K^+ \lambda [\exp \frac{\alpha w}{k_B T} - \exp \frac{-(1-\alpha)w}{k_B T}] = v_d \tag{4}$$

By the definition, the work needs to move an electron in a distance λ under an electric field, E, may be expressed as:

$$w = e\lambda E \tag{5}$$

Combining Eqs.4 and 5, one may obtain the velocity of an electron:

$$v_d = K^+ \lambda [\exp \frac{\alpha e \lambda E}{k_B T} - \exp \frac{-(1-\alpha) e \lambda E}{k_B T}] \tag{6}$$

Now, one may need to determine λ, the distance that an electron can travel from one equilibrium position to the next. It should be related to how much the free volume is

available for a conduction electron in systems. According to standard solid state physics, the Fermi wavevector (radius) k_F can be expressed as [20]:

$$k_F = (\frac{3\pi^2 N_v}{V_u})^{1/3} \tag{7}$$

Where N_v is the number of valence electrons in one unit cell and V_u is the volume of unit cell. Assume that the conduction electrons can only take the space outside the Fermi spheres and all electrons initially stay inside Fermi surface. In one unit cell, the free volume V_c available may be expressed as:

$$V_c = V_u - V_F \tag{8}$$

Where V_F is the volume of Fermi sphere that can be expressed as:

$$V_F = \frac{4\pi}{3} {k_F}^{-3} = \frac{4V_u}{9\pi N_v} \tag{9}$$

Thus Eq. 8 can be expressed as:

$$V_c = (1 - \frac{4}{9\pi N_v})V_u \tag{10}$$

If the number of unit cells in a material is N_u, and the total volume of the material under consideration is V_m, the total free volume V_f:

$$V_f = N_u V_c = (1 - \frac{4}{9\pi N_v})N_u V_u = (1 - \frac{4}{9\pi N_v})V_m \tag{11}$$

as $N_u V_u = V_m$ by definition. The V_f is the free volume that all conduction electrons can have in the whole material body, V_m. As mentioned in Section I, the electrons may be considered as spherical shape particles dispersed in a continuous "solid atomic lattice", similar to colloidal particles dispersed in a continuous liquid medium. In this scenario, we may be able to estimate the effective radius of an electron based on the free volume shown in Eq. 11 by utilizing a same analogous method for calculating the free volume in colloidal suspensions. Hao has developed a method for calculating the free volume of particulate systems using the inter-particle spacing (IPS) concept [11] [18] [22]. The inter-particle spacing (IPS) that scales the distance between two particle surfaces was used for estimating the free volume of whole systems to derive the viscosity of colloidal suspension systems [11] [18]. For estimating IPS, Hao [22] used Kuwabaras cell model [23] that was extended by many other researchers [24] [25][26] for calculating the electrophoretic and electroacoustic mobility of particles. The obtained IPS may be expressed as:

$$IPS = 2(\sqrt[3]{\phi_m/\phi} - 1)r \tag{12}$$

where r is the effective radius of an electron, ϕ_m is the maximum packing volume fraction achieved by the conduction electrons, and ϕ is the volume fraction of conduction electrons. Suppose that an electron can move three dimensionally on both left and right sides, the free volume of such an electron may occupy can be expressed as:

$$V_{fe} = (2IPS)^3 = 64(\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \tag{13}$$

Eq. 13 gives the free volume of each individual conduction electron. If the number of conduction electrons in the whole systemis is N_c , then the total free volume is:

$$V_f = V_{fe} N_c = 64 N_c (\sqrt[3]{\phi_m/\phi} - 1)^3 r^3 \tag{14}$$

Note that Eq.11 should be identical to Eq.14, one thus can obtain the effective radius of an electron:

$$r = \frac{1}{12(\sqrt[3]{\phi_m/\phi} - 1)} [\frac{(27\pi N_v - 12)V_m}{\pi N_c N_v}]^{1/3} \tag{15}$$

Since an electron may move both left and right sides with the distance of IPS, the equilibrium distance of an electron can travel, λ, may be expressed as:

$$\lambda = 2IPS = \frac{1}{3}[\frac{(27\pi N_v - 12)V_m}{\pi N_c N_v}]^{1/3} = [\frac{(9\pi N_v - 4)V_m}{9\pi N_c N_v}]^{1/3} \tag{16}$$

Now, we have the velocity of conduction electrons as shown in Eq. 6, the distance that a conduction electron can travel as shown in Eq.16, one may easily obtain the conductivity equation based on Eq.1:

$$\begin{aligned}
\sigma &= \frac{eN_c K^+ \lambda}{E} [\exp \frac{\alpha e \lambda E}{k_B T} - \exp \frac{-(1-\alpha) e \lambda E}{k_B T}] \\
&= \frac{e k_B T N_c^{2/3}}{hE} \exp(\frac{-\Delta G}{RT}) [\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3} [\exp \frac{\alpha e \lambda E}{k_B T} - \exp \frac{-(1-\alpha) e \lambda E}{k_B T}] \\
&= \frac{e k_B T N_c^{2/3}}{hE} \exp(\frac{-\Delta G}{RT}) [\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3} \\
&\quad [\exp \frac{\alpha e E}{k_B T} [\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3} - \exp \frac{-(1-\alpha) e E}{k_B T} [\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3}]
\end{aligned} \tag{17}$$

As one may see, the conductivity has complicated relationships with the number of valence electrons in unit cell, N_v; the number of conduction electrons in whole system, N_c; the volume of a material under study, V_m; A parameter related to the structures that electrons may form, α; the standard Gibbs free energy, ΔG; and the most importantly, the temperature,

T. In thermodynamics, the Gibbs free energy, ΔG, has a relationship with the equilibrium constant, K_{eq}:

$$-\Delta G = RT \ln K_{eq} \tag{18}$$

$$K_{eq} = \exp \frac{-\Delta G}{RT} \tag{19}$$

We may be able to use the equilibrium constant K_{eq} to replace the Gibbs free energy term in Eq.17. As we mentioned earlier, in condensed systems, α is related to the coordinate number of an electron in the system, c_n, with a simple relationship;

$$\alpha = \frac{1}{c_n} \tag{20}$$

When $c_n = 1$, then $\alpha = 1$. At this condition, electrons form pairs, and the conductivity equation Eq.17 may be written as:

$$\sigma = \frac{ek_BTN_c^{2/3}}{hE} \exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3}[\exp \frac{eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3} - 1] \tag{21}$$

When $c_n = 4$, then $\alpha = 1/4$. At this condition, electrons form tetrahedron lattice structure, and the conductivity equation Eq.17 may be written as:

$$\sigma = \frac{ek_BTN_c^{2/3}}{hE} \exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3} \\ [\exp \frac{0.25eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3} - \exp \frac{-0.75eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3}] \tag{22}$$

When $c_n = 8$, then $\alpha = 1/8$. At this condition, electrons form body-centered cubic (bcc) lattice structure, Wigner crystal at 3D [2], and the conductivity equation Eq.17 may be written as:

$$\sigma = \frac{ek_BTN_c^{2/3}}{hE} \exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3} \\ [\exp \frac{0.125eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3} - \exp \frac{-0.815eE}{k_BT}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3}] \tag{23}$$

We will evaluate all these situations in a more generic manner in next section, for the purpose of extracting what are the generic trends/correlations between the conductivity and all those parameters in the equations.

III. RESULTS

For illustrative comparison purpose, we may need to further simplify the conductivity equations listed above based on some approximations. First, let's focus on temperature dependence. The electron traveling distance, λ, should vary with temperature, on the basis of Fermi-Dirac distribution function with the relations $N_v \propto T^{3/2}$, $N_c N_v \propto T^3$, and $\lambda \propto T^{-1/2}$ approximately [27]. It will be assumed to be independent of temperature for clarity and easy evaluation purpose, assigned as about 100 nanometers as a starting point if the temperature variation range is not too wide in the consideration. So $eE\lambda/k_B$ is about 10 for a small electric field, 10 V/mm. The term ek_B/Eh is in the orders 10^{-13}. The number of conduction electrons per unit volume is $\sim 10^{23}$, about one conduction electron per atom. The equilibrium constant $\exp(\frac{-\Delta G}{RT})$ is usually a fairly large number, typically $\sim 10^4$. So the term $\frac{ek_B N_c^{2/3}}{hE}\exp(\frac{-\Delta G}{RT})[\frac{(9\pi N_v - 4)V_m}{9\pi N_v}]^{1/3}$ is $\sim 10^5$. The term $\frac{eE}{k_B}[\frac{(9\pi N_v - 4)V_m}{9\pi N_v N_c}]^{1/3}]$ is ~ 10. Under those approximations, the conductivity equation may be written as:

$$\sigma = AT[\exp\frac{10\alpha}{T} - \exp\frac{-10(1-\alpha)}{T}] \tag{24}$$

where A is a constant, $\sim 10^5$. For simplicity and easy comparison reason, A will be considered as 1 when we plot figures. Using Eq. 24, one may easily see how conductivity is going to change with temperature, which is shown in Fig. 2. Three electron condensation structures are evaluated: the electron pairs, the tetrahedron lattice, and the bcc lattice. First, under all those three conditions, there seem to be a sharp conductivity increase when the temperature approaches to zero: When electrons form pairs, the conductivity slowly increases with temperature decreases and suddenly starts to jump up when the temperatures reach a critical point, about 5 K, which may be the transition point for superconductivity. When electrons form tetrahedron lattice structure, the conductivity increases with the decrease of temperature in a much slower pace in comparison with that when electrons form pairs; however, there is still a sharp increase of conductivity but occurring at a little lower transition temperature, about 2 K. When electrons form Wigner crystal, bcc lattice structure, an abnormal phenomenon appears: The conductivity decreases with the decrease of temperatures and sharply increases when the temperature is very close to zero. Those findings at

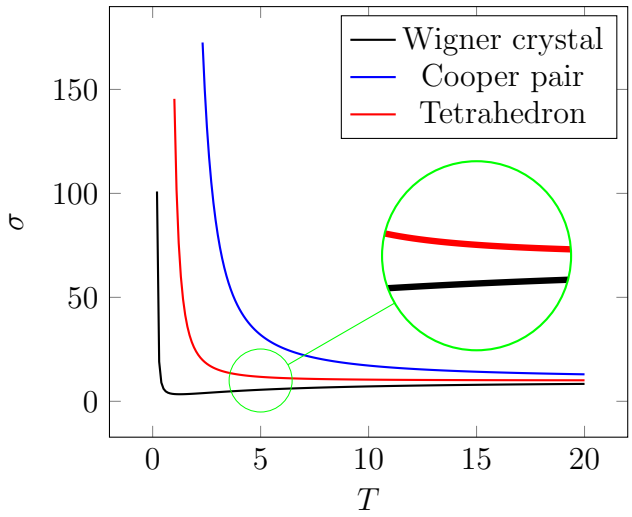

FIG. 2: Conductivity vs temperature at different lattice structures. The coordinate number is 1 for Cooper pair, 4 for tetrahedron, and 8 for Wigner crystal (bcc) lattice.

least demonstrate three things: 1) Electron pairs seem to favor superconductivity behaviors, which is in consistence with Cooper pair concept in BCS theory; 2) With electron coordinate numbers changing from 1 to 8, the transition temperatures move toward to lower ends, implying that electron trapping or localization from the formed crystalline structures may become a great hindrance for electron movements and thus lower the conductivity; Mott localization may come from the "crystalinity energy" created by other associated electrons; 3) When the Wigner crystal forms, the conductivity decreases rather than increases when the temperatures go lower, even though the electrons are assumed to travel such a long distance, 100 nm. This decrease may preclude the Mott transition phenomena if all other conditions are met, such as that the electrons can only travel a short distance.

For further elucidating the trends, we use 3D plots to illustrate the conductivity vs. both the temperature and α, first at the presumption that the electrons can still travel 100 nm from one equilibrium point to another, see Fig.3, and second at the presumption that the electrons may travel a smaller distance, 10 nm, see Fig.4. As clearly demonstrated in Fig. 3, the sharp conductivity increase that represents the superconductivity behavior, occurs at low temperatures and α is about 1; when temperatures and α are relatively high, the conductivity is flat and low. If the electron traveling distance is as lower as 10 nm, as shown in Fig.4, the conductivity is still higher when the temperatures are low and in addition α is about 1, but the increment is very limited. An intriguing thing happens when both

temperature and α are low, the conductivity actually decreases instead increases, which is opposite to superconductivity and may imply that Mott transition occurs at such conditions,

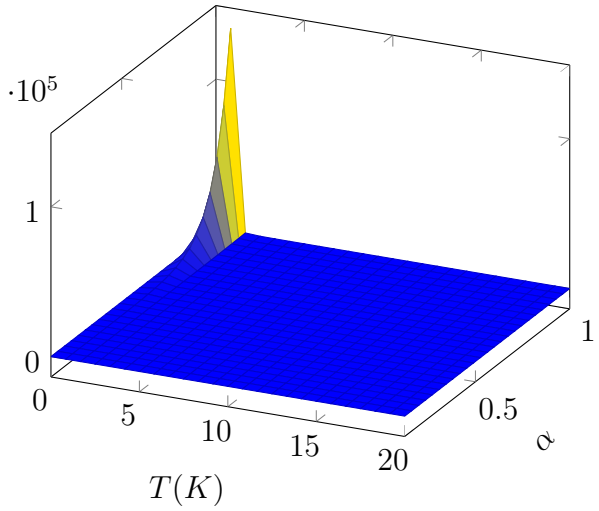

FIG. 3: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 100 nm

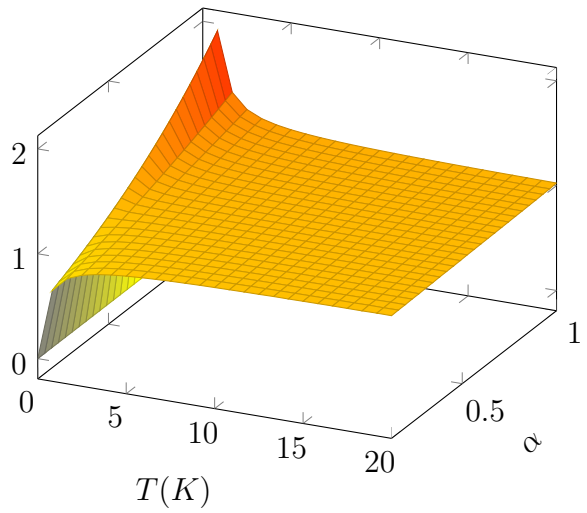

FIG. 4: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 10 nm

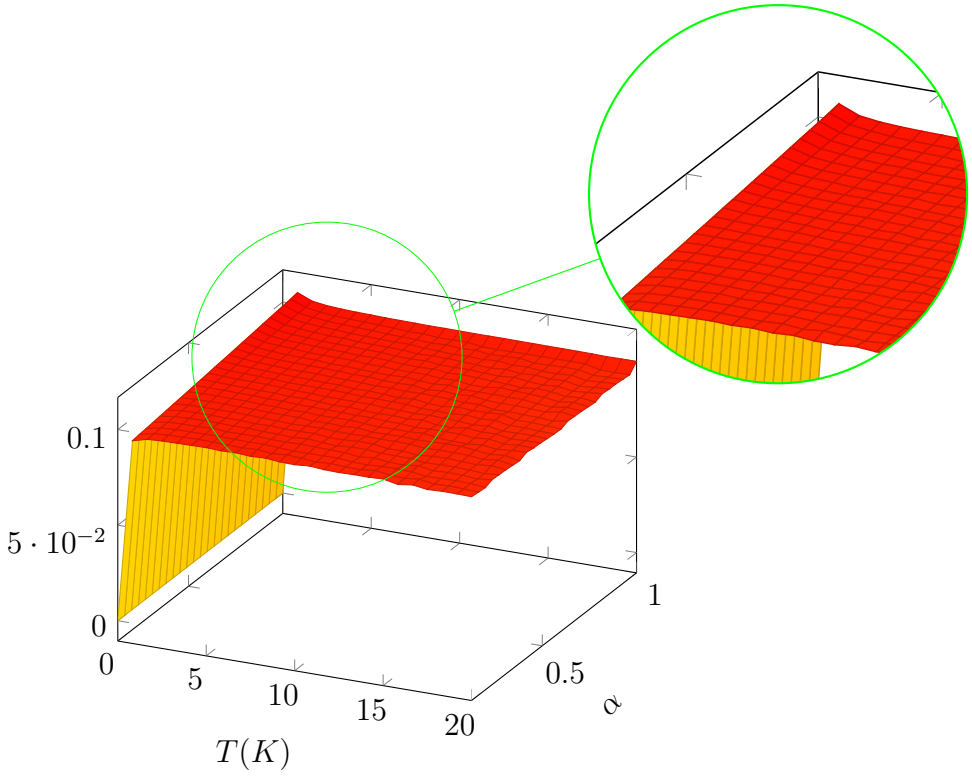

FIG. 5: Conductivity vs both temperatures and the structure related parameter α at electron traveling distance about 1 nm

where electrons are localized due to the interaction between electrons. Note that electrons are still assumed to travel a reasonable long distance at those conditions, 10 nm, further indicating that the electron crystallization may be responsible for Mott transition, the decrease rather than increase of conductivity at low temperatures. What happens if the electron traveling distance goes down to 1 nm? The illustrative graph is shown in Fig. 5. In such conditions, the conductivity goes down substantially even at high α, implying that even the Cooper pairs cannot prevent insulator transitions. Everything seems to completely stop due to the strong localization mainly resulted from the strong interferences between electrons, an Anderson localization. Again, the Mott localization may be resulted from crystalline structures formed in low temperature, corresponding to the low α region in Fig. 5; while the Anderson localization may be resulted from the strong interference between electrons at high α regions in Fig. 5. The most intriguing part is that when electron pairs form at $\alpha = 1$, the conductivity seems to slowly increase as temperature approaches to zero, go through a maximum, and then suddenly drop off. This seems to be the Kondo effect

observed in metallic alloy doped with magnetic impurities [28] and resulted from a strong spin-spin coupling between two electrons [29] [30], again, the electron pairs. Theoretically, Anderson localization model at low temperatures is found to be equivalent to what has been discussed for Kondo model [31] [32], and the similarity is again demonstrated in Fig. 5 at low temperatures and low traveling distances for electrons. The electron pairing could produce superconductivity when electrons are assumed to travel a relatively long distance as shown in Fig. 3; while it could induce Kondo insulator transition when electrons can only travel a very short distance as shown in Fig. 5. The Cooper pair that is the essence of BCS theory for superconductivity and the spin-spin coupling that is the cause for Kondo effect seem to contradict each other, but are seamlessly united in our current conductivity equation. The discovery may imply that Kondo insulators could potentially be very good superconductors, as the electron pairs are already formed and only thing needed is to make electrons travel a relatively long distance. Theoretically predicted and experimentally confirmed existence of topological insulators [33] [34] [35], where the surfaces show high conductivity even superconductivity properties and the interior is Kondo insulator, further confirm that the Kondo insulator and superconductor do co-exist together. In the interior of topological insulators all paired electrons are strongly localized probably due to the strong electron-phonon interactions; However, on the surfaces the electron-phonon interactions may become weak due to only half amount of atomic sites available to hinder the electron movements. If this physical picture is true, a material containing an element of a high electro-negativity (or high ionization energy like oxygen and fluorine) and an element of a low electro-negativity(or low ionization energy like Caesium, Barium, and Francium, etc.) may form a good topological insulator: an element of a high electro-negativity will ensure that electrons can be strongly pulled together to form pairs, while an element of a low electro-negativity will not hinder the electron movements too much, so electrons can travel a relatively long distance and the surfaces will show superconductivity. The ratio between those two elements could be critical, too, as we don't want too many atoms of a high electro-negativity in the systems to hold off the electron movements. In the meanwhile, since Kondo insulators are potentially good superconductors, any magnetic element, like Iron, Nickel, and Cobalt, that has unpaired electrons and can induce Kondo insulator as a dopant, could be a very good superconductor candidate once it is synthesized together with other proper elements of low electro-negativity. The discovery of Iron-based superconductors called ferropnictides [36] [37] [38] [39] further

supports the statements above derived from the conductivity equations.

It seems that the electron traveling distance plays a critical role here and it should be interesting to see how conductivity is going to change with λ, especially when Cooper pairs form, as this is the most favorable condition for superconductivity. As expected, the conductivity increases with the increase of λ, and superconductivity appears when the

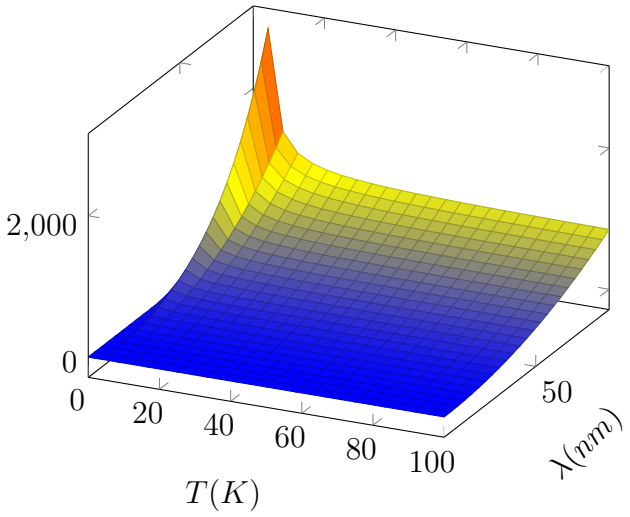

FIG. 6: Conductivity vs both temperatures and electron traveling distance, λ, when Cooper pairs form

.

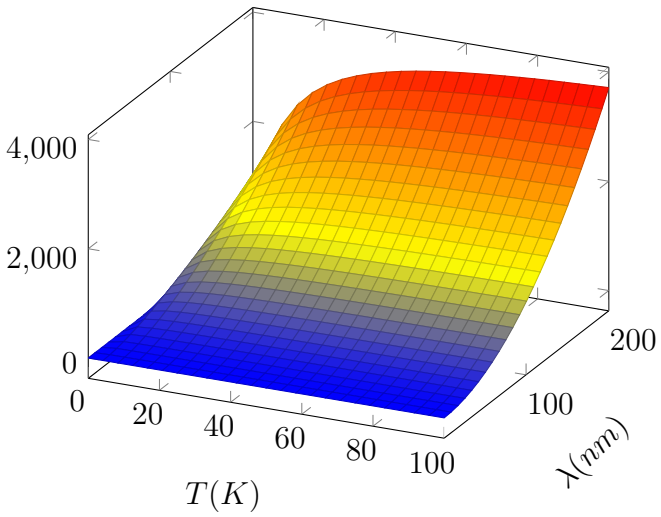

FIG. 7: Conductivity vs both temperatures and electron traveling distance, λ, when Wigner crystal forms

temperature is low. Note that the superconductivity transition temperatures seem to shift to higher regions when electrons are able to travel a long distance, which may give some clues on what drives high temperature superconductivity. In other words, if electrons can form Cooper pairs and are able to travel a relatively long distance, the superconductivity may appear at higher temperatures. For curiosity, what happens when Wigner crystal forms and λ is getting bigger? The graph is shown in Fig.7. With no surprise, the conductivity becomes larger when λ increases, but gets smaller when temperature goes down. A much more noticeable decrease occurs at higher λ, probably implying that electron interaction or localization may become more pronounced at low temperature and higher traveling distance.

The conductivity obviously has a complicated relationship with the volume of a material, the number of conduction electrons, and the number of valence electrons. We will use the conductivity equation under the assumption that Cooper pairs form for evaluation, as these equations will give more relevant information on superconductivity. The conductivity dependence on both temperature and the volume of a material is shown in Fig.8. The conductivity increases very slightly when the volume increases, and a relative large increase of conductivity happens only at low temperature regions. In this regards, the high pressure that typically makes material shrink will lower the conductivity, making the superconductivity transition temperature lower; However, under extremely high pressure, the electron density must increase for maintaining the stability of chemical bonds. Such an increase in electron density comes laterally from the region normal to the bond [40] [41], providing more valence electrons and making the superconductivity transition temperature higher. Those physical scenarios are qualitatively consistent with the experimental observation on how the pressure will change the superconductivity transition temperatures [42] [43]: Most time the high pressures lower superconductivity transition temperatures initially and raise it up once the pressures further increase. The impact of the numbers of both the valence electrons in unit cell and the conduction electrons in whole system is shown in Fig.9. The valence electrons only have an impact on conductivity at low temperature regions with a somewhat linear manner (see Fig.9 (b)) ; In contrast, the number of conduction electrons may have a deep impact: the conductivity dramatically increases when the number of conduction electrons reach a certain level, a phenomenon similar to the percolation transition observed in amorphous systems.

These new conductivity equations seem to be very consistent with experimental observa-

tions. The next important question will be how we can have a superconductor with higher transition temperatures?

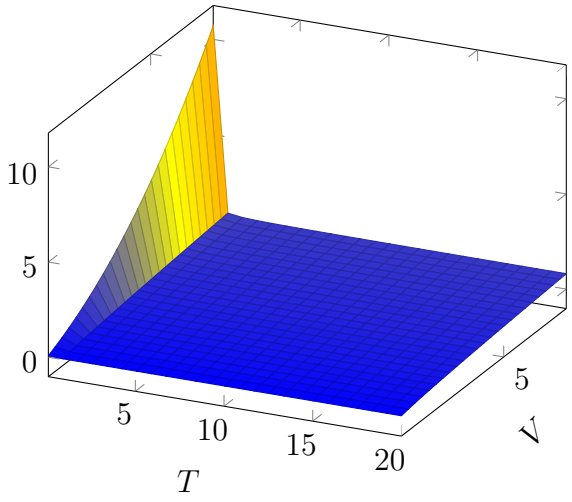

FIG. 8: Conductivity vs both temperature and the volume of a material

.

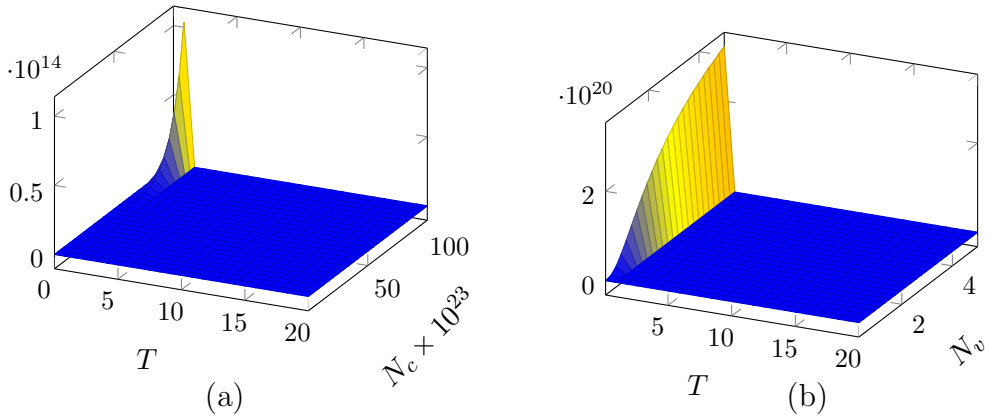

FIG. 9: (a) Conductivity vs both temperature and number of conduction electrons, N_c; (b) Conductivity vs both temperature and number of valence electrons, N_v.

.

Based on all figures showing from Fig. 2 to Fig. 9, we may say that the longer traveling distance for electrons, the larger number of conduction electrons, the larger number of valence electrons, and most importantly the electron pairing structure, will favor better superconductors with higher transition temperatures. From Fig.8, we may conclude that the volume reduction of a material (such as from the bulk to a thin film), the transition

temperature will be lowered, which has been confirmed experimentally [44][45][46]. We may not be able to control the electron condensation structure at this moment, but we may be able to do it in the future with new technologies that can help us better manipulate and monitor. If we can increase the numbers of both conduction and valence electrons using extremely thin epitaxy film deposited on a substrate, we may be able to increase the superconductivity transition temperatures, as confirmed experimentally [47].

IV. CONCLUSION

Using Eyring's rate process theory and the free volume concept, we come up conductivity equations under assumptions that electrons may have a spherical physical shape and the available free volume for each electron scales the traveling distance from one equilibrium position to the other; The electron traveling rate is assumed to obey Eyring's rate process theory. The conductivity has a complicated relationship with the electron condensation structure, the traveling distance, the numbers of both the conduction and the valence electrons, the volume of the material under investigation, and the most importantly, the temperature. When electrons form the Cooper pairs, the conductivity increases with the decrease of temperatures, and the superconductivity occurs when temperature is below a critical value; While when electrons form Wigner crystal (bcc lattice structure), the conductivity decreases when the temperature decreases, and the Mott transition, opposite to superconductivity, is predicted. However, even when Cooper pairs form but the electrons is only able to travel a short distance, the conductivity sharply decreases rather than increases, probably due to the Anderson localization resulted from the electron interference between each other, causing Anderson insulator transition. If the paired electrons can only travel a very short distance, the Kondo effect is predicted. The Anderson localization seems to have a lot of similarities as Kondo effect such as electron pairing and low traveling distances of electrons at low temperatures. The Cooper pair that is the essence of BCS theory for superconductivity and the spin-spin coupling that is the cause for Kondo effect seem to contradict each other, but are seamlessly united in our current conductivity equations. The topological insulators become the natural occurrences of our equations, as both Kondo insulator and superconductivity share a same physical origin–the electron pairs, but the electrons travel different distances at those two cases. We predict that a material containing an element

of a high electro-negativity (or high ionization energy) and an element of a low electro-negativity(or low ionization energy) may form a good topological insulator: an element of a high electro-negativity will ensure that electrons can be strongly pulled together to form pairs, while an element of a low electro-negativity will not hinder the electron movements too much, so electrons can travel a relatively long distance and the surfaces will show superconductivity. Any magnetic element, like Iron, Nickel, and Cobalt, that has unpaired electrons and can induce Kondo effect as a dopant, could be a very good superconductor candidate once it is synthesized together with other proper elements of low electro-negativity, forming pnictide superconductors as an example. As expected, the conductivity increases with the electron traveling distance, no matter which structures form (Cooper pair or Wigner crystal). It increases with the volume of the material, the numbers of both the conduction and the valence electrons. Anything that can change the volume of the material like the pressure and the thin film and can change the numbers of the conduction and the valence electrons, could potentially change the conductivity. For obtaining a superconductor with higher transition temperatures, electrons may better form Cooper pair and are able to travel a relatively long distance. Our equations are qualitatively in consistent with the currently observed rich conductivity phenomena.

Acknowledgments

The author sincerely appreciate Yingqin Li for her generous help and encouragement.

---

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Microscopic Theory of Superconductivity, Phys. Rev. **106**, 162-164(1957).

[2] E. Wigner, On the Interaction of Electrons in Metals, Phys. Rev. **46**, 1002(1934).

[3] J. S. Van Dyke, F. Massee, M. P. Allan, J. C. S. Davis, C. Petrovic, and D. K. Morr, Direct Evidence for a Magnetic f-electron-mediated Pairing Mechanism of Heavy-fermion Superconductivity, Proc. Natl. Acad. Sci., **111**, 11663(2014)

[4] B. A. Poit, Z. Jiang, C. R. Dean, L. W. Engel, G. Gervais, L. N. Pfeiffer, and K. W. West, Wigner Crystallization in Quasi-three-dimensional Electronic System, Nature Phys., **4**, 936(2008)

[5] D. Zhang, X. Huang, W. Dietsche, K.von Klitzing, and J. H. Smet, Signatures for Wigner Crystal Formation in the Chemical Potential of a Two-Dimensional Electron System, Phys. Rev. Lett. **113**, 076804(2014).

[6] J. J. Hudson, D. M. Kara, I. J. Smallman, B. E. Sauer, M. R. Tarbutt, E. A. Hinds, Improved Measurement of the Shape of the Electron, Nature, **473**, 493(2011)

[7] T. Chen, R. N. Zitter, and R. Tao, Laser Diffraction Determination of the Crystalline Structure of Electrorheological Fluids, Phys. Rev. Lett. **68**, 2555(1992).

[8] A. Yethiraj and A. van Blaaderen, A Colloidal Model System with an Interaction Tunable Hard Sphere to Soft and Dipolar, Nature, **421**, 513(2003)

[9] Y. Kim, A. A. Shah, and M. J. Solomon, Spatially and Temporally Reconfigurable Assembly of Colloidal Crystals, Nature Comm. **5**, 3676(2014)

[10] W. B. Russel, D. A. Saville, W. R. Schowalter, Colloidal Dispersions (Cambridge Monographs on Mechanics), Cambridge University Press, March 27, 1992

[11] T. Hao, Electrorheological Fluids: The Non-aqueous Suspensions, Elsevier, December 19, 2005

[12] N. M. Wereley, Ed., Magnetorheology: Advances and Applications, Royal Society of Chemistry, RSC Smart Materials, Cambridge, UK, 2014

[13] T. Hao, and Yuanze Xu, Conductive Behaviors of Polymer-Based Electrorheological Fluid under Zero and Oscillatory Mechanical Fields, J. Coll. Interf. Sci, **181**, 581(1996).

[14] T. Hao, Y. Chen, Z. Xu, Y. Xu, and Y. Huang, Percolation Transition in Electrorheological Fluids, Chinese J. Poly. Sci, **12**, 97(1994)

[15] H. Eyring, The Activated Complex in Chemical Reactions, J. Chem. Phys, **3**, 107(1935).

[16] P. Hanggi, P. Talkner, and M. Borkvec, Reaction-rate Theory: Fifty Years after Kramers, Rev. Mod. Phys., **62**, 251(1990)

[17] K. J. Laidler, and M. C. Klng, The Development of Transition-State Theory, J. Phys. Chem., **87**, 2657-2664(1983)

[18] T. Hao, Viscosities of Liquids, Colloidal Suspensions, and Polymeric Systems under Zero or Non-zero Electric Field, Adv. Coll. Interf. Sci. **142**, 1(2008).

[19] S. Glasstone, K. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw Hill; 1st Ed., 1941.

[20] C. Kittel, Introduction to Solid State Physics, Wiley, November 11, 2004

[21] F. H. Ree, T. Ree, and H. Eyring, The Relaxation Theory of Transport Problems in Condensed

Systems, Ind. Eng. Chem., **50**, 1036(1958)

[22] T. Hao, and R. E. Riman, Calculation of Interparticle Spacing in Colloidal Systems, J. Coll. Interf. Sci., **297**, 374-377(2006).

[23] S. Kuwabara, The Forces Experienced by Randomly Distributed Parallel Circular Cylinders or Spheres in a Viscous Flow at Small Reynolds Numbers, J. Phys. Soc. Jpn., **14**, 527-532(1959)

[24] M. W. Kozak, and E. J. Davis, Electrokinetic Phenomena in Fibrous Porous Media, J. Coll. Interf. Sci., **112**, 403-411(1986).

[25] S. Levine, and G. H. Neale, The Prediction of Electrokinetic Phenomena within Multiparticle Systems. I. Electrophoresis and Electroosmosis, J. Coll. Interf. Sci., **47**, 520-529(1974).

[26] H. Ohshima, Dynamic Electrophoretic Mobility of Spherical Colloidal Particles in Concentrated Suspensions, J. Coll. Interf. Sci., **195**, 137-148(1997).

[27] J. Colinge, and C. A. Colinge, Physics of Semiconductor Devices, Kluwer Academic Publishers, 2002

[28] J. Kondo, Resistance Minimum in Dilute Magnetic Alloys, Prog. Theor. Phys., **32(1)**, 37-49(1964).

[29] A. C. Hewson, The Kondo Problem to Heavy Fermions, Cambridge University Press, Cambridge, 1997.

[30] Y. Zhang, S. Kahle, T. Herden, C. Stroh, M. Mayor, U. Schlickum, M. Ternes, P. Wahl1, K. Kern, Temperature and Magnetic Field Dependence of a Kondo System in the Weak Coupling Regime, Nature Comm., **4**, 2110(2013)

[31] J. R. Schrieffer and P. A. Wolff, Relation between the Anderson and Kondo Hamiltonians, Phys. Rev., **149**, 491 (1966)

[32] B. Mhlschlegel, Relation between the Anderson and Kondo Hamiltonians for the Case of Degenerate Impurity Orbitals, Zeitschrift fur Physik, **208**, 94-103(1968)

[33] C. L. Kane, and E. J. Mele, Z_2 Topological Order and the Quantum Spin Hall Effect, Phys. Rev. Lett., **95** 146802(2005)

[34] M. Knig, S. Wiedmann, C. Brne, A. Roth, H. Buhmann, L. W. Molenkamp, X. Qi, S. Zhang, Quantum Spin Hall Insulator State in HgTe Quantum Wells, Science, **318**, 766-770(2007).

[35] J. E. Moore, The Birth of Topological Insulators, Nature, **464**, 194-198(2010)

[36] Y. Kamihara, H. Hiramatsu, M. Hirano,R. Kawamura, H. Yanagi, T. Kamiya,H. Hosono, Iron-Based Layered Superconductor: LaOFeP, J. Am. Chem. Soc., **128 (31)**, 10012-10013(2006).

[37] J. C. Davis, and P. J. Hirschfeld, Iron-Based Superconductors: Enigmatic Nematic, Nature Physics, **10**, 184-185 (2014).

[38] E. P. Rosenthal, E. F. Andrade, C. J. Arguello, R. M. Fernandes, L. Y. Xing, X. C. Wang, C. Q. Jin, A. J. Millis, and A. N. Pasupathy, Visualization of Electron Nematicity and Unidirectional Antiferroic Fluctuations at High Temperatures in NaFeAs, Nature Physics, **10**, 225-232(2014)

[39] Y. Luo, L. Pourovskii, S. E. Rowley, Y. Li, C. Feng, A. Georges, J. Dai, G. Cao, Z. Xu, Q. Si, N. P. Ong, Heavy Fermion Quantum Criticality and Destruction of the Kondo Effect in a Nickel Oxypnictide, Nature Materials, **13**, 777 (2014)

[40] G. V. Gibbs, J. W. Downs, and M. B. Boisen, The Elusive SiO bond. In: Silica: Physical Behavior, Geochemistry, and Materials Applications. P.J. Heaney, C.T. Prewiit, G.V. Gibbs GV, Ed., Rev. Mineral, **29**, 331-368(1994)

[41] C. T. Prewitt, and R. T. Downs, High-Pressure Crystal Chemistry, Reviews in Mineralogy, 37, Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior, Russell J. Hemley, Ed., Mineralogical Society of America, Washington DC, 283-317(1998)

[42] B. Lorenz, and C. W. Chu, High Pressure Effects on Superconductivity, Frontiers in Superconducting Materials, 459-497(2005)

[43] S. Gabni, I. Takov, G. Prist, E. Gao, K. Flachbart, T. Mori, D. Braithwaite, M. Mek, K. V. Kamenev, M. Hanfland, and P. Samuely, High-pressure Effect on the Superconductivity of YB_6, Phys. Rev. B, **90**, 045136(2014)

[44] D. G. Naugle, R. E. Glover, W. Moormann, Thickness Dependence of the Transition Temperature of Superconducting Films, Physica, **55**, 250-255(1971)

[45] O. Crauste, C. A. Marrache−Kikuchi, L. Berge, D. Stanescu, and L. Dumoulin, Thickness Dependence of the Superconductivity in Thin Disordered NbSi Films, J Phys.: Conf. Ser. **150**, 042019(2009)

[46] Ze-Lei Guan, Yan-Xiao Ning, Can-Li Song, Jian Wang, Jin-Feng Jia, Xi Chen, Qi-Kun Xue, and Xucun Ma, Sample-size Dependence of the Superconducting Transition of Ribbon-shaped Pb Nanocrystals Studied by Scanning Tunneling Spectroscopy, Phys. Rev. B, **81**, 054516(2010).

[47] A. T. Bollinger, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich, and I. Boovi, Superconductor−insulator Transition in $La_{2-x}Sr_xCuO_4$ at the Pair Quantum Resistance, Nature, **472**, 458-460 (2011).

[48] Y. Ivry, Chung-Soo Kim, A. E. Dane, D. De Fazio, A. McCaughan, K. A. Sunter, Q. Zhao, K. K. Berggren, Universal Scaling of the Critical Temperature for Thin Films near the Superconducting-to-insulating Transition, 22 Jul 2014, arXiv:1407.5945 [cond-mat.supr-con].