

Half-century of Efros-Shklovskii Coulomb gap. Romance with Coulomb interaction and disorder.

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The Efros-Shklovskii (ES) Coulomb gap in the one-electron density of localized states and the ES law of the variable range hopping conductivity were coined 50 years ago. The theory and its first confirmations were reviewed in SE monograph published 40-years ago. This paper reviews the subsequent experimental evidence, theoretical advancements, and novel applications of the ES law. Out of hundreds of experimental validations of the ES law in a diverse range of materials, I focus on those where the dynamic range of conductivity exceeds four orders of magnitude. These include three- and two-dimensional semiconductors under both zero and high magnetic fields, localized phases in the quantum Hall effect, granular metals, nanocrystal arrays, and conducting polymers. Additionally, I discuss the non-ohmic ES law and the Coulomb gap near insulator-metal transition. Recent developments of other concepts of the ES book are also discussed.

I. INTRODUCTION

50 years ago Efros and Shklovskii (ES) penned the paper [1] “Coulomb gap and low temperature conductivity of disordered systems”. It elucidated how Coulomb interaction between localized electrons in semiconductors creates the power law Coulomb gap of the one-electron density of states near the Fermi level and changes temperature dependence of Mott variable hopping conductivity to the ES law.

Localized electron states in lightly doped semiconductors are formed by randomly positioned donors. Typically semiconductors are compensated, i. e. n -type semiconductor with concentration of donors N_D has a concentration $N_A < N_D$ of acceptors. At low temperatures each acceptor captures an electron from a donor and becomes negative. As a result N_A donors become positive while $N_D - N_A$ donors are still neutral. Charged donors and acceptors create a random potential which shifts energy of the donor i up or down by a value ϵ_i . This broadens the originally δ -functional peak of the density of donor states. At low temperature lower energy occupied donor levels are separated by the Fermi level (chemical potential) μ from higher empty levels. Before 1975 it was believed that near the Fermi level μ the density of states (DOS) $g(\epsilon) = g(\mu) = \text{Const.}$ ES showed [1] that due to the Coulomb interaction between electrons

$$g(\epsilon) = \frac{\pi \kappa^3 (\epsilon - \mu)^2}{3 e^6}. \quad (1)$$

in a three-dimensional (3D) semiconductor and

$$g(\epsilon) = \frac{\pi \kappa^2 |\epsilon - \mu|}{2 e^4}. \quad (2)$$

in a two-dimensional (2D) one. Here κ is the dielectric constant of the semiconductor (and in 2D of its environment), e is the proton charge and coefficients $\pi/3$ and $\pi/2$ were found with help of the self-consistent approximation [2]. Thus, the density of states has a power law gap at the Fermi level, which is termed the Coulomb gap by ES. One can say that the Coulomb gap originates due to the exciton effect, i. e. attraction between an electron excited from occupied to an empty in the ground state donor to the hole it left at the original donor. The major consequence of this gap is replacement of the Mott variable

range hopping conductivity law

$$\sigma = \sigma_0 \exp \left\{ - \left(\frac{T_M}{T} \right)^p \right\}, \quad (3)$$

with $p = 1/4$ for three-dimensional (3D) and $p = 1/3$ for 2D cases by the ES law

$$\sigma = \sigma_0 \exp \left\{ - \left(\frac{T_{ES}}{T} \right)^{1/2} \right\}, \quad (4)$$

valid for both 3D and 2D cases. Here T is the temperature in energy units, $T_M = 22/g(\mu)\xi^3$ for 3D and $T_M = 13/g(\mu)\xi^2$ for 2D, ξ is the localization length of localized states at the Fermi level (for a lightly doped semiconductors ξ is equal to the Bohr radius of a donor a), and

$$T_{ES} = \frac{C e^2}{\kappa \xi}, \quad (5)$$

where $C = 2.8$ in 3D and $C = 6$ in 2D [3, 4].

Derivations of Eqs. (1) and (4) and first experimental and numerical conformations of them are discussed at length in Shklovskii-Efros (SE) book [3]. The Russian original of SE book was published in 1979, while the updated and extended English translation was published in 1984, 40 years ago. SE book is still widely used. I devote this article to the double 50/40 years anniversary. The main part of the article reviews new observations, generalizations and applications of Eqs. (1) and (4) while the second part briefly mentions developments of other ideas of SE book. I try to avoid repetitions of the SE book.

The plan of this short article is as follows. I dwell on major experimental confirmations of the ES Coulomb gap and ES law in Section II. Section III is devoted to non-Ohmic generalization of the ES law. In Section IV I discuss new advances of the Coulomb gap and ES law theory. I focus on the evolution of the Coulomb gap near metal-insulator transition in Section V. Section VI goes beyond the Coulomb gap and SE book and dwells on related problems of Coulomb interaction and disorder physics. I comment on developments of ideas of specific chapters of the SE book in Section VII.

II. NEW EXPERIMENTAL CONFIRMATIONS OF COULOMB GAP AND ES LAW

An experimental verification of ES law Eq. (4) is done by plotting $\ln \sigma$ as a function of $T^{-1/2}$ and checking whether this plot can be fitted by a straight line. In order to reliably discriminate the ES law from Eq. (3) with $p = 1/4$ and particularly in 2D case with $p = 1/3$ the dynamic range of measured conductivity should cover approximately 3 orders of magnitude. In this review I dwell only on the most spectacular data which cover at least 4 orders of magnitude.

I start from observations of the ES law in 3D elementary semiconductor crystals Ge and Si. First high quality data for compensated Ge were discussed Chapters 9 and 10 of the SE book. Later the ES law was observed in neutron-transmutation-doped p -Ge in 4 orders of magnitude range [5] and even in 6 orders of magnitude range [6]. Similar high quality data were obtained in Si samples in 5 orders of magnitude range [7]. It is remarkable that the data [5, 7] were obtained in the process of development of Ge and Si based bolometers for astrophysics and dark matter research.

Other spectacular 3D data for the ES law were obtained in the mixed valence cuprate LiCu_3O_3 in 7 orders of magnitude range [8], in CdSe nanocrystal arrays in 6 orders of magnitude range [9], in ZnO nanocrystal films in 4 orders of magnitude range [10], in magnetite nanocrystal arrays in 7 orders of magnitude range [11], in ceramics [12] in 5 orders of magnitude range, in granular metals in insulator in 4-8 orders of magnitude ranges [13, 14], in different conducting polymers [15–21] in 4-10 orders of magnitude ranges, and in graphene oxide thin films [22, 23] in 4-5 orders of magnitude ranges.

Due to scattering of a tunneling electron on intermediate donors the ES law should work even in strong magnetic fields [24]. This happens because the scattering changes asymptotic behavior of a donor electron wave function in the orthogonal to magnetic field plane from $\exp(-\rho^2/4\lambda^2)$ to $\exp(-\rho/\lambda)$. Indeed, the data obtained on InSb samples [25] (see SE Fig. 9.2b) demonstrates excellent agreement with the ES law in 7 orders of magnitude range of resistance. Similar magnetoresistance data were obtained for Ge samples in 6 orders of magnitude range [6].

Let us now switch to 2D systems with localized electron states. The ES law was observed in 6 orders of magnitude range in the gated GaAs/GaAlAs low mobility heterostructures in strong a orthogonal magnetic fields [26] which shrinks localized state wave functions and makes electron hops shorter. At smaller magnetic fields, where the hop length becomes as large as the distance to the gate the authors observed the transition from ES law (4) to 2D Mott law (3) with $p = 1/3$. They interpreted this transition as a result of screening of electron-electron interactions in two-dimensional electron gas (2DEG) by the metallic gate. This observation confirms that ES law results from the Coulomb interaction between electrons.

Discovery of the Quantum Hall effect (QHE) in higher mobility samples lead to observations of ES law in 4 orders of magnitude range of the diagonal conductivity σ_{xx} at integer filling factors ν , where the electron states at the Fermi level are localized [27, 28]. Ref. [29] argued that at low enough

temperatures the ES law should be observed not only at integer ν , but everywhere between two neighboring half-integer ν_c where electron states are still localized. The localization length ξ diverges at a Landau level as $\xi \propto |\nu - \nu_c|^{-\gamma}$ with $\gamma = 7/3$ leading to vanishing $T_{ES}(\nu)$ at all half-integers. At a finite T equation $T_{ES}(|\nu - \nu_c|) = T$ defines the temperature dependent half-width $|\nu - \nu_c| \propto T^{1/\gamma}$ of a the peak of the resistivity ρ_{xx} near ν_c in agreement with experimental data [30–32].

Predictions of Ref. 29 were also confirmed by comprehensive studies of ES variable range hopping in GaAs [33, 34] and graphene [35]. In these papers ES law for σ_{xx} was observed in 4-5 orders of magnitude dynamic range and the localization length $\xi(\nu)$ was extracted from measured values of T_{ES} . It was found to diverge at ν_c with the theoretical critical index $7/3$. Ref. 35 also studied transition from ES to Mott law due to screening of Coulomb interaction by the gate, again confirming the Coulomb origin of ES law. (In the absence of screening the ES law may yield to the Mott law only when bare (non-Coulomb) DOS $g(\mu)$ is very small, so that the Coulomb gap width determined by equating Eqs. (1) and (2) to $g(\mu)$ is narrower than the band of energies around the Fermi level involved in the variable range hopping. Such a situation takes place in amorphous semiconductors, where the Mott law was originally observed. Even there the ES law should work at low enough temperatures, but this requires measuring unrealistically large resistances.)

So far we talked about the integer QHE. The ES law was observed also in the middles of the fractional QHE plateaus [36]. One can interpret such an observation assuming that fractional charges q (say $q = -e/3$) bound to donors form the Coulomb gap of DOS. The variable range hopping of these fractional charges then obeys the ES law with $T_{ES} = Cq^2/\kappa\xi$, where ξ is the localization length of a charge q . Small values of q lead to a very small T_{ES} in agreement with experiment [36]. Then, a straightforward extension of the logic of Ref. 29 leads to the ES law for σ_{xx} everywhere in a fractional plateau. The divergence of the localization length near the filling factor border between two neighboring fractions leads to the prediction of the same behavior of widths of ρ_{xx} peaks with growing temperature as in the integer QHE. This prediction agrees with experimental results [37–40].

III. NON-OHMIC ES LAW

So far we discussed the Ohmic variable range hopping conductivity in small electric fields. It was shown theoretically [41, 42] that at very low temperatures the strong electric field E acts as the effective temperature $T_E = e\xi E/2$. The origin of T_E can be understood using the concept of the electron quasi-Fermi level $\mu(x) = \mu(0) - eEx$ created by the electric field E directed oppositely to the x -axis. Then an electron hopping from an occupied donors at $x = 0$ with the energy close to $\mu(0)$ to an empty donor at the distance x finds itself above the local Fermi level by energy $\epsilon = eEx$. Probability of such a hop is $P = \exp(-2x/\xi) = \exp(-\epsilon/T_E)$ determines the generation rate of electrons with energy ϵ . Assuming that their energy relaxation rate is a weaker function of energy we

arrive at the Boltzmann energy distribution with $T_E = e\xi E/2$.

As a result Eqs. (1) and (2) lead to the exponential growth of the current I with E (the non-Ohmic ES law)

$$I = I_0 \exp \left\{ - \left(\frac{E_0}{E} \right)^{1/2} \right\}, \quad (6)$$

where

$$E_0 = \frac{2T_{ES}}{e\xi} = \frac{2Ce}{\kappa\xi^2}. \quad (7)$$

Fitting the lowest temperature data with Eq. (7) and the temperature dependence of the Ohmic conductivity with Eq. (4) and using the resulting T_{ES} and E_0 one can find unknown ξ and κ . This is particularly important [29] in 3D cases where most measurements are done close to the insulator-metal transition at which both ξ and κ diverge [3]. The non-Ohmic ES law was observed in large dynamic ranges of currents in Refs. 9, 22, and 23. These authors then found both ξ and κ .

Eq. (7) was also generalized for the low temperature variable range hopping in the quantum Hall effect, where the role of electric field E is played by the Hall electric field [29]. This allowed to predict that the half-width $|\nu - \nu_c|$ of ρ_{xx} peaks at a half-integer ν_c grows as $I^{1/2\gamma}$ with the current I . This prediction was confirmed by Refs. 33–35, and 43. Temperature and current dependencies of ρ_{xx} peak widths based on the ES law [29] provide the microscopic interpretation to the scaling theory [44].

IV. COULOMB GAP AND ES LAW: NEW THEORETICAL DEVELOPMENTS

Multiple numerical studies of the Coulomb gap density of states confirmed power laws Eqs. (1), (2) for three- and two-dimensional systems [45–50]. However, they did not find exponential depletion of the one-electron density of states at smallest energies due to the electron polaron effects predicted for three-dimensional case [2] and discussed in Chapter 10 of the SE book. This puzzle was resolved in Ref. 51. In two dimensions the ES law was confirmed by the direct numerical modelling of the variable range hopping conductivity [52].

As we saw in Sec. II the ES law is observed in many granular metals and nanocrystal arrays [9, 10, 13, 14, 53]. The theory of the Coulomb gap and the ES law in such systems was developed later than for lightly doped semiconductors, because it required understanding of the origin of disorder. For the hopping conductivity in arrays of metal granules disorder is related to randomly positioned charged impurities in the insulator surrounding metallic granules [54–56]. The role of charged impurities in a system of isolated long metallic needles or flexible wires dispersed and frozen in an insulator was studied in Ref. 57 and 58. On the other hand, in a periodic epitaxially connected nanocrystal array the disorder originates from random number of donors in individual nanocrystals [59–61]. An interesting, but more complicated case of quasi-one-dimensional crystals with impurities was studied in Refs. 62 and 63.

As we saw above, the ES law data allows us to find the localization length of localized states with energy close to the Fermi level. This required the development of a new theory of the localization length. It was shown that in granular metals the long distance tunneling happens through a chain of neighboring granules or, in other words, via relay co-tunneling [54–58, 64, 65]. In epitaxially connected nanocrystals similar relay co-tunneling happens through necks connecting nearest neighbor nanocrystals [59–61].

In doped semiconductors the related concept of tunneling with virtual scattering on intermediate impurities was developed in Ref. 24, 66–68. Later it was applied to theories of negative magnetoresistance, Aharonov-Bohm oscillations and mesoscopic transport in the range of ES law [69–73]. In QHE the localization length of localized states between two half-integers is formed by a chain of virtually scattered electron cyclotron orbits [74].

Theory of the variable range hopping thermopower was developed for the Mott law [75] and the ES law [76]. The hopping thermopower originates from a small residual asymmetry of the density of localized states [75, 76] or of the localization length [77] near the Fermi level μ which does not allow electron and hole contributions to completely cancel each other. Experimental confirmation of these theories, however, remains controversial [78–80].

V. COULOMB GAP NEAR METAL-INSULATOR TRANSITION

The shape of the Coulomb gap of DOS in a doped 3D semiconductor with concentration of donors N close to the critical concentration N_c of the MIT was studied in Ref. 81 both theoretically and experimentally. It is known [3] that on the insulator side of MIT the long wavelength dielectric constant κ diverges, so that according to Eq. (1) close to N_c DOS $g(|\epsilon - \mu|)$ parabola becomes very steep. On the other hand, on the metallic side of MIT metal $g(\epsilon)$ is large and weakly energy dependent at small $|\epsilon - \mu|$. In order to understand how crossover between these two limits happens it was assumed [81] that at MIT $\kappa(q) = \kappa/qa$ and the Coulomb potential $V(r) = e^2 a / \kappa r^2$, where a is the Bohr radius of the donor. (I use the scaling ansatz [81] with $\eta = 2$ which is in good agreement with experiments). Then, using ES arguments of Ref. 1 we arrive at the critical Coulomb gap DOS, shown in Fig. 1 by the thick line

$$g_c(\epsilon) = \frac{\kappa^{3/2} |\epsilon - \mu|^{1/2}}{a^{3/2} e^3}. \quad (8)$$

In the vicinity of the MIT at $|1 - N/N_c| \ll 1$ the large correlation (localization) length $\xi = a|1 - N/N_c|^{-\nu}$ truncates the growth of the dielectric constant $\kappa(q)$ at $\kappa = \kappa(1/\xi)$ and defines the energy scale $T_{ES} = e^2 / \xi \kappa(1/\xi)$. Then at $|\epsilon - \mu| < T_{ES}$ on the insulating side of the MIT we recover Eq. (1) with $\kappa = \kappa(1/\xi)$, while on the metallic side $g(\epsilon) = g_c(T_{ES}) = \text{Const}$ (see Fig. 1). ES law is valid at $T < T_{ES}$ because it uses only the parabolic part of DOS. Remarkably McMillan [83] arrived essentially at the same scaling

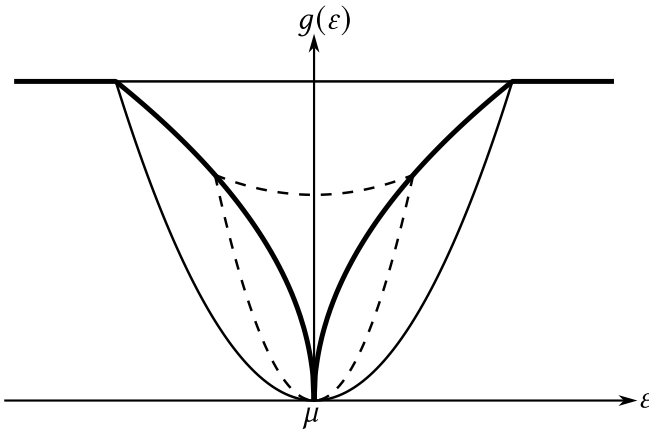


Figure 1. Schematic plot of the DOS $g(\epsilon)$ in the vicinity of the critical concentration N_c of the metal-insulator transition [81]. The DOS $g(\epsilon)$ at $N = N_c$ is shown by the thick line. Thin lines show $g(\epsilon)$ way from the critical region at $N = 2N_c$ and $N = N_c/2$. Dashed lines show $g(\epsilon)$ for $N = 1.25N_c$ and $N = 0.8N_c$ at $|\epsilon - \mu| < T_{ES}$ where they deviate from the thick line. On the metallic side the Altshuler-Aronov dip [82] at $\epsilon = \mu$ is not shown.

ansatz but only for the metallic side of the MIT. The McMillan-Shklovskii scaling ansatz was supported by two recent theoretical papers [84, 85]. The Coulomb gap evolution near the MIT was studied by direct tunneling into Si crystals [81] with impurity concentrations $0.9N_c < N < 1.1N_c$. Results of this experiment are in agreement with McMillan-Shklovskii scaling ansatz.

The McMillan-Shklovskii scaling ansatz is based on the absence of the local screening of the Coulomb gap in a given realization of random coordinates of donors and acceptors discovered in numerical experiment Ref. 86, discussed in Ref. 81 and later supported by Refs. 50 and 87. Indeed, when we bring a new electron on an empty donor in the center of a lightly doped semiconductor sample it induces polarization either zero or small number of pairs, i. e. transitions of other electrons from occupied to empty donors. These pairs typically form a chain moving an electron charge away from the center in a particular direction, so that potential of the central new electron at distance r remains of the order $e^2/\kappa r$, but may change its sign. Thus, in a system of localized states the local screening is absent and does not affect the Coulomb gap. To arrive at the exponential Yukawa screening of the Coulomb potential we have to average over many realizations of random coordinates of surrounding central electron donors and acceptors. Such a procedure leads to averaging over many directions of polarization chains and makes the central electron polarization cloud spherically symmetric, but apparently it has nothing to do with the local ES law physics. On the other hand, when one calculates the thermodynamic DOS describing penetration of the uniform electric field into the orthogonal macroscopic slab of a lightly doped semiconductor, the averaging of local polarization over its surface makes perfect sense and leads to the finite DOS and the exponential Yukawa screening with the screening radius of the order of average distance between donors [86].

It is believed that in two-dimensional semiconductor there is no delocalization transition with the growing two-dimensional concentration of donors n_D . Instead the localization length ξ of states near the Fermi level steeply grows with n_D . The Coulomb gap near the Fermi level then can be described assuming that effective dielectric constant κ does not change much [29]. Namely, for the shrinking with n_D energy range $|\epsilon - \mu| < T_{ES}$, where the characteristic distance of the important Coulomb interaction $e^2/\kappa|\epsilon - \mu|$ is larger than ξ , Eq. (2) remains valid, while at $e^2/\kappa|\epsilon - \mu| < \xi$ the Coulomb interaction is so weak that at $|\epsilon - \mu| > T_{ES}$ the DOS sharply returns to its non-Coulomb value. The ES law with T_{ES} decreasing with ξ and n_D then remains valid at all $T < T_{ES}$. These predictions qualitatively agree with the data on tunneling into very thin Be films and on their conductivity [88], but details of the observed DOS shape are still not understood.

VI. BEYOND THE COULOMB GAP

A. High frequency conductivity

In this section I dwell on problems with the Coulomb interaction and disorder which are practically missing in the ES book. As we saw above, the Coulomb gap of the one-electron DOS determines the DC variable range hopping conductivity and the tunneling current into a semiconductor. On other hand, the high frequency the phononless hopping conductivity $\sigma(\omega)$ is determined by electron hopping in compact resonance pairs of donors with small arms r_ω populated by one electron only. The density of states of these pairs does not have a Coulomb gap and is (with logarithmic accuracy) constant at small excitation energies [1, 3]. So at the first sight the Coulomb interaction is not important here and the low temperature terahertz range phononless conductivity $\sigma(\omega) \propto \omega^2$ as proposed by Mott [89] and Berezinskii [90]. However, we predicted [91] that at gigahertz frequencies when the Coulomb energy of two electrons repulsion $e^2/\kappa r_\omega$ exceeds $\hbar\omega$ one power of $\hbar\omega$ should be replaced by $e^2/\kappa r_\omega$, what leads to $\sigma(\omega) \propto \omega$. This happens because the concentration of pairs having one electron is proportional to $g(\mu)e^2/\kappa r_\omega$. We are talking about the case when $e^2/\kappa r_\omega$ is larger than the width of the Coulomb gap $(e^6 g(\mu)/\kappa^3)^{1/2}$. Multiple experiments [92–97] confirmed this prediction.

Above we talked only about phononless absorption of photons by compact donor pairs. At lower frequencies microwave absorption has a phonon assisted relaxation nature [98]. The calculation of $\sigma(\omega)$ in Ref. 98 automatically included interaction between two electrons of a pair of donors. But later in application to amorphous semiconductors [99] this interaction was ignored. Efros [100] took electron-electron interaction into account for amorphous semiconductors and showed that this interaction weakens the temperature dependence of the relaxation absorption. Comprehensive review of the theory of both phononless and relaxation high frequency hopping conductivity can be found in Ref. 101.

Compact pairs are also responsible for the electron contribution to the specific heat of systems with localized states [102].

Far on the other side of the frequency spectrum, at very low frequencies there is the $1/f$ noise of the hopping conductivity. It was studied experimentally [7] and theoretically [103–105].

B. Back to strong electric fields

The hopping conductivity in strong electric fields is another big field practically missing in the SE book. In Section III we dealt with very low temperature and very strong electric field where electric field leads to the linear growth of the effective temperature. However, there are many intermediate cases. At a strong disorder, large concentrations of carriers and low temperatures the current always exponentially grows with the applied electric field [106–111]. This growth can be interpreted as the effect of reduction of large hopping energy barriers by the applied electric field. However, at small concentrations of carriers, modest disorder and large enough temperatures the current decreases in a strong electric field. This counter-intuitive behavior happens because a very strong electric field does not allow electrons to use return parts in optimal tortuous percolation chains of the ohmic conductivity [112, 113] creating geometrical traps for electrons, such as “parachutes” [112] or “toilets” [113] from them. Then electrons spend most of their time in these traps and only rarely leave them. Predicted negative differential conductivity was discovered in lightly doped and weakly compensated Si samples [114], where it led to new Gunn-effect-like current oscillations.

Hopping down the energy ladder of localized states plays important role in many relaxation phenomena in semiconductors. We studied the energy relaxation via hopping in nonradiative recombination of electrons and holes [115, 116] and in the hopping photoconductivity [117–120]. Spin polarization relaxation via hopping conductivity was discussed in Ref. 121.

C. Stripes and bubbles in QHE

Correlated arrangement of electrons in a lightly doped semiconductor leading to the Coulomb gap DOS is similar to a hierarchy of pinned by disorder Wigner crystals of different spacial scales. Therefore, I returned to Wigner crystals several times [122–125]. While studying spin splitting of Landau levels in 2DEG [126] we were wondering whether electrons of a spin split high Landau level can form a Wigner crystal. We discovered [127, 128] that instead the peculiar box type of the electron-electron repulsion potential at a partially filled Landau level with quantum number $N \geq 2$ should lead to the stripe phase at its filling factor $0.4 < \nu < 0.6$ and to bubble phases at $\nu < 0.4$ and $\nu > 0.6$. Predicted phases were discovered in Refs. 129 and 130. See the review of first 6 years of stripes and bubbles [131].

Following ideas of the Ref. 132 we recently calculated the resistivity anisotropy in a stripe phase and found that it should grow with the magnetic field B as B^4 . This result is in a good agreement with the experimental data for cleanest GaAs samples where the resistance anisotropy reaches 3000 [133]. We also studied what the scattering by a short range disorder

does to a stripe phase and its resistivity tensor. We discovered “hidden stripe phases” where the stripe order survives a growing short range disorder, but the resistivity is already isotropic [134, 135]. Multiple bubble phases with different number of electrons per bubble were recently observed in GaAs [136, 137] and graphene [138, 139]. They are direct relatives of the low density Wigner crystal.

D. Negative compressibility

Another our theory [140] predicted that the compressibility of a low-density 2DEG in the Wigner crystal and Wigner-crystal-like liquid states is negative. When a 2DEG with very small concentration n is on one side of a capacitor with opposite metallic electrode at the distance d a negative compressibility leads to small negative correction for d , namely d is replaced by $d^* = d - 0.12n^{-1/2}$.

The negative compressibility was discovered in Refs. 141 and 142 and studied in Refs. 143–146. Many authors working with relatively small $r_s = (\pi n)^{-1/2} a_B^{-1} < 5$, where a_B is a semiconductor Bohr radius, found a satisfactory agreement with result of the Hartree-Fock approximation and claimed that the negative compressibility is the exchange driven phenomenon. Indeed, exchange makes compressibility negative [147] starting at $r_s > 2.2$ and leads to $d^* = d - 0.064n^{-1/2}$. Thus, the exchange negative compressibility correction is roughly twice smaller than in the Wigner crystal limit. Actually both the Pauli principle driven exchange between same spin electrons and the direct Coulomb repulsion between all electrons keep electrons apart reducing their energy. At $r_s > 5$ the role of the exchange energy decreases, while the role of the correlation energy increases, so that at $r_s > 10$ in the energy of the liquid state is practically equal to that of the Wigner crystal, where exchange contribution is exponentially small.

Thinking about the Wigner crystal and Wigner-crystal-like liquid at $r_s > 10$ we studied [148] what happens at a very small d when $nd^2 \ll 1$. We found that in this case $d^* = 2.7d(nd^2)^{1/2}$, so that capacitance becomes much larger than geometrical. This limit has not been achieved yet, but 40% and 60% growth of the capacitance above geometrical was observed in Refs. 149 and 150.

Strong magnetic field enhances the negative compressibility near integer filling factors where the concentration of electrons or holes at the topmost Landau level is very small [141, 142]. This effect was studied theoretically in GaAs [151, 152] and graphene [153]. 20% increase of capacitance above geometrical in strong magnetic field was observed in graphene [153].

It was also predicted that a 3D array of epitaxially connected nanocrystals gated by a penetrating inside the array ionic liquid counterions may abruptly get a finite charge at some critical gate voltage [154]. At this critical gate voltage the differential capacitance of the array is infinite.

E. Charge inversion of DNA and gene delivery

We also used the concept of a classical Wigner crystal beyond the solid state physics, namely in the chemistry and biology of water solutions with multivalent positive ions, for example, short positive polyelectrolytes. We showed that the Wigner-crystal-like correlated liquid of multivalent counterions adsorbed at the surface of a negative macroion such as the double-helix DNA inverts the DNA net charge making DNA positive [155]. This charge inversion is driven by attraction of an extra counterions to their correlation holes (images) in the surface of DNA already neutralized by absorbed Wigner liquid of counterions. The net positive charge of DNA grows until its repulsion compensates counterion-hole attraction. Charge inversion can be also interpreted as a result of the classical fractionalization of the polyelectrolytes driven by elimination of its self energy [156]. We deal with a multivalent strongly charged counterions because interaction energy of monovalent ions in water is much weaker and they can not form Wigner-crystal-like correlated liquid at room temperature.

Membranes of biological cells are usually negative and repel all approaching strongly negative naked DNA molecules, while a charge inverted positive DNA is allowed to enter the cell. Therefore, DNA charge inversion by positive polyelectrolytes is used for delivery of normal genes to the cells with abnormal genes producing defected proteins [157, 158]. This paradigm of the modern medicine is called the gene therapy. The similar charge inversion of a mRNA molecule by positive lipids is used in modern COVID-19 Pfizer and Moderna mRNA vaccines [159].

In another biology related theory understanding of correlations of monovalent ion in a narrow biological ion channel allowed us to solve the puzzle of the deconfinement of pairs of strongly attracting each other positive and negative ions which leads to practically zero activation energy of the channel ion conductivity at ambient conditions [160, 161]. This deconfinement is similar to the deconfinement of quarks in a hot quark-gluon plasma produced in heavy ion collisions [162].

VII. SE BOOK AT 40. COMMENTS TO ITS CHAPTERS

Chapter 2. Substantial progress in identifying the metal-insulator transition (MIT) point and its critical indexes is achieved by analyzing the distribution function $P(s)$ of the nearest level spacing s . It was conjectured and confirmed numerically [163] that on the top of two known universal functions $P(s)$, the Wigner-Dyson and the Poisson ones, exactly at the MIT there is the third universal function $P(s) = P_c(s)$ which is an interesting hybrid of the first two. Namely, it was found to behave as the Wigner-Dyson one at $s < 1$ and as the Poisson $P(s) \propto \exp(-As)$ at $s \gg 1$. Here $A > 1$ due to the level repulsion. Later study of much larger 3D lattices [164] confirmed the $s \gg 1$ asymptotic of $P_c(s)$ with $A = 1.9 \pm 0.1$.

We showed that for the Anderson transition one can char-

acterize the function $P(s, W, L)$ for each disorder strength W and the system size L by the area $\gamma(W, L)$ of its $s > 2$ tail. Then doing the finite size analysis for the function $\gamma(W, L)$ we found the transition point and the correlation length exponent [163]. Thus, to find an MIT one does not need to study participation ratio of wave functions, but can study only the energy spectrum. The finite size analysis of $\gamma(W, L)$ was used to identify MIT transitions until a new more convenient way of characterizing $P(s, W, L)$ called r -method was invented [165] and replaced the use of $\gamma(W, L)$. One can also use the spectral rigidity [166–168] to find an MIT threshold [169].

Recently we extended the finite size analysis to the non-Hermitian analog [170] of Anderson Hamiltonian where complex diagonal elements are distributed randomly in a square with the side W in the complex plane. Generalizing r -method for analysis of complex energies we discovered the non-Hermitian Anderson transition in three-dimensions and showed that there is no Anderson transition in two-dimensions [171, 172].

Chapter 3. Calculation of the activation energy of the nearest neighbor hopping conductivity of a 3D weakly compensated semiconductor was generalized for the 2D case [173]. The goal was to describe the experimental data for the surface hopping conductivity of Si induced by room temperature ion liquid gating with a positive metallic gate which pushes positive ions of the ion liquid to Si surface. Inside of the Si crystal these ions play the role of surface donors which due to compensation by bulk acceptors provide surface hopping conductivity.

Chapter 4. Hall effect for the hopping conductivity was theoretically studied and compared with previous results in Ref. 174.

Chapter 5. A new application of percolation theory was proposed [175, 176] to describe bulk magnetization induced by ion liquid gating of an oxide film.

Chapter 12. SE book section (12.3) deals with filtering of a random potential from its small scales via the wave function averaging. Recently a new way to do the filtering was suggested [177] and later compared with the conventional one [178].

Chapter 13. The theory of nonlinear screening of a long-range potential developed in Chapters 3 and 13 was applied to nonlinear screening of the random potential of remote impurities by 2DEG in QHE devices [126, 179–188]. The concepts of strongly or completely compensated semiconductor found an application to topological insulators [189–193], to other narrow gap semiconductors subjected to a strong 3D Coulomb disorder [194, 195] and to the superconductor-insulator transition in high T_c superconductors [196].

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