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SCIENTIFIC LEGACY OF PETRO TOMCHUK IN THE FIELDS OF THEORETICAL PHYSICS AND CONDENSED MATTER PHYSICS

In this paper, the main scientific results of the outstanding Ukrainian theoretical physicist Petro Tomchuk (January 2, 1934–October 7, 2024) are reviewed. P.M. Tomchuk worked in various areas of condensed matter physics, including semiconductor physics, metal physics, soft matter physics, and nanophysics. This review article on the scientific legacy of P.M. Tomchuk focuses on his research of kinetic and optical phenomena in semiconductors, carrier transport in semiconductor structures, electron-lattice energy transfer and hot electrons in semiconductors and metal island films, optical properties of metal nanoparticles and their ensembles, liquid crystals and colloids, and molecular structures with hydrogen bonds.

K e y w o r d s: theoretical physics, condensed matter physics, solid state physics, nanophysics, semiconductors, hot electrons, liquid crystals, hydrogen bonds, polaron, proton conductivity.

1. Introduction

Petro Mykhailovych Tomchuk (January 2, 1934–October 7, 2024) was an outstanding Ukrainian theoretical physicist, Doctor of Science in physics and mathematics (1973), Professor (1980), Corresponding Member of the National Academy of Sciences of Ukraine (2000), and Honored Worker of Science and Engineering of Ukraine (1997). He was undoubtedly one of the most famous Ukrainian theoretical physicists in the late 20th and early 21st century in the field of condensed matter physics and solid state physics. Petro Tomchuk spent his entire scientific life at the Institute of Physics of the National Academy of Sciences of Ukraine, where he headed the Department of Theoretical Physics for 50 years. Under his supervision, 7 doctoral and 19 candidate theses were defended. You can learn about P.M. Tomchuk's life path from the book "The Life Credo is Science" [1], which was published on his 80th birthday, and congratulatory articles on his 90th birthday [2, 3].

P.M. Tomchuk was a graduate of the Physics and Mathematics Faculty of Chernivtsi State University (in 1957), where the supervisor of his diploma thesis was Arnold Markovych Kosevych, a well-known specialist in the field of condensed matter physics (later, in 2009, P.M. Tomchuk became an honorary doctor of this university). The supervisor of P.M. Tomchuk's PhD thesis "Problems of the Theory of Hot Electrons in Atomic Semiconductors" (1962) was Isaak Markovych Dykman, who worked in the scientific group of the famous theoretical physicist Solomon Isakovych Pekar, at that time the head of the Department of Theoretical Physics at the Institute of Physics. It was owing to the influence of I.M. Dykman and S.I. Pekar, both the prominent representatives of the school of theoretical physics at that time, that the main direction of Petro Tomchuk's scientific activity was formed. Throughout his subsequent scientific life, P.M. Tomchuk studied the effects associated with hot electrons in various semiconductor and metal structures.

His doctoral dissertation entitled "Research on the Theory of Transfer Phenomena and Collective Processes in Nonequilibrium Semiconductor Plasma"

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(1972) dealt with kinetic phenomena and fluctuations in nonequilibrium systems, another topic that laid the basis for his further scientific work. Later, Petro Tomchuk's scientific achievements were recognized with two state prizes in the field of science and engineering: in 1986 as a team member for the series of works "Size Effects in Small Particles of A Solid" and in 1995 as a team member for the series of works "Physical Mechanisms of Degradation and Ways to Enhance the Reliability of Optoelectronic Devices". In 2008, for the series of works "Hot Electrons and New Optical Phenomena in Multi-Valley Semiconductors and Nanoparticles", P.M. Tomchuk, together with his colleagues, was awarded the A.F. Prykhotko Prize of the National Academy of Sciences of Ukraine.

Petro Tomchuk can be characterized as a very versatile theoretical physicist. The scientific breadth of his research was favored by the diverse topics of theoretical research at the Institute of Physics: crystal optics, electron-phonon interaction, band structure of semiconductors and spin phenomena, transport processes, size effects, nonlinear effects in laser fields, acoustoelectronics, and semiconductor materials. His scientific results are important for the physics of semiconductors and metals, as well as for the description of physical processes in liquid crystals and biological molecular structures.

In the domain of semiconductor physics, P.M. Tomchuk, together with I.M. Dykman, was the first to develop the theory of carrier heating in semiconductor structures [4–6]. He also developed the theory of superlattices on hot electrons in multi-valley semiconductors (together with O.O. Chumak) [7] and an analytic method for calculating fluctuations and wave scattering on them in nonequilibrium electron-phonon systems (together with V.A. Shenderovskyi) [8].

While studying the properties of metal nanoparticles and their ensembles, Petro Tomchuk proposed and substantiated the concept of hot electrons in metal nanoparticles. It was used as a basis for the theory of nonlinear current-voltage characteristics and the theory of electron and photon emission from metal island films in the case of current flowing through them [9, 10] or in the case of laser heating of electrons [11]. P.M. Tomchuk also developed the theory of the optoacoustic effect in metal island films; it consists in the sound generation by metal islands under the action of a modulated light flux [12]. Moreover, he constructed the theory of optical absorption by small metal particles and showed an anomalously high absorption sensitivity to the nanoparticle shape in the infrared spectral interval [13, 14]. Based on this theory, the dependence of the width of plasma resonances on the shape of metal nanoparticles was determined [15].

In the field of liquid crystal physics, P.M. Tomchuk, together with B.I. Lev, applied a microscopic approach to the theory of liquid crystals and showed how the microscopic theory can be associated with the phenomenological one [16]. He, together with Ye.D. Bilotsky and B.I. Lev, also proposed an orientational mechanism for the formation of the effective mass of an ion in a liquid crystal, which was confirmed experimentally [17]. In addition, together with Ye.D. Bilotsky, he constructed the theory of dissipative structures that can be formed in nematic liquid crystals under the action of an external electric field [18]. Finally, P.M. Tomchuk, together with B.I. Lev, developed the theory of interaction between macroscopic particles immersed in a liquid crystal and analyzed the possibilities of creating supramolecular structures in systems of such macroimpurities [19, 20].

In regard to the properties of molecular chains, of high importance is the proton polaron model proposed by Petro Tomchuk to describe the conductivity of hydrogen bond chains. This model was used, in particular, to construct the theory of transmembrane proton transport through biological membranes. Another important result of P.M. Tomchuk, which was obtained together with V.V. Krasnoholovets, is the theory of quantum tunneling repolarization in finite chains of hydrogen bonds [24].

Summarizing the scientific achievements of P.M. Tomchuk, it is worth mentioning that he is a co-author of two monographs [25, 26] and the author or co-author of more than 300 scientific papers [27]. Among his most cited works, it is worth marking the review article on the emission of electrons and light from metal island films and the generation of hot electrons in nanoparticles, which was published in Physics Reports [28] together with R.D. Fedorovych and A.G. Naumovets; the articles in Physical Review E on the interaction between extraneous macrodroplets in nematic liquid crystals and induced supramolecular structures [20] and on the symmetry breaking and the interaction of colloidal particles in nematic liquid crystals [29] (co-authored with B.I. Lev and other colleagues); the articles in Phy-

sical Review B on size effects and the influence of particle shape on the energy absorption by small metal particles [15] and on the optical and transport properties of spheroidal metal nanoparticles with allowance for surface effects [30] (co-authored with M.I. Grigorchuk); and the article in Surface Science on electron-phonon interaction and hot electrons in small metal islands [31] (co-authored with Ye.D. Bilotsky). It is also worth mentioning the review article in Advances in Chemical Physics on the proton transfer and coherent phenomena in molecular structures with hydrogen bonds [32], which was written together with V.V. Krasnoholovets and S.P. Lukyanets.

The main directions of P.M. Tomchuk's scientific research can thematically be divided into the following categories:

1) kinetic and optical phenomena in semiconductors,

2) hot electrons in metal island films,

3) optical properties of metal nanoparticles and their ensembles,

4) liquid crystals and colloids,

5) molecular structures with hydrogen bonds.

In the subsequent sections of this review, each of these directions is considered separately. Basic points of each indicated topic are presented, current problems are outlined, and Petro Tomchuk's contribution is demonstrated. The conclusions briefly point to the prospects for further research based on P.M. Tomchuk's scientific legacy.

2. Kinetic and Optical Phenomena in Semiconductors

2.1. General information

In the second half of the last century, the dominant place in solid state physics was occupied by the physics of *semiconductors* together with its various directions that emerged due to the wide possibilities of their practical application in technology. The task of creating a theory of kinetic effects that would involve the *band structure* of specific semiconductors, the specificity of the mechanisms of carrier scattering, and lattice vibrations and defects became urgent.

Let us recall that the electrical and optical properties of semiconductors are a result of the fact that the filled electron states in the valence band are separated from the vacant states in the conduction band by a forbidden *band gap*, in which electron states are absent. The band gap width (in energy units) largely determines the electronic properties of a particular semiconductor. The smaller the band gap, the easier it is for electrons to move into the conduction band, and the better the semiconductor conducts current as temperature increases. Depending on the band gap width, semiconductors are divided into *wide-band* semiconductors (if the band gap width exceeds a certain conditional value, the semiconductor properties become actually lost, and the corresponding material is classified as an insulator) and *narrow-band* semiconductors (they are also called *narrow-gap* semiconductors, and, in the limiting case of zero band gap width, *gapless* semiconductors). The current carriers in semiconductors are electrons in the conduction band and holes in the valence band. In pure semiconductors, the motion of an electron in the conduction band corresponds to the motion of a hole in the forbidden band gap. This type of conductivity is called *intrinsic*. Impurities and defects can cause the appearance of local electronic levels in the forbidden gap and, accordingly, change the conductivity toward the electron-type (n-type semiconductors, donor impurities) or hole-type (p-type semiconductors, acceptor impurities). The structure of the bands in semiconductors is determined by the law of dispersion of current carriers in them. Energy minima in the conduction band are called *valleys*, and semiconductors with several equivalent minima are called *multi-valley* semiconductors [33, 34].

2.2. Physical kinetics

The quantitative description of kinetic phenomena in semiconductors is based on the methods of statistical physics [25]. Here, the main equation of the theory is the *Boltzmann kinetic equation* [35]

$$\frac{\partial f}{\partial t} + \frac{\partial \boldsymbol{r}}{\partial t} \cdot \nabla_{\boldsymbol{r}} f + \frac{\partial \boldsymbol{p}}{\partial t} \cdot \nabla_{\boldsymbol{p}} f = \mathcal{I}(f), \tag{1}$$

which describes a change in the distribution function $f(\boldsymbol{r}, \boldsymbol{p}, t)$ of charge carriers in the phase space of coordinates $\boldsymbol{r}$ and momenta $\boldsymbol{p}$ due to the motion of carriers (the second term), the influence of external fields (the third term), and collisions between the particles, which are taken into account through the so-called collision integral $\mathcal{I}(f)$. Making allowance for the interaction of electrons, lattice vibrations, and various scattering mechanisms considerably complicates the

solution of the kinetic equation, which is an integro-differential equation in the general case. One of the approaches to solve the kinetic equation is the variational method [35].

Petro Tomchuk was among the first who applied the variational approach in the kinetic theory of solids. In work [36], he first applied the variational method to calculate kinetic coefficients in anisotropic condensed media. The originality of this work consisted in choosing the appropriate functional, the extreme value of which coincided with the Joule power divided by the electron temperature. Therefore, in crystals with arbitrary scattering potential anisotropy, anisotropic energy dispersion law, and carrier statistics, the extreme value of the functional can be determined through the conductivity tensor.

This fact made it possible to apply the theory of kinetic and fluctuation processes in nonequilibrium electron-phonon systems to semiconductors with various band structures and the dominant role of electron-electron interactions [37]. Various cases were considered: semiconductors with the parabolic and isotropic dispersion law of carrier energy under the isotropic scattering mechanisms; multi-valley semiconductors with ellipsoidal isoenergetic surfaces and anisotropic scattering; semiconductors with a nonparabolic dispersion law and narrow-gap semiconductors. The dependences of the kinetic coefficients, the fluctuation characteristics, and the cross-section of wave scattering by fluctuations on the carrier scattering rate and the band structure features in typical semiconductors were also found [38]. Generalized expressions were obtained for the electrical conductivity, the Hall effect, the thermoelectric power, and the electron thermal conductivity in multi-valley silicon and germanium, as well as for various kinetic coefficients in semiconductor crystals with low symmetry, and a comparison with experimental data was made.

2.3. Hot carriers and electric field effect

Hot carriers are nonequilibrium charge carriers (electrons and holes), whose average kinetic energy exceeds the equilibrium thermal energy corresponding to the lattice temperature. If some power is introduced into the electronic subsystem in one way or another, the thermodynamic equilibrium between the electronic and lattice subsystems becomes violated. Electrons become "hot" when their average energy exceeds the equilibrium energy. The higher the input power and the lower the intensity of electron-phonon interaction, the higher is the degree of electron heating [39]. The heating of charge carriers is manifested not only in known kinetic effects, but also leads to the appearance of new phenomena, which are characteristic only of the hot carrier gas state (the Gunn effect, negative differential resistance, anisotropy of conductivity in cubic crystals, and so forth) [40].

When studying the influence of an electric field on the electron temperature, the electrical conductivity, and the thermionic emission in atomic and ionic semiconductors, P.M. Tomchuk, together with I.M. Dykman, first determined the electron distribution function by solving the kinetic equation, where the presence of an electric field, the interaction of electrons with lattice vibrations and impurity centers, and the Coulomb electron-electron interaction were taken into consideration [4]. It is important to note that an analysis of the literature on the theory of hot carriers at that time showed that none of the works correctly considered the influence of electron-electron interaction on the transfer phenomena. It was in work [4] where a method for solving the kinetic equation for finding the electron distribution function was first proposed, and where it was shown that, under certain conditions, the electron-electron interaction leads to an approximately Maxwellian distribution with an effective temperature T different from the lattice temperature. The dependences of the conduction current magnitude on the electric field and the semiconductor parameters were obtained. Since the temperature T can substantially exceed the lattice temperature (which corresponds to the "heating" of the carriers), this effect is especially pronounced in the magnitude of the thermionic emission current (see also works [5, 6]).

In work [41], the case of strong electric fields was considered, when the charge carriers are substantially nonequilibrium, and the electron distribution function is largely determined by the conduction band shape.

Another important result obtained by P.M. Tomchuk (together with V.A. Shenderovskyi) concerned the processes of scattering and transformation of waves on fluctuations in nonequilibrium plasma of semiconductors with an anisotropic energy band [8]. The intensity of wave scattering is determined by

both the level of fluctuations and the intensity of the incoming wave. If the plasma is nonequilibrium with a high fluctuation level, then the cross-section of the wave scattering and transformation can be quite large. In strong electric fields, the plasma in solids can become substantially nonequilibrium (especially in materials with a high carrier mobility). Furthermore, in semiconductors with a carrier energy dispersion law different from the isotropic parabolic one, the frequencies and decrements of intrinsic oscillations become dependent on the magnitude and orientation of the external electric field. A consequence of the nonequilibrium state of plasma and anisotropy is the emergence of anomalously large fluctuations at frequencies close to the natural ones. Since the magnitude and character of fluctuations in a semiconductor plasma in the nonequilibrium case considerably depend on the scattering mechanisms and the shape of energy bands, studying the processes of wave scattering and transformation on these fluctuations can provide valuable information on the mechanisms of hot carrier scattering and the details of the energy band shape.

It was found that in a nonequilibrium semiconductor plasma with a complicated carrier dispersion law the wave scattering (transformation) cross-section substantially depends on the shape of energy bands and the field orientation. For certain field directions (an external field or the fields of the incoming and scattered waves), the scattering cross-section can reach anomalously large values, which is associated with the appearance of anomalously large fluctuations in the nonequilibrium plasma at those field orientations. Taking into account the deviation of the energy dispersion law from the isotropic parabolic behavior and the presence of a field that heats the carriers brings about the emergence of a specific current that causes the additional wave scattering (transformation) – the so-called band-structure effect. This additional contribution to the wave scattering (transformation) coefficient can be noticeably larger than the ordinary contribution associated only with fluctuations in the carrier concentration in plasma. For this reason, in particular, the scattering and transformation coefficients at high electric fields in semiconductors of the p-Ge type at low temperatures (when the carrier distribution function is noticeably elongated along the field) are strongly anisotropic, and they may have anomalously large values in certain directions. The appearance of anomalously large scattering cross-sections (with regard for their strong anisotropy) can be used for the frequency conversion at Raman scattering. The importance of this result was indicated, in particular, in work [42].

Current fluctuations in semiconductors in strong electric fields, when the quantum effects caused by the level splitting due to the Stark effect (the quantizing electric field) begin to affect the behavior of electrons, were studied in work [43] written by P.M. Tomchuk together with S.S. Rozhkov. It is known that the fluctuation-dissipation theorem is obeyed for systems in thermodynamic equilibrium. This theorem implies that the problem of fluctuations can be reduced to calculating the linear response of the system to an external action. For nonequilibrium systems, such a general theorem does not exist, so that calculating the fluctuations requires a special consideration in every specific case [26]. P.M. Tomchuk and his co-authors developed the theory of fluctuations for nonequilibrium electron-phonon systems and proposed a method for calculating the fluctuations on the basis of the equation of motion for a quantum analog of the microscopic distribution function. This method makes it possible to introduce external fluctuation sources into the equation for the fluctuating part of the distribution function without any additional assumptions, except for those used while deriving the corresponding kinetic equations.

Thus, spatially uniform fluctuations of the transverse current with respect to a strong electric field were calculated [43]. It was found that the quantization arising due to the Stark effect considerably changes the character of fluctuations, and their intensity can substantially exceed the intensity of equilibrium fluctuations. Such fluctuations were shown to depend on the parameters of the scattering system and the band gap width. This result allows certain conclusions to be drawn about the energy dissipation in semiconductors and their band structure.

2.4. Optical phenomena

Of importance for optical phenomena in semiconductors are the studies by P.M. Tomchuk (conducted together with I.M. Dykman) on the influence of coherent light beams on free carriers [44, 45]. P.M. Tomchuk and I.M. Dykman considered a superlattice formed in a semiconductor by a standing laser wave and analyzed the influence of a constant electric field,

which heats electrons, on this superlattice. Special attention was paid to the consideration of wave interference because it is the phenomenon that gives rise to the superlattice formation and the appearance of additional light pressure on the electron gas. In work [46], the results were generalized to the case where a semiconductor with electrons heated by a constant electric field is illuminated with a beam of coherent light waves. In this case, static and high-frequency superlattices of electron concentration, electron temperature, and additional electric field are formed in the semiconductor. These superlattices are rather noninertial, which allows their control by means of an applied constant electric field.

In work [47], a system of kinetic equations was obtained that describes the electron-magnon system of a ferromagnetic semiconductor when several coherent light beams fall on it, both in the presence and absence of a constant external electric field. It was shown that in ferromagnetic semiconductors there arise superlattices on nonequilibrium electrons and magnons as a result of the interference of coherent light beams.

Another fundamentally important result obtained by P.M. Tomchuk together with O.O. Chumak while studying the nonlinear propagation of infrared radiation in *multi-valley semiconductors* [7] is also worth mentioning. It is known that the isoenergy surfaces of free electrons in multi-valley semiconductors of the germanium or silicon type are strongly prolate ellipsoids of revolution. This circumstance is often responsible for a non-trivial dependence of the semiconductor response to an external action. Since external forces (a magnetic or an electric field, elastic deformation, and so forth) are generally directed at various angles to the axes of the ellipsoidal isoenergy surfaces, electrons in different valleys react differently to this action, and the stationary state of the system is achieved at different fillings of the valleys with the carriers. When considering the interaction of electrons in multi-valley semiconductors with strong electromagnetic radiation, it is actually necessary to study the intervalley redistribution of electrons in the field of a strong electromagnetic wave. In this case, in addition to the fact that different heating of electrons in different valleys takes place, a contribution to the effect can be made by unequal energy shifts of the valleys due to electron oscillations in the wave field. The distribution of carriers over the valleys will depend on the coordinate; therefore, the contribution of free electrons to the refractive index of the crystal can be appreciable. The calculation of the relevant kinetic effects was reduced to finding the electron distribution functions and the integral of intervalley collisions, in which the change of the electron spectrum in the wave field was taken into account. The intervalley redistribution of the carriers leads to a variation of the crystal refractive index, so that a superlattice of the refractive index and the self-diffraction of beams might be realized. Conditions under which multivalley semiconductors can be used as nonlinear media for dynamic holography in the infrared spectral interval were established.

Petro Tomchuk also built the theory of light absorption and emission by free electrons in multi-valley semiconductors of the n-Ge and n-Si types [48]. General expressions for the coefficient of light absorption by free carriers and the intensity of spontaneous light emission by hot electrons were obtained. These expressions depend on the electron concentration in individual valleys and their temperatures. The anisotropy of the dispersion law and the mechanisms of electron scattering were taken into account. The impurity-driven and acoustic scattering mechanisms were considered. The polarization dependence of the spontaneous emission of hot electrons was found.

The polarization dependence of the spontaneous emission of hot electrons associated with their intervalley redistribution in multi-valley semiconductors was also considered in paper [49], which P.M. Tomchuk published together with V.M. Bondar and O.G. Sarbey. The polarization dependences of light emission by free electrons in n-Ge at liquid helium temperatures were considered, and a qualitative agreement of numerical calculations with experiment was obtained [50]. The angular dependences of spontaneous emission by hot electrons in multi-valley semiconductors were analyzed by an example of n-Ge [51]. It was shown that the angular dependence of emission in the case where electrons in all the valleys have the same concentration and temperature is associated with the violation of the symmetry of the electron energy distribution function.

In work [52], the angular dependences of hot electron emission were considered in the high-frequency *terahertz range* in the case where the electric field is orientated in the symmetric direction with respect to the locations of valleys in n-Ge. The influence of

anisotropic scattering mechanisms on the polarization dependences of terahertz radiation emission by hot electrons in semiconductors of the same type was considered in work [53]. It was shown that the change of the anisotropic mechanism of electron scattering by ionized impurities to the anisotropic mechanism of their scattering by acoustic phonons leads to the transformation of maxima into minima in the periodic polarization angular dependence of the intensity of hot electron radiation. A comparison with the experiment was made. In papers [54, 55], the influence of a weak magnetic field on the intensity of terahertz radiation by hot electrons in n-Ge was investigated.

2.5. Optoelectronics

A separate prominent direction of theoretical research by Petro Tomchuk in the field of semiconductor physics concerned the physical mechanisms of *degradation of optoelectronic devices*.

In work [56], which was published by a group of co-authors with the participation of P.M. Tomchuk, the kinetics of injection-stimulated transformation of defects in semiconductor light-emitting diode structures GaAs : Si was studied [1]. During the injection of electric current into a semiconductor, the injected charge carriers can interact with defects available in the semiconductor. This interaction can lead to the transformation of defects, which affects the service life of optoelectronic materials and devices and results in their gradual degradation. It was shown that the non-monotonic kinetics of changes in the luminescence efficiency of the examined structures under injection conditions can be explained by the processes of recombination-stimulated decay of simple impurity–intrinsic defect complexes, subsequent diffusion of intrinsic defects, and their combination into complicated multi-particle complexes. A theoretical model for the defect transformation under injection conditions was proposed, which made it possible to describe a non-monotonic change of the luminescence intensity of LED structures.

[1] This work was published in the journal "Physics and Technics of Semiconductors" in 1989. It was recognized as one of the best works in solid-state physics published in this journal in 1989–1990 and was included in the collection of articles republished in English by the World Scientific Publishing House [57].

Degradation of optoelectronic materials is also possible because of the action of pulsed laser irradiation. In works [58, 59] with Petro Tomchuk as a co-author, it was shown that the reduction in the strength threshold of optically transparent materials under repeated laser irradiation can occur because of the thermal diffusion of locally heated inhomogeneities in the material. An increase in the inhomogeneity radius leads to even stronger heating (the accumulation effect) and thermal deformation of the material near the inhomogeneity. The local heating of an inhomogeneity occurs owing to the recombination of photoexcited nonequilibrium charge carriers in the material.

For his contribution to the theoretical research of the physical mechanisms of degradation in optoelectronic devices, Petro Tomchuk was awarded the State Prize of Ukraine in Science and Engineering (in 1995), as a member of the author's team. This award is a fair recognition of the substantial contribution made by P.M. Tomchuk to the development of semiconductor physics.

3. Hot Electrons in Metal Island Films

3.1. Metal island films

Island films are systems of small (nano-sized) metal particles that are located on a dielectric substrate and do not contact with one another. Small metal particles, when in close thermal contact with the substrate, can withstand large power fluxes without destruction. This property, together with the weakening of the electron-phonon interaction intensity as the particle size decreases, allows the electron gas in small metal particles to be heated. As a result, *hot electrons* are obtained. The appearance of hot electrons (when there is a current passing or laser irradiation applied) stimulates electron emission of such films and their luminescence [60].

The properties of metal island films differ significantly from those of bulk metals and even solid metal films. This occurs due to their nanoscale size and discrete structure. The greatest efforts in the study of such physical objects were directed to the description of the mechanism of electrical conductivity and the nature of anomalous optical properties [28]. It was Petro Tomchuk who, using the theory of hot electrons, managed to give an excellent theoretical explanation to the observed experimental data.

3.2. Electron and photon emission under the action of electric current

The story began with the discovery made by P.G. Borziak, O.G. Sarbey, and R.D. Fedorovych at the Institute of Physics in 1963. They observed the phenomenon of *electron emission* and *luminescence* of metal island films when an *electric current* passed through them. The scientists reported about their discovery in the work published in 1965 [61]. They found that when applying a voltage of several tens of volts, separate points begin to glow, but only in the films with an island structure. The glow of those points had various colors: from red to blue. Comparing the total radiation spectrum from all luminescence centers with the radiation spectrum from an incandescent lamp, the authors pointed out that the film radiation most likely had a non-temperature character. Further research was focused on a more detailed clarification of the luminescence nature of the above-mentioned phenomenon. Radiation from a film in a vacuum was found to appear simultaneously with electron emission at the voltages for which the current-voltage characteristic of the conduction current began to deviate from the linear law [62].

After the discovery of electron emission and luminescence of metal island films, P.G. Borziak addressed P.M. Tomchuk with a request to develop a theory of the observed phenomena. By applying his scientific intuition, Petro Tomchuk formulated the idea that the emission of electrons and photons from metal island films can be associated with the availability of nanometer-sized metal islands in the emission centers (Fig. 1). He was the first who showed theoretically that the energy exchange between electrons and the atomic lattice is drastcally weakened in nanoparticles whose size is smaller than the mean free path of electrons in metal, as the electrons are mainly scattered by the nanoparticle surface. As a result, it is possible to heat the electron gas to temperatures much higher than the lattice temperature. Hence, hot electrons are emitted into a vacuum, although the nanoislands themselves remain unheated. This phenomenon ensures the long-term operation of metal island film emitters without destruction of the film itself [63]. A substantiation of the concept of hot electrons in metal island films and the nonlinearity of the current-voltage characteristics observed under those circumstances was given by P.M. Tomchuk in works

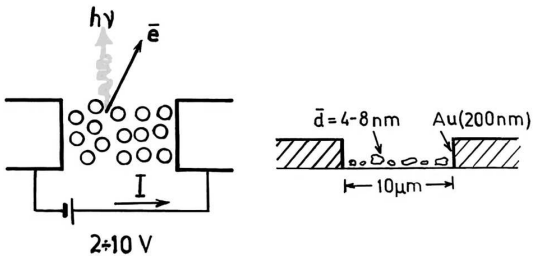

Fig. 1. Electron and photon emission from a metal island film under the action of an electric current (the hand-drawn illustration by P.M. Tomchuk)

[9, 10] published together with R.D. Fedorovych in 1966. Later, experimental and theoretical results on the emission of hot electrons from metal island films were presented in a joint paper by P.G. Borziak and P.M. Tomchuk [64].

In his subsequent works, Petro Tomchuk detailed his theory and summarized it in a preprint of the Institute of Physics published in 1987 [65]. He showed that if some power is introduced into the electron subsystem interacting with lattice vibrations, a violation of the thermodynamic equilibrium between electrons and phonons can occur, i.e., the electron subsystem becomes "hotter". The degree of thermodynamic equilibrium violation depends on the power magnitude and the electron-phonon interaction strength. In the case of a weak electron-phonon interaction, rapid heating of electrons takes place at the initial stage of power input (due to a relatively low heat capacity of the electron subsystem as compared to phonons), which is accompanied by an increase in the power transferred from electrons to phonons. In the case of further stationary power input, the electron subsystem either enters a stationary (but non-equilibrium) state or stays in a quasi-stationary state, depending on what happens to the phonon subsystem. The electron concentration is high in massive metals, so that the input power per electron required to heat the subsystem to a given temperature might substantially exceed the power in semiconductors. As a result, rapid heating of the electron and phonon subsystems takes place, and the metal melts. Therefore, hot electrons in metals could be observed only at the initial moment of applying short but powerful light pulses.

A completely different situation arises in metal island films, where the concentration of electrons is high, but it is concentrated in small island vol-

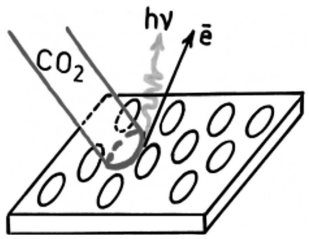

Fig. 2. Electron and photon emission from a metal island film under the action of a CO_2 laser with a wavelength of 10.6 μm (the hand-drawn illustration by P.M. Tomchuk)

umes. An island of small radius is able to withstand, without destruction, powers that are considerably larger than the power that a massive piece of the metal can withstand. However, if the size of islands is smaller than the electron mean free path, the mechanism of electromagnetic radiation absorption by the electron gas also changes. For such islands, if the film has a certain structure, the specific power of electromagnetic radiation in the infrared range can exceed the specific power absorbed by a massive metal by several orders of magnitude. All those factors, together with some weakening of the electron-phonon coupling in small islands, contribute to the appearance of hot electrons in metal island films at relatively low flux densities incident on the film. In turn, hot electrons stimulate electron emission from such films and their luminescence in a wide frequency interval.

3.3. Electron and photon emission under the action of laser radiation

Electron and photon emission from island films deposited on a dielectric substrate was also observed under the action of *laser radiation* [66, 67]. Gold and copper island films were chosen for the experiment, as emission phenomena occurring when an electric current passes through them were most completely studied. In order to restrict the contribution of multi-quantum effect, a CO_2 laser with a wavelength of 10.6 μm in the infrared spectral interval was used (Fig. 2). Electron and photon emissions from the islands occurred under the action of pulsed radiation with flux powers ranging from 5×10^4 to 5×10^6 W/cm^2 and a pulse duration of 10^{-6} s. For continuous films made of the same material, no similar emission phenomena were observed under the same conditions.

Neither the single-quantum photoeffect (because the laser quantum energy was an order of magnitude lower than the electron work function) nor a multi-quantum process (since the probability of a high-order nonlinear effect is insignificant for the powers used in the experiment) can explain such electron emission from island films. Furthermore, the shape of the electron emission pulse was close to the shape of the laser pulse, i.e., the emission was almost stationary (the pulse duration was an order of magnitude longer than all characteristic relaxation times). The destruction of the film structure did not occur during the observation of electron emission. P.M. Tomchuk was engaged in the explanation of the experimental data, and he suggested that the observed emission of electrons and photons from island films under the laser action can be explained by the heating of electrons, as in the case of heating by current [67].

A theoretical explanation of the possibility of the electron heating in metal island films under the action of laser radiation was given by Petro Tomchuk in work [11] (this theory was further developed in works [31,68,69]). To this end, he proposed a thermal model of the electron-phonon interaction in metal island films. The power transmitted to the electron subsystem in a metal island (using a laser, current, or an electron beam) is then transferred to the phonon system via electron-phonon interaction and transferred to the substrate. The system of equations describing the time evolution of the electron and phonon temperatures looks like

$$\begin{aligned} &\partial_t\big(C_eT_e\big) = \mathrm{div}\big(K_e\nabla T_e\big) - \alpha\big(T_e - T\big) + Q, \\ &\partial_t(CT) = \mathrm{div}(K\nabla T) + \alpha\big(T_e - T\big). \end{aligned} \tag{2}$$

Here, C_e and C are the heat capacities of electrons and phonons, respectively; K_e and K are the thermal conductivity coefficients of electrons and phonons, respectively; and Q is the specific power absorbed by the island. The coefficient α describes the electron-phonon interaction, and the product $\alpha\big(T_e - T\big)$ determines the power transferred from electrons to phonons (here, the temperature difference $T_e - T$ is assumed to be small). These equations must be supplemented with boundary conditions that describe the heat transfer process from the metal island to the substrate.

To analyze this system of equations, P.M. Tomchuk proposed a graphical model of coupled vessels,

which illustrates the energy transfer between the electron and phonon subsystems as well as the nonequilibrium heating of the electron gas in a small island on the substrate. The model consists of two interconnected cylindrical vessels nested one inside another (Fig. 3). The narrow vessel is responsible for the electron gas, and the wider one for the phonon subsystem (the lattice). The cross-sections of the vessels are proportional to the heat capacities C_e and C. The heights of a liquid in the narrow and wide vessels correspond to the electron (T_e) and phonon (T) temperatures, respectively. The height of the wide vessel corresponds to the lattice melting temperature T_n. The narrow vessel is inserted into the wider one and is quickly filled with liquid, and this process corresponds to a rapid temperature growth in it. The narrow vessel has a gap that simulates the interaction between the electron and phonon subsystems. The width of this gap is determined by the electron-phonon interaction coefficient α, and its narrowness demonstrates that the energy exchange between electrons and phonons is predominantly weak. Similarly, holes in the wide vessel simulate the interaction with the substrate, namely, the intensity of the heat exchange between the island lattice and the substrate. The liquid is fed into the narrow vessel (the term Q in the equation), which corresponds to the thermal power transfer to the electron subsystem. The narrower the gap in the narrow vessel (the smaller the electron-phonon interaction coefficient α), the less liquid enters the wide vessel per unit time. The liquid level in the wide vessel is stabilized by means of the liquid leakage from it, which simulates the thermal contact between the island and the substrate. As a result, the phonon temperature is maintained at a level where the substrate material is not destroyed. In addition, the thermal stability of small metal islands on a thermally conductive substrate can be substantially higher, if the power Q is supplied in the pulsed mode.

The specific heat capacity of the electron subsystem (C_e) is much lower than that of the phonon subsystem (C). Therefore, the characteristic relaxation time for the electron temperature, $\tau_e \approx C_e/\alpha$, is estimated to be of the order of 1 ps, which is much shorter than the corresponding time for phonons, estimated to be of the order of 100 ps. For this reason, the phonon temperature cannot change considerably during the time $t < \tau_e$, and the electrons behave themselvelves as if they were thermally isolated during this

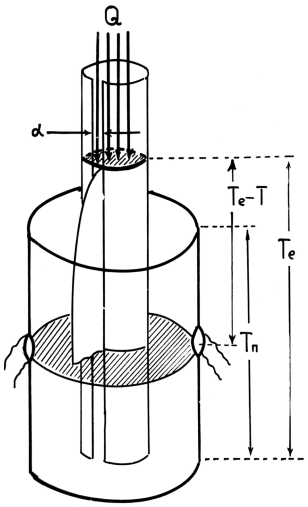

Fig. 3. A graphical model proposed by P.M. Tomchuk to explain the phenomenon of electron gas heating in a small metal island (particle) on a substrate. The narrow vessel is responsible for the electron gas, and the wider one for the phonon subsystem

time interval. If a quasi-equilibrium state is reached within a time interval of the order of τ_e, the difference between the electron and phonon temperatures stabilizes (as much liquid flows into the narrow vessel as flows out of the wider one) and becomes equal to

$$T_e - T \approx Q/\alpha. \tag{3}$$

Theoretical estimates of the electron temperature T_e made by P.M. Tomchuk gave values of the order of 10^3 K, whereas the lattice remained almost unheated ($T \approx 10^2$ K). This result coincides with experimental data [28, 70]. In this case, the thermionic emission current can be determined using the well-known Richardson formula

$$I_e \sim \exp\Big(-\frac{\varphi}{kT_e}\Big), \tag{4}$$

where φ is the electron work function from the island.

An essential difference between island and continuous films, especially between island films and massive metals, is manifested at the stage of energy redistribution between the electron gas (the electron subsystem), the metal lattice (the phonon subsystem), and the dielectric substrate. The energy flow from electrons to the lattice increases as the temperature difference $T_e - T$ grows. However, as the lattice temperature increases, there begins an intensive removal of

the energy to the substrate (where it is distributed over a large volume), which does not occur in a massive metal.

An island film is principally different from a continuous film by the character of the heat transfer into the substrate. In particular, in metal islands with a size smaller than the critical one, there are no energy losses associated with the generation of longitudinal acoustic waves such as Cherenkov radiation, as was described in detail in P.M. Tomchuk's works [71, 72], written jointly with Ye.D. Bilotsky. The Cherenkov radiation of acoustic waves is the main channel of energy losses by hot electrons in massive metals. In the absence of such losses in metal island films, the electron heating can occur at lower input powers. Theoretical estimates presented in works [73, 74] showed that the electron-phonon energy exchange in a system of small metal particles, such as metal islands in a film, is two orders of magnitude weaker than in massive metals. This result was also confirmed experimentally [75].

Thus, Petro Tomchuk showed that the electron and photon emissions from a metal island film in the case of its heating with current or laser irradiation are of the same nature. The difference lies only in the mechanisms of power input. In the case of current transmission, hot electrons arise due to high current densities (along the current lines) and some weakening of the electron-phonon interaction. In the case of pulsed laser irradiation, the power is introduced only into the electron subsystem of the island, and the electron temperature increases almost non-inertially following the irradiation power density, which leads to the electron gas heating and the emission of hot electrons.

Later, the electron emission from island films obtained by sputtering silver and gold nanoparticles and irradiated with a femtosecond laser was detected as well, and P.M. Tomchuk's theory was also applied to explain this experiment [76].

3.4. Optoacoustic effect

Besides the theory explaining the emission of electrons and photons from metal island films, Petro Tomchuk also built the theory of sound generation by metal island films under the action of a modulated light (laser) flux [12]. This effect was called *optoacoustic*. If the electron temperature T_e substantially exceeds the lattice temperature, the electrons create additional pressure on the metal particle surface and deform it (even the particle destruction is possible). Additional electron pressure and the heat flux from hot electrons can generate acoustic waves propagating in the dielectric substrate. In the case of electron temperature modulation occuring as a result of the modulated laser flux acting on the island film, additional electron pressure induces surface vibrations of the metal island (particle) rather than its destruction, as in the case of unmodulated flux. A characteristic feature of this sound generation mechanism is the appearance of a double harmonic and the quadratic dependence of the sound wave amplitude on the light flux intensity. It is significant that the acoustic wave shape does not depend on the island shape, but the light absorption cross-section may depend very strongly on it and change by several orders of magnitude. In this case, a metal island film can absorb light much more efficiently than a continuous film.

In work [77], the theory of optoacoustic effect was extended to the case of laser irradiation in the ultrashort (femtosecond) interval; additionally, the problem was considered in a more general formulation involving a system of metal nanoparticles embedded into a dielectric matrix. In works [78, 79], the influence of laser irradiation on metal nanoclusters in a dielectric matrix was considered. The energy absorbed by the clusters propagates in the dielectric matrix in the form of heat and generates sound waves via the thermodeformation mechanism. A high sensitivity of the sound wave amplitude to the shape of metal clusters as well as to such parameters of laser radiation as frequency, polarization, and intensity was found. The behavior of the sound vibration amplitude in the region of *surface plasmon* excitation [2] was investigated in detail. It was found that if light is absorbed by a discrete metal film (a system of clusters in a matrix) in the spectral interval of plasmon resonances, this amplitude can be several orders of magnitude larger than the corresponding amplitude in the case of a continuous metal film.

3.5. Size effects

The latest series of works by Petro Tomchuk and coauthors on the theory of hot electrons in metal is-

[2] Recall that *surface plasmons* are collective oscillations of electron plasma in metals. They are excited near the metal surface by an incident external electromagnetic wave [80].

land films (in essence, this is an ensemble of metal nanoparticles in a dielectric matrix) is related to the study of size effects in such systems [81–84].

The authors of paper [81], which was a continuation of works [71, 72], demonstrated that the intensity of the electron-lattice energy exchange in the bulk (associated with the Cherenkov mechanism of sound generation) decreases and tends to zero for certain particle sizes as the size of metal particles (islands) decreases. An expression was obtained for the energy lost by an electron per unit time to initiate acoustic vibrations in the lattice. In paper [82], the bulk and surface components of electron-phonon energy exchange in metal nanoislands were considered. It was found that the bulk energy exchange exhibits non-monotonic oscillations depending on the particle size. The amplitude of such oscillations increases with particle size decreasing until the particle size reaches a critical value. Oscillations disappear below this value, the bulk energy exchange ceases, and only the surface mechanism of energy exchange remains in force. It was confirmed that there is an interval of particle sizes for which the total energy exchange is several orders of magnitude lower than in massive bulk metals.

The electron-lattice energy exchange was found to substantially depend on the electron temperature for certain particle sizes called "magic" [83]. The effect of size dependences of the electron-lattice energy exchange on the temperature of hot electrons was analyzed in work [84] for the case of a system approaching a critical size. A high sensitivity of electron temperature to the size of metal nanoparticle in the vicinity of critical values was revealed. The results of computational experiments were presented, and they confirmed the main assumptions of the theory.

4. Optical Properties of Metal Nanoparticles and Their Ensembles

4.1. General background

In the last few decades, the physics of *metal nanoparticles* has undergone significant development. This was due to the so-called plasma resonances associated with the collective motion of conduction electrons (in particular, in the visible spectral interval) that manifested themselves in systems of such particles [85]. Studying the physical properties of metal nanoparticles is challenging in a wide range of problems that are not only of purely academic but also of practical interest. For example, this concerns the study of colloidal solutions of metals, the development of paints with finely dispersed metal particles, the design of optical metamaterials with nanosized metal inclusions, and so forth [86].

The studies of the optical properties of small metal particles have a history spanning over a century. One of the milestones in this history is the classic article by Gustav Mie "Contribution to the optics of turbid media, particularly of colloidal metal solutions" [87] published in 1908. It is where a solution to the problem of the plane electromagnetic wave scattering by a homogeneous spherical particle was presented. The results obtained by G. Mie still constitute a theoretical basis for describing and analyzing the optical properties of particles of various sizes (both small and comparable to the length of the incoming light wave).

At first, in his work on the physics of metal island films, Petro Tomchuk considered small metal particles as structural elements of such films, as was indicated in the previous section. Later, in the 1990s, he moved on to consider isolated nanoparticles and their ensembles as separate research objects, independent of the island film problem. In the works by P.M. Tomchuk and his co-authors on the optical properties of metal nanoparticles that were published over the past three decades, effects that had previously been little studied or not studied at all were analyzed.

The choice of the research direction in this series of works was based on the idea that the character of light interaction with metal particles changes qualitatively whenever two (or more) characteristic dimensions – for example, the incident wave length, the particle size, the mean free path of conduction electrons in the particle material or their de Broglie wavelength, and the skin layer depth – become the same or comparable. Petro Tomchuk not only determined the applicability limits of the Mie theory, but he also obtained some new results in the problem of light scattering and absorption by small metal particles. Here, we review the most significant results obtained by P.M. Tomchuk in this direction.

4.2. Spheroidal metal nanoparticles

The light absorption by metal nanoparticles with the shape of *ellipsoids of revolution* (prolate or oblate,

spherical particles being a particular case) was considered in works [13, 14] [3]. Such particles are also called *spheroidal* or *spheroid*. Both the electric component of absorption (associated with the currents excited directly by the electric field of the incoming wave inside the particle) and the magnetic component (associated with the Foucault currents induced by the oscillating magnetic field of the wave) were taken into account. The estimates showed that the magnetic component of absorption can be considerable for nanoparticles even under quite standard (non-exotic) conditions. For instance, for spherical gold particles with a diameter of 60 nm, the magnetic absorption at the emission frequency of a CO_2 laser turns out to be twice as large as the electric one. In the case of prolate or oblate particles, the ratio between two absorption mechanisms also becomes dependent on the incoming wave polarization with respect to the directions of ellipsoid axes.

In the works cited above, the dependence of total absorption on the nanoparticle size was analyzed using the kinetic equation for the distribution function of conduction electrons over their velocities in ellipsoidal nanoparticles in an external electromagnetic field. The both possible cases of the relationship between the electron mean free path l in the particle and the particle size d were analyzed, namely, $l < d$ and $l > d$. Variations in the shape of metallic ellipsoidal nanoparticles were demonstrated to affect the total absorption as well as the ratio between the electric and magnetic absorption components by several orders of magnitude. Analytic expressions for the electric and magnetic components of absorption, as well as for the components of the particle conductivity tensor, were obtained for the first time for particles smaller than the electron mean free path.

Later, these results were developed in the studies of optical absorption by metallic nanoparticles in the frequency interval near the particle's plasma resonances [15]. For ellipsoidal particles with different sizes of all three axes, expressions for the electric absorption component were obtained in terms of the depolarization coefficients and the components of the optical conductivity tensor of the particle.

[3] Some ideas of those works were also presented in the earlier paper [88]. It is also worth noting that paper [14] was written by P.M. Tomchuk in co-authorship with his son Bohdan, and this is their only joint work.

Further studies also concerned the optical absorption of ultrashort laser pulses by spheroidal particles [89, 90]. They are of importance for the experimental study of the femtosecond dynamics of the electron gas in nanoparticles. Besides the geometric parameters of the particles, this problem involves new parameters that have effect on the optical absorption by particles, namely, the carrier frequency as well as the laser pulse duration and power. The pulse carrier frequency coinciding with the frequency of the particle's surface plasmons was considered, as well as the carrier frequency being higher or lower. Analytic expressions for the coefficients of light absorption by particles were obtained depending on the initial problem parameters. It was shown that the effective light absorption in the case of highly prolate or oblate particles can be achieved at a carrier pulse frequency close to the frequency of either of two plasma resonances in such particles, or under the condition of a spectrally broad pulse whose frequency "covers" the both plasma resonance peaks. The interaction of small spheroidal metal particles with double ultrashort laser pulses was considered in work [91]. It was shown that the energy scattered by the particles in this case reveals an oscillatory behavior with a change in the time delay between the pulses.

The behavior of optical and transport properties (namely, the refractive index and the electrical conductivity) of spheroidal metal nanoparticles was analyzed in detail in paper [30]. A wide range of initial problem parameters was considered: the frequency of incident wave, the particle size, the ratios between the particle axis lengths, and the particle orientation with respect to the direction of the wave electric field vector. It was shown, based on the analysis of kinetic equation, that if the size of a nanoparticle decreases to the value of the electron mean free path or below, collisions of electrons inside the particle with its walls begin to play a decisive role. The optical and transport properties of nanoparticles undergo substantial variations (up to two orders of magnitude) in comparison with the values calculated on the basis of the real and imaginary parts of the dielectric permittivity of the particle material when using the formula of classical Drude–Sommerfeld theory

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = 1 - \frac{\omega_{\rm pl}^2}{\omega^2 + \nu^2} + i\frac{\nu}{\omega}\frac{\omega_{\rm pl}^2}{\omega^2 + \nu^2}. \quad (5)$$

Here, ω is the incident wave frequency, $\omega_{\rm pl}$ is the plasma frequency of the particle material, and ν is the frequency of electron collisions in the particle bulk (ν^{-1} is the relaxation time of conduction electrons in the bulk material of the particle). The plasma frequency is determined by the formula

$$\omega_{\rm pl} = \sqrt{\frac{4\pi n e^2}{m}}, \tag{6}$$

where n is the concentration of conduction electrons in the material, and e and m are the electron charge and mass, respectively. The imaginary part of ϵ is related to the electrical conductivity σ of the particle material in a well-known way,

$$\epsilon''(\omega) = \frac{4\pi}{\omega}\sigma(\omega). \tag{7}$$

This relationship, as was shown in work [30], becomes violated for particles whose size is comparable to or smaller than the mean free path of electrons in the particle. Namely, it becomes dependent on the particle size and on the orientations of the electric and magnetic field strength vectors of the incident wave with respect to the particle symmetry axis. Therefore, the quantities ϵ'' and σ transform into tensors for which analytical expressions were obtained in some limiting cases.

The tensor character of optical conductivity was used by P.M. Tomchuk in work [92], where he further developed the theory of the light scattering by ellipsoidal metal nanoparticles to the case where the particle sizes are smaller than the electron mean free path in the particle and considerably smaller than the electromagnetic wavelength. The angular dependence of the light intensity scattered by a spheroidal particle is determined by the mutual orientations of the polarization vector of the output light flux, the spheroid symmetry axis, and the observation direction (Fig. 4). Making allownce for this angular dependence, Petro Tomchuk obtained an analytic expression for the cross-section of light scattering by a spheroidal metal particle, which involves not only the influence of particle shape on the frequencies of plasma resonances, but also its influence on the halfwidths of plasma resonances. It was shown that this effect is fundamentally important and cannot be reduced to small corrections of the known results for a spherical particle. In work [93], the theory was generalized to the case of ensembles of nanospheroids that are chaotically oriented in space.

4.3. Ultrasmall metal nanoparticles and nanoparticle ensembles

Nonlocal effects that can be observed in extremely small (or otherwise ultrasmall) metal nanoparticles (10 nm and smaller in diameter) were investigated in work [94]. The simplest case of a spherical particle was considered. In the framework of kinetic approach, the current induced by an external wave field was shown to depend on the spatial derivatives of the local field inside the particle. Such a dependence can be explained by a large contribution of the particle surface to the scattering of free electrons in the particle in the case when the particle size is substantially smaller than the mean free path of electrons. As a result, the relationship between the current density and

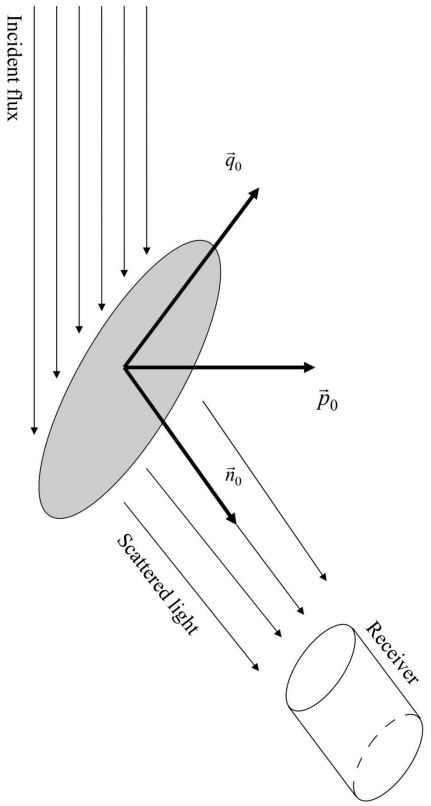

Fig. 4. Schematic diagram of electromagnetic wave screening at a small spheroidal particle used by P.M. Tomchuk to analyze the influence of the particle shape on the scattering cross-section. The vector $\boldsymbol{n}_0$ determines the observation direction, the vector $\boldsymbol{p}_0$ specifies the polarization of the outgoing light flux, and the vector $\boldsymbol{q}_0$ specifies the orientation of the spheroid symmetry axis (reproducted from work [92])

the electric field inside the particle becomes nonlocal,

$$\boldsymbol{j}(r,\,\omega) = \boldsymbol{j}^{(\mathrm{loc})} + \boldsymbol{j}^{(\mathrm{nl})} = \sigma(\omega)\boldsymbol{E}(\boldsymbol{r},\omega) + \boldsymbol{j}^{(\mathrm{nl})}, \qquad (8)$$

which means the violation of Ohm's law and requires a modification of the Mie theory for nonlocality. The nonlocal term $\boldsymbol{j}^{(\mathrm{nl})}$ is a function of the derivatives of the vector $\boldsymbol{E}$ length in the electron velocity direction and lateral direction. In the work cited above, the dependence of the nonlocal contribution on the incident wave frequency and the particle size was analyzed.

In paper [95], the problem of calculating the optical properties of extremely small metal particles was formulated in terms of an integral equation for the electric field in the particle. Approximate analytic solutions for this equation were found in the cases of spherical and ellipsoidal particles, provided that the field nonuniformity inside the particles is neglected. If the field nonuniformity is considered, the solution can be found numerically. The obtained results were consistent with the known experimental data for the optical properties of metal nanoclusters.

The optical properties of the systems (ensembles) of metal nanoparticles were considered in works [96, 97]. Systems of spheroidal particles randomly arranged in a dielectric matrix were analyzed, assuming that all the particles have the same volume but different shapes. The particle distribution function was defined in terms of the particle shape parameter, namely, the eccentricity of the generating ellipse. At the same time, the particle size (the largest of the two sizes of any particle in the system) was limited so that it was smaller than the electron mean free path. The coefficients of light absorption and scattering by the system of particles were calculated as the averages over the ensembles of corresponding coefficients for individual particles. The optical spectra obtained numerically for the particle system under consideration had features that are also characteristic of the spectra measured experimentally; in particular, these are two peaks of plasma resonances for the systems of ellipsoids of rotation.

4.4. Final remarks of the section

The influence of the magnetic dipole moment of an asymmetric metal nanoparticle on the electromagnetic radiation scattering was studied in the framework of kinetic approach in work [98]. The contribution made by the magnetic moment to the scattering was shown to be of the same order of magnitude as that made by the electric moment in the frequency interval far from plasma resonances. In this case, the ratio between the magnetic and electric scattering cross-sections becomes maximum for a spherical particle. In paper [99], the dependences of the magnetic absorption by spheroidal metal nanoparticles on the ratio between their curvature radii and on the angle between the spheroid symmetry axis and the magnetic field vector of the electromagnetic wave were considered. An interesting result of this study is that the energy absorption by a spheroidal nanoparticle grows as its disk-likeness increases.

A separate research direction for Petro Tomchuk was investigating the optical properties of metal nanotubes and nanoshells. These are small composite clusters consisting of a dielectric core and a metal cylindrical or spherical shell. In particular, the optical conductivity (electrical absorption) of such shells was calculated in the one-electron approximation and for frequencies far from the plasmon resonance region [100].

We hope that the studies of the optical properties of metal nanoparticles carried out by P.M. Tomchuk will be continued, and the theoretical approaches developed by him will be used to explain new experimental data.

5. Liquid Crystals and Colloids

5.1. General properties and the story of discovery

Liquid crystals are thermodynamically stable states of matter that have physical properties that are intermediate between those of a liquid and a solid [101]. Liquid crystals are formed by particles (molecules or molecular groups) with a prolate shape. The most general properties of liquid crystals are the presence of long-range orientational order in the arrangement of molecules and the absence (complete or partial) of translational order in the arrangement of the centers of mass of molecules. Therefore, a liquid crystal is an intermediate state of matter (the so-called *mesophase*) between a solid and a liquid, in which the orientational ordering of long molecules is possible without complete spatial ordering of their centers of mass [102]. The average equilibrium direc-

tion of orientation of molecules in liquid crystals is called *director*.

Depending on the structure of molecules, liquid crystals are divided into two groups, *lyotropic* and *thermotropic*. In the former, the orientational ordering of molecules arises as the concentration increases, and in the latter as the temperature grows [102]. Thermotropic liquid crystals are classified into three groups according to their properties: *nematics*, in which only an orientational ordering (along the director) of the long axes of mesophase molecules takes place, with no spatial ordering; *cholesterics*, in which the director forms a helix in space; and *smectics*, in which the molecules form parallel layers with an orientational ordering.

The properties of liquid crystals are very sensitive to various external factors (temperature, electric or magnetic field, mechanical stresses, and so forth). The mesophase properties also change if macroscopic inclusions of other substances are introduced into it, for example, in the form of solid particles or liquid droplets. Such systems are called *liquid crystal colloids*. A possibility of changing the material parameters to a significant degree by using weak external influences is a factor that determines a significant practical interest to liquid crystals and colloids.

Unusual properties of a transitional phase between the crystalline and liquid phases were first demonstrated by the Austrian scientist Julius Planer in his work [103] published in 1861. At that time, he worked at Lviv University and studied the optical properties of a cholesterol derivative (an organic substance) [4]. More details about this discovery can be found in works [108, 109].

Since the second half of the 20th century, liquid crystals have found a wide application in display technologies [110] and the chemical industry, in particular, in the production of liquid crystal polymers [111]. Nowadays, the scope of liquid crystal research has been expanded even further.

[4] J. Planer's work was published in German; the English translation can be found in the reference [104]. Note that the discovery of liquid crystals is often ascribed to another Austrian scientist, Friedrich Reinitzer [105]. He published his research much later (in 1888), with the work by J. Planer cited therein. The term "liquid crystal" was first introduced by the German physicist Otto Lehmann in the variations "flowing crystal" [106] and "crystalline liquid" [107].

5.2. Foundational studies

Petro Tomchuk was a pioneer in theoretical research on liquid crystals at the Institute of Physics [5]. Together with his disciple B.I. Lev, he applied a microscopic approach to the theory of liquid crystals and showed how the microscopic theory can be related to the phenomenological one [16]. In the phenomenological approach, the deformation of the director in the nematic liquid crystal's bulk is described in terms of the free energy. In the simplest case (where the surface deformations are neglected), the latter can be written in the form

$$F = \frac{1}{2}\int dV \Big(K_{11}\,(\operatorname{div}\boldsymbol{n})^2 + K_{22}\,(\boldsymbol{n}\cdot\operatorname{rot}\boldsymbol{n})^2 + \\ + K_{33}\,(\boldsymbol{n}\times\operatorname{rot}\boldsymbol{n})^2\Big), \tag{9}$$

where the unit vector $\boldsymbol{n}$ denotes the director orientation. This expression is called the *Frank free energy*, [6] and the constants K_{11} (responsible for splaying), K_{22} (responsible for torsion), and K_{33} (responsible for bending) are called Frank elastic constants.

Using the BBGKY method, [7] B.I. Lev and P.M. Tomchuk obtained a chain of equations for the particle distribution functions (single-particle, two-particle, and so on) that depend on the position and spatial orientation of the liquid crystal molecules. Further, they obtained hydrodynamic equations for describing the liquid crystal dynamics, proposed a scheme for obtaining the phenomenological Frank

[5] Experimental studies on liquid crystals at the Institute of Physics were first initiated by M.V. Kuryk, with whom P.M. Tomchuk was on friendly terms [112]. Scientific discussions with Mykhailo Kuryk were a starting point for Petro Tomchuk's research on the physics of liquid crystals.

[6] Sir Frederick Charles Frank was a British theoretical physicist who built the general theory of elasticity for molecularly uniaxial liquid crystals [113]. The expression for the free energy of a liquid crystal is also called the Frank–Oseen energy, paying tribute to the Swedish theoretical physicist Carl Wilhelm Oseen, who built the theory of elasticity of liquid crystals and obtained an expression for the free energy earlier than F.C. Frank did [114]. The corresponding historical reference can be found, in particular, in work [115].

[7] This method was named after M.M. Bogolyubov, M. Born, G.S. Green, J. Kirkwood, and J. Yvon, who independently developed a statistical approach to describe the dynamics of many-particle systems with interaction, which is based on the reduction of the Liouville equation for the particle distribution function.

elastic constants in terms of the microscopic parameters of the theory, and estimated one of those constants (K_{22}).

In works [17, 116, 117], P.M. Tomchuk (together with Ye.D. Bilotsky and B.I. Lev) built the theory of the effective mass and mobility of ions in a nematic liquid crystal. The electric field of an ion acts on the liquid crystal molecules and orients them along the field so that a deformation shell appears around the ion (which can also be called a deformation "coat"). It was assumed that the deformation shell adiabatically follows the moving ion (a similar assumption was used by S.I. Pekar to build the polaron theory, which is described in more detail in the next section). Then, during the ion motion, the rotation energy of the director in the deformation shell is added to the ion's kinetic energy. Accordingly, the ion's (effective) mass becomes substantially (by several times) bigger. This result is consistent with experimental data. Thus, the above authors first put forward the concept of the orientational mechanism describing the formation of the ion effective mass in a liquid crystal.

5.3. Nonequilibrium dissipative structures

In work [18], the theory of formation of stationary nonequilibrium dissipative structures in a nematic liquid crystal film under the action of a transverse external electric field was built. The formation of such structures occurs when the external field strength exceeds a certain critical value. This fact was first noticed by the American physicist R. Williams [118, 119], who observed the formation of one-dimensional domains in the form of elongated rolls in a liquid crystal. Accordingly, such structures in liquid crystals are called *Williams domains*. In the work by other American physicists, the formation of two-dimensional twisted (helical) structures in the presence of an additional transverse electric field modulated in the longitudinal direction with a period different from the period of the Williams domains was experimentally established [120].

P.M. Tomchuk, together with Ye.D. Bilotsky, showed that such nonequilibrium structures are formed due to the electrohydrodynamic instability accompanied by the loss of mechanical equilibrium in the liquid crystal [18]. For this purpose, the theory of perturbations near the external-field critical point was developed for a system of equations that describes the liquid crystal dynamics in the hydrodynamic approximation and has to be solved together with Maxwell's equations for the electric field. The twisted nonequilibrium structures formed due to instability are described using a generalized thermodynamic potential. The minima of this potential determine stationary nonlinear dissipative nonequilibrium structures, whereas the free energy determines equilibrium structures. Further, the perturbation magnitude was found to be almost constant, and only the perturbation phase was changing, so that a generalized thermodynamic potential for the phase could be written. By analyzing this potential, the authors of work [18] concluded that in the case of a modulated electric field whose period is not constant, but incommensurate with the period of Williams domains, there arises a two-dimensional helicoidal periodic structure in the system. Thus, the experimental data from work [120] were explained. This topic was further developed in work [121].

The authors of paper [122] considered the problem of the formation of nonequilibrium dissipative structures in nematic liquid crystals from the viewpoint of the group-theoretical analysis. The same generalized thermodynamic potential was found as in work [18], but this was done using the method of Lie algebras. The corresponding algebra and Lie group were found by analyzing a linearized system of differential equations describing the Williams domains in a nematic liquid crystal. This algebra was used to derive a nonlinear differential equation that also was the Euler equation for the sought generalized thermodynamic potential describing nonlinear dissipative structures in the Williams domain system. In particular, a generalized thermodynamic potential was obtained that describes the low-frequency regime of electrohydrodynamic instability. The theory of high-frequency nonlinear dissipative structures was developed in paper [123].

5.4. Liquid crystal droplets

In papers [124, 125] written by a group of colleagues with the co-authorship of Petro Tomchuk, the effect of an external electric field on the nematic liquid crystal droplets freely suspended in an isotropic liquid polymer was studied. The shape of a liquid crystal droplet was deformed under the action of the field. As the field strength increased, the equilibrium droplet shape transformed into a prolate ellipsoid. The experimental dependence of the droplet size on the elec-

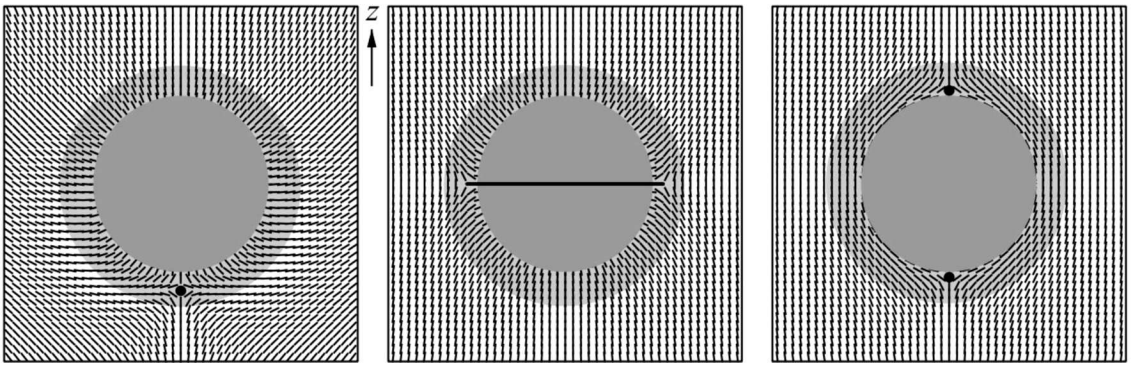

Fig. 5. Possible director configurations around a spherical particle: a hyperbolic hedgehog around a point defect (*a*), a ring of Saturn around a linear defect (*b*), and boojums around a pair of point defects (*c*). The shaded region between the particle and the liquid crystal (the so-called *deformation coat*) contains topological defects and strong director deformations (reproduction of Fig. 5.1 from work [102])

tric field strength was analyzed and conditions for the droplet to lose its stability were determined. The droplet shape and critical field strength were found to depend on the ion concentration in the polymer liquid and a theoretical explanation of the observed effect was proposed.

5.5. Liquid crystal colloids and elastic deformations

P.M. Tomchuk's scientific achievements in the field of liquid crystals also include the studies of micron-sized colloidal particles immersed into a nematic liquid crystal [19, 20, 29, 126, 127]. If a particle is embedded into a nematic liquid crystal, the molecules of the latter interact with the particle surface. This interaction is determined by the anisotropic part of the surface tension, which depends on the orientation of liquid crystal molecules with respect to the particle surface. Such anisotropic interaction of liquid crystal molecules with external surfaces is called *adhesion* (or *anchoring*) [102]. In the phenomenological approach, the surface energy of the interaction between a liquid crystal and a particle immersed into it is determined by the integral over the particle surface

$$F_s = \oint ds\, W(\boldsymbol{s})\big(\boldsymbol{n}(\boldsymbol{s})\cdot\boldsymbol{\nu}(\boldsymbol{s})\big)^2, \tag{10}$$

where $\boldsymbol{\nu}$ is the vector normal to the particle surface at the surface point $\boldsymbol{s}$, and the anchoring coefficient W determines the adhesion force of the director to the surface (the case $W<0$ corresponds to the normal orientation of the director on the particle surface, and $W>0$ to the tangential orientation). The bulk energy of deformations is determined via the Frank free energy. If there are several particles in a liquid crystal, each of them creates deformations that overlap. As a result, the elastic interaction originating between the particles leads to the formation of various structures. Depending on the value of the coefficient W, the director deformations can be strong enough for topological defects to emerge around the particle (Fig. 5).

The region around the particle where the director deformations are substantial (and where topological defects are present) can be separated from the region where the director deformations are small. Such a region with topological defects around the particle can be called a "*deformation coat*", as was proposed in work [29]. Outside this region (far zone), deformations are weak, implying that the director field can be considered as a small perturbation $\delta\boldsymbol{n}(\boldsymbol{r})$ of the equilibrium distribution of the director $\boldsymbol{n}_0$ in the absence of inclusions,

$$\boldsymbol{n}(\boldsymbol{r}) = \boldsymbol{n}_0 + \delta\boldsymbol{n}(\boldsymbol{r}), \quad |\delta\boldsymbol{n}| \ll 1, \tag{11}$$

with $\delta\boldsymbol{n}(\boldsymbol{r})\perp\boldsymbol{n}_0$ in the linear approximation. Then, the director field at a supposed surface of a colloidal particle with a coat can also be approximately represented as a gradient expansion in a small perturbation of the equilibrium distribution [20],

$$\boldsymbol{n}(\boldsymbol{s}) = \boldsymbol{n}_0 + \delta\boldsymbol{n}(\boldsymbol{r}_c) + (\boldsymbol{\rho}\cdot\nabla)\,\delta\boldsymbol{n}(\boldsymbol{r}_c) + \\ + \frac{1}{2}(\boldsymbol{\rho}\cdot\nabla)^2\,\delta\boldsymbol{n}(\boldsymbol{r}_c). \tag{12}$$

Here, $\boldsymbol{\rho}$ is the vector drawn from the particle center $\boldsymbol{r}_c$ to the surface point $\boldsymbol{s}$, $\boldsymbol{r}(\boldsymbol{s}) = \boldsymbol{r}_c + \boldsymbol{\rho}$. This representation makes it possible to reduce a real particle to some point source of deformations in a liquid crystal.

Next, the corresponding gradient expansion can be obtained for the surface energy. It can be expressed in terms of a set of certain tensor characteristics of the deformation coat. These tensors characterize various possible symmetry violations of the director field near the particle and determine the interaction potential features in the far zone [20]. It is also possible to calculate the pairwise interaction energy between two particles. For particles of arbitrary shape, this energy depends on the Frank elastic constants (the volume component of energy) and the corresponding tensor characteristics of surface deformations (the surface component of energy). Depending on the particle symmetry, this interaction in the far zone can be of the Coulomb, dipole-dipole, or quadrupole-quadrupole types [29].

An equation for the director distribution can be obtained from the condition of the minimum of the total energy functional (volume plus surface). In the far zone and in the case of the so-called single-constant approximation ($K_{11} = K_{22} = K_{33}$), the Laplace equation is obtained. Its solution can be written in the form of a *multipole expansion*, as is done in electrostatics [102, 128],

$$n_i(\boldsymbol{r}) = \frac{q_i}{r} + \sum_{\alpha} \frac{p_i^{\alpha} r_{\alpha}}{r^3} + \frac{1}{2} \sum_{\alpha,\beta} \frac{Q_i^{\alpha\beta} r_{\alpha} r_{\beta}}{r^5} + ..., \quad (13)$$

where the subscript i runs through the values 1 and 2 (the coordinates x and y; the unperturbed director is considered to be directed along the z-axis), and the indices α and β run through the values 1, 2, and 3 (the coordinates x, y, and z). The quantities q_i, p_i^{α}, and $Q_i^{\alpha\beta}$ are called elastic charges (monopoles), dipoles, and quadrupoles, respectively.

The results obtained by P.M. Tomchuk together with a group of his co-authors in the theory of liquid crystal colloids are undoubtedly important, which is confirmed by their wide recognition among the scientific community. In particular, it was shown how one can build a theory of elastic interactions between macroparticles in a liquid crystal [19, 20]. The broken director symmetry in the near zone of a colloidal particle (near the deformation coat) was demonstrated to affect the nature of the interaction between the particles in the far zone [29]. The deformation coat around the particle confines the region of topological defects and strong deformations. Outside the coat, there are no topological defects and the director deformations are small. In a nematic liquid crystal, colloidal particles interact through elastic deformations of the director field, which can lead to the formation of spatially modulated structures. Some examples of such structures were considered and modeled in work [126]. In paper [127], the theory was applied to explain the formation of a two-dimensional hexagonal structure of glycerol droplets introduced into a nematic cell.

6. Proton Conductivity in Molecular Structures with Hydrogen Bonds

6.1. Proton conductivity

In the early 1970s, it was known that *injected protons* are charge carriers in some hydrogen compounds [129]. Such compounds include some inorganic crystals (for example, ice, potassium dihydrogen phosphate KH_2PO_4, lithium sulfate monohydrate $Li_2SO_4 \cdot H_2O$, and others [130]) and certain organic compounds (imidazole, dry alcohols, carbohydrates, and biopolymers [129]). A distinctive feature of these compounds is the presence of three- or two-dimensional networks of *hydrogen bonds* (H-bonds) in them and H-bond chains ...A–H...A–H... in some of them (here, A stands for O, N, F, or other atoms).

At the same time, some chemical compounds with H-bond chains, such as lithium hydrazine sulfate $Li(N_2H_5)SO_4$ (LiHzS), triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ (TAHS), and others, demonstrate a strong anisotropy of their specific proton conductivity, which is three orders of magnitude larger along the H-bond chains than in perpendicular directions [32]. This fact testifies that H-bond chains significantly contribute to the motion of protons.

A bright example of proton conductivity is the functioning of biological membranes in living organisms, which is a subject of study in molecular biophysics [131]. Proton transport is performed along proton channels, which are essential components of biological membranes of all types. Playing a major role in the bioenergetics of living organisms, this process maintains a constant difference between the electrochemical potentials in the aqueous media on both sides of the membrane. The process of proton transport occurs precisely along the H-bond chain that is

formed by the end groups of side radicals in the amino acid residues of protein [132] [8].

6.2. Proton polaron model

It was the possibility of applying the methods of theoretical physics in biophysics that motivated Petro Tomchuk to join the study of proton conductivity in hydrogen bond chains. The task was to research the proton transport in order to develop the microscopic theory of proton transfer along an H-bond chain. When studying the process of proton motion in compounds with hydrogen bonds, P.M. Tomchuk noticed that their conductivity was not similar to the conductivity of metals or semiconductors. The conductivity mechanism here was more reminiscent of *polaron* (hopping) *conductivity*, which is caused by the interaction of charge carriers with polarization vibrations in the crystal.

The term "*polaron*" was introduced by S.I. Pekar in 1946 [135] for a quasiparticle that describes the state of a conduction electron localized in the polarization potential well formed by the displacements of surrounding ions [136]. If the potential well is formed by small displacements of a large number of ions (so that the well's radius substantially exceeds the interatomic distance), then we speak of a *strongly coupled* (or large-radius) *polaron*. If the potential well is formed by the displacements of the equilibrium positions of a small number of ions (for example, the two closest ones), then we speak of a *small-radius polaron*. The theory of such "small" polarons was proposed by T. Holstein in 1959 [137]. The presence of a potential well drastically reduces the probability of electron tunneling to neighboring sites, and the velocity of current carrier motion is determined by thermally activated electron jumps between neighboring sites.

It was the hopping mechanism of charge carrier transport (such as the polaron electron conductivity, which has an activation nature) that Petro Tomchuk took as the basis for describing the proton conductivity in H-bond chains [9]. Such a mechanism, based on the model of a quasiparticle like a small-radius polaron, was earlier proposed by American chemists [130], mainly to describe the proton motion in ice crystals. Together with his colleagues, P.M. Tomchuk used the small-radius polaron model to describe the transport of charged defects (excess protons or proton holes, Fig. 6) along the H-bond chains [21, 22]. At first, the theory of proton conductivity in a chain of weak H-bonds located in a strong electric field (up to the field strengths achievable in biomembranes) was developed [21]. Then, taking into account the renormalization due to the phonon-phonon interaction, an expression for the proton conductivity was obtained in the case of a strong defect coupling with longitudinal optical polarization phonons and longitudinal acoustic phonons [22]. To this end, the chain polarization was assumed not to be affected by the motion of the ionic state, which is a charge carrier in the system examined. This assumption is valid as long as the proton rotates around the proton-binding atom much faster than the charge carrier migrates along the chain.

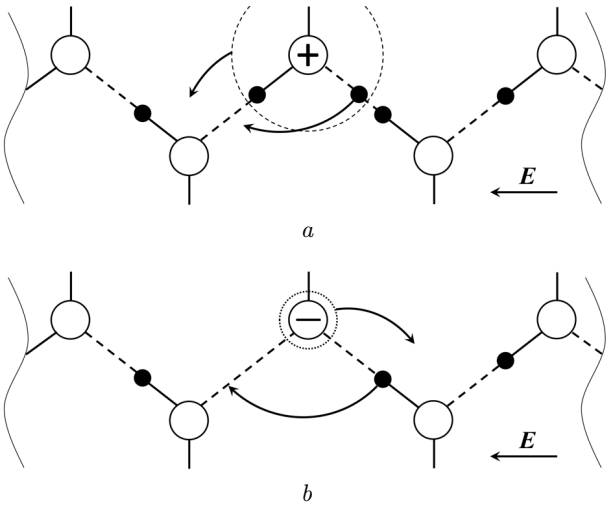

Fig. 6. Schematic diagram of charged defect (ionic state) transfer along an H-bond chain in an external electric field **E** [22, 23]. Charged defect: (*a*) an excess proton, (*b*) a proton hole. Notations: ◯ is an atom (e.g., O, N, or F), • is a proton (H^+), - - - is a hydrogen bond, and —— is a covalent bond

The hopping conductivity along the chain is described by the trace of the current density operator,

$$I = \mathrm{Tr}\ (\widehat{\rho}_E\, \widehat{j}), \tag{14}$$

where I is the "hopping" proton current density (the hopping mechanism dominates at temperatures of

[8] This fact was first pointed out in papers [133, 134] by Lars Onsager, an American physicist-chemist of Norwegian origin, the Nobel Prize laureate in chemistry.

[9] Note that there were other models of energy transfer in molecular chains at that time; e.g., the soliton mechanism of propagation of collective intramolecular excitations proposed by O.S. Davydov and M.I. Kislukha [138].

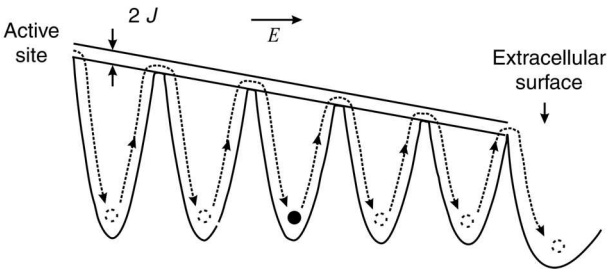

Fig. 7. Schematic diagram of the hopping motion of an excess proton along a chain of polaron wells, which corresponds to its motion along a chain of hydrogen bonds in an external electric field (reproduced from work [144] by permission from Elsevier). Notations: $2J$ is the width of a narrow polaron zone, E is the applied electric field strength

about 300 K, when phonons play the role of an activation system), $\widehat{j}$ is the current density operator calculated via the tunnel Hamiltonian in the second quantization representation, and $\widehat{\rho}_E$ is a correction to the density matrix operator that involves the interaction with the external electric field E. Based on this expression, the activation energy for the proton polaron jump was obtained in the explicit form as a function of the proton coupling constant with crystal lattice vibrations and the resonance integral of the overlap of the proton wave functions in the H-bond chain. These two fitting parameters can be determined from a comparison with experimental data in every specific case. Taking the anharmonicity into account improves the agreement with the results of proton conductivity measurements [139].

In addition, the influence of Coulomb correlations, i.e., the interaction of conductivity protons with one another in the H-bond chain, local inhomogeneities [140], and external factors such as electromagnetic radiation and ultrasound [141] on the proton conductivity was analyzed.

6.3. Applications in biophysics

An important result of those works was a conclusion that an H-bond chain does not repolarize after the passage of a proton along it. Such a behavior is typical for H-bond chains in the proton channels of transmembrane proteins. It was P.M. Tomchuk who, together with co-authors, proposed the polaron mechanism to describe the proton transport along a proton channel through the membrane in the protein complex of the ATP synthase enzyme [23]. This enzyme catalyzes the synthesis of adenosine triphosphate (ATP), the molecule responsible for the intracellular energy transfer in living organisms. Further studies of the structure and proton conductivity of the transmembrane protein bacteriorhodopsin, which is found in some microorganisms belonging to the class of halobacteria (*H. halobium*) and acts as a proton pump due to light energy, confirmed that the proton motion in the proton protein channels of living organisms occurs in accordance with the predictions of the small-polaron theory [142–144].

For instance, a polaron state can arise at any node of the H-bond chain along which an excess proton moves. In this state, the charge carrier remains bound to the chain node for a short time (of the order of a microsecond), though sufficient for the chain to deform and a potential (polaron) well to appear. Then, the excess proton "jumps" from one polaron well to another, which corresponds to its motion along the H-bond chain from the active center to the extracellular membrane surface under the electric field action [144]. A schematic diagram of such a proton hopping motion is shown in Fig. 7.

6.4. Pseudospin chains, repolarization effects

Having returned from a business trip to Germany in 1990, Petro Tomchuk was hooked on the idea of considering the behavior of a hydrated layer on the metal film surface. It was experimentally found by his German colleagues that such a layer substantially affected the electrical parameters of the metal film [145]. P.M. Tomchuk, together with V.V. Krasnoholovets, proposed a theoretical explanation of this effect in the framework of the pseudospin operator approach, which makes it possible to describe oscillations of polar water molecules [146].

As a continuation of this study, the polarization dynamics of a pseudospin H-bond chain was considered with allowance for the chain anisotropy [24]. It was shown, using the time-dependent mean-field approximation, that the repolarization of hydrogen bonds (i.e., switching the orientation of OH groups to the opposite direction) can take place *in a finite chain* due to the macroscopic quantum tunneling of the chain polarization. An expression for the tunneling probability was obtained, and this probability was shown to decrease as the number of H-bonds in

the chain inceases. Therefore, repolarization does not take place in sufficiently long H-bond chains.

In the subsequent series of papers published by P.M. Tomchuk on this topic [147–149], this time together with S.P. Lukyanets, another mechanism of tunnel repolarization of a short H-bond chain was considered, with allowance for coherent reorientation of ionic groups. Using the quasiclassical approximation (also known as the WKB method),[10] they estimated the frequency of such reorientation of ionic groups, which turned out to be independent of the temperature. Therefore, coherent reorientation can be observed at low temperatures, at which the tunnel repolarization of the H-bond chain prevails over the thermally activated one.

6.5. Final remarks of the section

The quintessence of P.M. Tomchuk's research on the conductivity of molecular H-bond chains was the large review article he published together with his colleagues in Advances in Chemical Physics in 2003 [32]. This review article was invited by the editors of the Advances in Chemical Physics series, the well-known physicists I. Prigogine and S.A. Rice.

Note also that the polaron mechanism of proton conductivity was later confirmed experimentally in work [150] using the quasielastic neutron scattering (QENS) method in hydrated yttrium oxide substituted by barium cerate (BCY20), which is an inorganic compound, and in work [151] by analyzing low-temperature Raman spectra of oxalic acid dihydrate, which is an organic compound. Both of those experimental works contain references to articles coauthored by P.M. Tomchuk. The results obtained there testify to the correctness of Petro Tomchuk's scientific intuition in choosing a model to describe the proton conductivity in H-bond chains.

7. Conclusions

In this paper, the main scientific results obtained by the outstanding Ukrainian theoretical physicist Petro Tomchuk in such domains as the physics of semiconductors, metal island films and nanoparticles, liquid crystals and colloids, and molecular structures with hydrogen bonds were considered.

In the field of semiconductor physics, Petro Tomchuk built the theory of hot electrons with a dominant role of electron-electron interaction and a complex structure of energy bands. He predicted non-trivial field dependences of the kinetic coefficients, which were later experimentally confirmed, and built the theory of superlattices on hot electrons in semiconductors. P.M. Tomchuk also developed the theory of physical mechanisms of degradation in optoelectronic devices.

Petro Tomchuk was the founder of the theory of hot electrons in metal island films and nanoparticles, especially in the context of the electron emission and energy transfer. His work became fundamental for understanding those processes. The possibility of obtaining hot electrons at relatively low powers can explain why, in the stationary regime, hot electrons can be obtained only in island films and cannot be obtained in continuous films or massive metals. Due to the intensive electron-lattice energy exchange in continuous films and massive metals, thermal destruction of the material occurs before the electron temperature "breaks away" from the lattice temperature. Therefore, to avoid thermal destruction of such materials, hot electrons can be obtained there only if short and powerful laser pulses are applied.

P.M. Tomchuk's theory laid the foundations for the quantitative description of nonequilibrium electronic processes in nano-sized metals. His approach combined classical solid-state physics with quantum effects, which became crucial for modern research in nanophotonics and quantum electronics. P.M. Tomchuk's works on the optical properties of metal nanoparticles and their systems formed a basis for understanding the processes that govern the optical response of particles of various sizes: from tens of nanometers, as in the long-used paints based on colloidal gold or silver, to several nanometers, as in the structural elements of modern metamaterials for plasmonics. From the viewpoint of the increasing miniaturization of the element base of electronics and optoelectronics, the significance of the theoretical results obtained by Petro Tomchuk will only grow.

The works co-authored by P.M. Tomchuk in the field of liquid crystals laid the foundations for understanding many processes in liquid crystals and liquid crystal colloids, and they can certainly be used in future studies. In particular, one can think about biaxial liquid crystals (with two average orientatio-

[10] The method was named after the physicists G. Wentzel, H.A. Kramers, and L. Brillouin, who developed it independently of one another in 1926.

nal axes), ferroelectric nematics (consisting of long molecules with a dipole moment, where a transition to a state with spontaneous polarization is possible; the polarization sign can be changed by an external electric field, which leads to the hysteresis effect), polar nematics (which have spontaneous polarization, but its sign cannot be changed by an external field; i.e., there is no hysteresis), and twist-bend nematics. An important direction of further research is also the study of three-dimensional topological defects in liquid crystals, such as skyrmions, thorons, and so forth.

To describe the proton conductivity in the molecular chains of hydrogen bonds, Petro Tomchuk used the small-radius polaron model, which describes the hopping mechanism of charge carrier transport due to the interaction of carriers with polarization phonons. The proton polaron model was used to describe the proton transport along proton channels through biological membranes in protein complexes. The polaron mechanism of proton conductivity in some inorganic and organic compounds was subsequently confirmed in experiments made by various research groups. Together with his colleagues, P.M. Tomchuk also built the theory of repolarization of hydrogen bonds in finite-size chains based on the quantum tunneling and coherence effects. Petro Tomchuk's work on the proton conductivity in H-bond chains has received the wide international recognition.

The vast majority of P.M. Tomchuk's research in the field of theoretical physics and condensed matter physics, which was considered in this review, dealt with nonequilibrium systems and processes. Kinetic theory, distribution function, fluctuations, microscopic approach, density matrix – these are the key concepts that can most often be found in the works by P.M. Tomchuk. That is why his research can be used in the future in such a modern direction of condensed matter physics as active soft matter, in particular, active liquid crystals. This is a substance that contains components (for example, bacteria, cells, actin cytoskeleton, motor proteins, active colloids) that take energy from the environment and use it for movement, deformation, or flow generation. Active environments are in a nonequilibrium state, even when it is a stationary state, and they are capable of self-organization. Such studies may probably help one to discover new physical principles in order to better understand relations between living and nonliving matter.

During his long scientific activity, P.M. Tomchuk collaborated with many theoretical physicists and experimenters. His works were aimed at explaining specific effects observed in the experiment. He was always open to discussing the results with his colleagues or other scientists who turned to him for advice. P.M. Tomchuk contributed to the scientific maturing of many theoretical physicists. A lot of his disciples continued to develop the ideas of their teacher in their further scientific works. This is a sign of the formation by Petro Tomchuk of his scientific school in the field of theoretical physics and condensed matter physics.

Petro Tomchuk was an example of a person who devoted his entire life to science. He was a man of the highest decency and virtue, a democrat, and a patriot. This is how his colleagues and disciples will remember him.

Finally, we would like to note that this review is not an exhaustive record of all scientific achievements of Petro Tomchuk. Here, we primarily focused on those results that he himself considered the most significant, and which received wide recognition within the scientific community. Other works by P.M. Tomchuk, which have not been paid enough attention, can be considered elsewhere.

Authors' contribution. *I. Gandzha: idea, concept, article structure; introduction, conclusions, general editing, and detailing of all sections; V. Shenderovskyi: introduction, section 2; L. Barabash: section 3; V. Gozhenko: section 4; V. Krasnoholovets: section 6; S. Chernyshuk: section 5. All the authors participated in writing the conclusions.*

1. *The Life Credo is Science: To the 80th Anniversary of the Birth of Petro Mykhailovych Tomchuk.* Edited by I. Gandzha, V. Shenderovskyi (Prostir Publishing House, 2014) (in Ukrainian).
2. V. Shenderovskyi, O. Polevetska. From a pleiad of outstanding modern Ukrainian theoretical physicists (to the 90th anniversary of the birth of Professor Petro Tomchuk). *Svitohlyad* **6** (104), 35 (2023) (in Ukrainian).
3. M.V. Bondar, I.S. Gandzha, A.G. Zagorodny, B.I. Lev, V.M. Starkov, V.A. Shenderovskyi. Petro Mykhailovych Tomchuk (to the 90th anniversary of his birth). *Ukr. J. Phys.* **69**, 66 (2024).
4. I.M. Dykman, P.M. Tomchuk. Effect of electric field on the temperature of electrons, electrical conductivity, and thermoionic emission of semiconductors. I. Atomic semiconductors. Development of the method. *Fiz. Tverd. Tela* **2**, 2228 (1960) (in Russian).

5. P.M. Tomchuk. Effect of electric field on the temperature of electrons, electrical conductivity, and thermionic emission of semiconductors. II. Accounting for plasma oscillations and close collisions. *Fiz. Tverd. Tela* **3**, 1019 (1961) (in Russian).
6. I.M. Dykman, P.M. Tomchuk. Effect of electric field on the temperature of electrons, electrical conductivity, and thermionic emission of semiconductors. III. Thermionic emission. *Fiz. Tverd. Tela* **3**, 632 (1961) (in Russian).
7. P.M. Tomchuk, A.A. Chumak. Nonlinear propagation of infrared radiation in multi-valley semiconductors. *Fiz. Tekh. Poluprovodn.* **19**, 77 (1985) (in Russian).
8. P.M. Tomchuk, V.A. Shenderovskii. Scattering and transformation of waves by fluctuations in a nonequilibrium plasma in a semiconductor with an anisotropic energy band. *Zh. Èksp. Teor. Fiz.* **62**, 1131 (1972) (in Russian).
9. P.M. Tomchuk, R.D. Fedorovich. Emission of hot electrons from thin metal films. *Fiz. Tverd. Tela* **8**, 276 (1966) (in Russian).
10. P.M. Tomchuk, R.D. Fedorovich. Conductivity of thin metal films having an island structure. *Fiz. Tverd. Tela* **8**, 3131 (1966) (in Russian).
11. P.M. Tomchuk. Electron emission from metal island films under the influence of laser infrared radiation (theory). *Izv. Akad. Nauk SSSR Ser. Fiz.* **52**, 1434 (1988) (in Russian).
12. P.M. Tomchuk. Optoacoustic effect in the systems of island metal film on a dielectric, metal impurities in dielectric. *Ukr. J. Phys.* **38**, 1174 (1993) (in Ukrainian).
13. P.M. Tomchuk. Light absorption by island metal films in the infrared range. *Surf. Sci.* **330**, 350 (1995).
14. P.M. Tomchuk, B.P. Tomchuk. Optical absorption by small metallic particles. *J. Exp. Theor. Phys.* **85**, 360 (1997).
15. P.M. Tomchuk, N.I. Grigorchuk. Shape and size effects on the energy absorption by small metallic particles. *Phys. Rev. B* **73**, 155423 (2006).
16. B.I. Lev, P.M. Tomchuk. On the relation between phenomenological and microscopic approaches in the theory of liquid crystals. *Teor. Mat. Fiz.* **32**, 101 (1977) (in Russian).
17. E.D. Belotskiĭ, B.I. Lev, P.M. Tomchuk. Effective ion mass in a liquid crystal. *JETP Lett.* **31**, 539 (1980).
18. E.D. Belotskiĭ, P.M. Tomchuk. Incommensurable and helicoidal structures in nematic liquid crystals in electric fields. *Sov. Phys. JETP* **61**, 974 (1985).
19. B.I. Lev, P.M. Tomchuk. Supramolecular structures in liquid crystals induced by macrodroplets. *Ukr. J. Phys.* **44**, 135 (1999) (in Ukrainian).
20. B.I. Lev, P.M. Tomchuk. Interaction of foreign macrodroplets in a nematic liquid crystal and induced supermolecular structures. *Phys. Rev. E* **59**, 591 (1999).
21. P.M. Tomchuk, V.V. Krasnogolovets, N.A. Protsenko. Proton conductivity of a chain of hydrogen bonds in a strong electric field. *Ukr. J. Phys.* **28**, 767 (1983) (in Russian).
22. V.V. Krasnogolovets, P.M. Tomchuk. On the proton conductivity mechanism in systems containing hydrogen-bonded chains. *Phys. Status Solidi B* **123,** 365 (1984).
23. P.M. Tomchuk, N.A. Protsenko, V.V. Krasnogolovets. Quantum-mechanical descriptions of proton transfer in biosystems containing hydrogen-bonded chains. *Biochim. Biophys. Acta* **807,** 272 (1985).
24. P.M. Tomchuk, V.V. Krasnoholovets. Macroscopic quantum tunneling of polarization in the hydrogen-bonded chain. *J. Mol. Struct.* **416**, 161 (1997).
25. I.M. Dykman, P.M. Tomchuk. *Transport Phenomena and Fluctuations in Semiconductors* (Naukova Dumka, 1981) (in Russian).
26. A.A. Tarasenko, P.M. Tomchuk, A.A. Chumak. *Fluctuations in the Bulk and on the Surface of Solids* (Naukova Dumka, 1992) (in Russian).
27. I.S. Gandzha, O.V. Polevetska, L.M. Barabash, V.V. Gozhenko, V.A. Shenderovskyi. Scientific legacy of Petro Tomchuk. Bibliography. *Ukr. J. Phys.* **70**, 738 (2025).
28. R.D. Fedorovich, A.G. Naumovets, P.M. Tomchuk. Electron and light emission from island metal films and generation of hot electrons in nanoparticles. *Phys. Rep.* **328**, 73 (2000).
29. B.I. Lev, S.B. Chernyshuk, P.M. Tomchuk, H. Yokoyama. Symmetry breaking and interaction of colloidal particles in nematic liquid crystals. *Phys. Rev. E* **65**, 021709 (2002).
30. N.I. Grigorchuk, P.M. Tomchuk. Optical and transport properties of spheroidal metal nanoparticles with account for the surface effect. *Phys. Rev. B* **84**, 085448 (2011).
31. E.D. Belotskii, P.M. Tomchuk. Electron-phonon interaction and hot electrons in small metal islands. *Surf. Sci.* **239**, 143 (1990).
32. V.V. Krasnoholovets, P.M. Tomchuk, S.P. Lukyanets. Proton transfer and coherent phenomena in molecular structures with hydrogen bonds. *Adv. Chem. Phys.* **125**, 351 (2003).
33. A.L. Efros. Semiconductors. In *Solid State Physics: Encyclopedic Dictionary, Vol. 2.* Edited by V.G. Baryakhtar *et al.* (Naukova Dumka, 1998) (in Russian).
34. N.P. Gavaleshko, P.N. Gorley, V.A. Shenderovsky. *Narrow-Gap Semiconductors. Production and Physical Properties* (Naukova Dumka, 1984) (in Russian).
35. P.N. Gorley, V.A. Shenderovsky. *Variational Method in Kinetic Theory* (Naukova Dumka, 1992) (in Russian).
36. P.M. Tomchuk. Variational method for determining electrical conductivity with allowance for the Coulomb interaction of carriers. *Fiz. Tverd. Tela* **3**, 1258 (1961) (in Russian).
37. I.M. Dykman, P.M. Tomchuk. Effect of electric field and energy dispersion law on plasma oscillations in semiconductors. *Zh. Èksp. Teor. Fiz.* **54**, 592 (1968) (in Russian).
38. P.M. Tomchuk, V.A. Shenderovskii, P.N. Gorley, N.P. Gavaleshko, L.S. Solonchuk. Galvanomagnetic properties of anisotropic semiconductors of the *p*-Te type. *Phys. Status Solidi B* **71**, 41 (1975).

39. M. Ashe, P.M. Tomchuk. Hot electrons. In: *Solid State Physics: Encyclopedic Dictionary, Vol. 1.* Edited by V.G. Baryakhtar *et al.* (Naukova Dumka, 1996) (in Russian).
40. V. Denis, Yu. Pozhela. *Hot Electrons* (Mintis, 1971) (in Russian).
41. I.M. Dykman, P.M. Tomchuk. Distribution function and electron mobility in polar semiconductors in the case of a nonparabolic dispersion law. *Fiz. Tverd. Tela* **8**, 1343 (1966) (in Russian).
42. M.V. Klein. Electronic Raman scattering. In: *Light Scattering in Solids. Topics in Applied Physics, Vol. 8.* Edited by M. Cardona (Springer, 1975).
43. S.S. Rozhkov, P.M. Tomchuk. Current fluctuations in semiconductors in the presence of a quantizing electric field. *Zh. Èksp. Teor. Fiz.* **72**, 248 (1977) (in Russian).
44. I.M. Dykman, P.M. Tomchuk. Kinetic equation and parameters of a superlattice formed by a standing laser wave in a semiconductor with heated carriers. *Ukr. J. Phys.* **27**, 1023 (1982) (in Russian).
45. I.M. Dykman, P.M. Tomchuk. Effect of a constant field on the parameters of a superlattice formed in a semiconductor by a standing laser wave. *Fiz. Tverd. Tela* **24**, 3255 (1982) (in Russian).
46. I.M. Dykman, P.M. Tomchuk. Effect of coherent light beams on free carriers in semiconductors. *Fiz. Tverd. Tela* **26**, 2729 (1984) (in Russian).
47. A.E. Levshin, A.Yu. Semchuk, P.M. Tomchuk. Superlattices formed in ferromagnetic semiconductors by coherent light beams. *Sov. Phys. Solid State* **28**, 229 (1986).
48. P.M. Tomchuk. Peculiarities of the light absorption and emission by free electrons in multivalley semiconductors. *Ukr. J. Phys.* **49**, 681 (2004).
49. V.M. Bondar, O.G. Sarbey, P.M. Tomchuk. Polarization dependence of the spontaneous radiation of hot electrons. *Fiz. Tverd. Tela* **44**, 1540 (2002) (in Russian).
50. V.M. Bondar, A.E. Levshin, P.M. Tomchuk. Polarization dependencies of light emitted by free electrons in multivalley semiconductors. *Ukr. J. Phys.* **51**, 178 (2006).
51. P.M. Tomchuk, V.M. Bondar. Polarization effects at emission and absorption of light by hot electrons in multivalley semiconductors. *Ukr. J. Phys.* **53**, 666 (2008).
52. V.M. Bondar, P.M. Tomchuk. Polarization effects in the terahertz emission by hot electrons in multivalley semiconductors. *J. Phys. Stud.* **13**, 2705 (2009).
53. P.M. Tomchuk, V.M. Bondar, O.E. Levshin. Influence of anisotropic scattering mechanisms on polarization dependences of terahertz radiation emitted by hot electrons. *Ukr. J. Phys.* **59**, 505 (2014).
54. V.M. Bondar, P.M. Tomchuk, G.A. Shepels'kii. Effect of weak magnetic field (∼300 Gs) on the intensity of terahertz emission of hot electrons in n-Ge at helium temperatures. *Ukr. J. Phys.* **55**, 1020 (2010).
55. V.M. Bondar, P.M. Tomchuk, G.A. Shepelskii. Effect of weak magnetic field on terahertz radiation of hot electrons in n-Ge. *Phys. Status Solidi B* **250**, 344 (2013).
56. B.I. Lev, T.V. Torchinskaya, P.M. Tomchuk, M.K. Sheikman. Kinetics of injection-stimulated transformation of defects in light-emitting GaAs : Si structures. *Sov. Phys. Semiconductors* **23**, 949 (1989).
57. *Best of Soviet Semiconductor Physics and Technology (1989–1990).* Edited by M. Levinshtein, M. Shur (World Scientific, 1995).
58. N.N. Grigorev, T.A. Kudykina, P.M. Tomchuk. Thermal diffusion spreading of inclusions and accumulation effect in the destruction of laser materials. *Kvant. Elektron.* **37**, 84 (1989) (in Russian).
59. N.N. Grigor'ev, T.A. Kudykina, P.M. Tomchuk. Laser-induced degradation of transparent solids. *J. Phys. D* **25**, 276 (1992).
60. P.M. Tomchuk, S.A. Nepiyko. Island films. In *Solid State Physics: Encyclopedic Dictionary, Vol. 1.* Edited by V.G. Baryakhtar *et al.* (Naukova Dumka, 1996) (in Russian).
61. P.G. Borziak, O.G. Sarbej, R.D. Fedorovich. Neue Erscheinungen in sehr dünnen Metallschichten. *Phys. Status Solidi* **8**, 55 (1965).
62. P.G. Borziak, Yu.A. Kulyupin. *Electronic Processes in Metal Island Films* (Naukova Dumka, 1980) (in Russian).
63. A. Naumovets. Electronic engineer Petro Mykhailovych Tomchuk. In: *The Life Credo is Science: To the 80th Anniversary of the Birth of Petro Mykhailovych Tomchuk.* Edited by I. Gandzha, V. Shenderovskyi (Prostir Publishing House, 2014) (in Ukrainian).
64. P. Borziak, Yu. Kulyupin, P. Tomchuk. Electron processes in discontinuous metal films. *Thin Solid Films* **30**, 47 (1975).
65. P.M. Tomchuk. *Hot Electrons in a Metal Island Film. Preprint No. 22* (Institute of Physics, Kyiv, 1987) (in Russian).
66. L.I. Andreeva, A.A. Benditskii, L.V. Viduta, A.B. Granovsky, Yu.A. Kulyupin, M.A. Makedontsev, G.I. Rukman, B.M. Stepanov, R.D. Fedorovich, M.A. Shoitov, A.I. Yuzhin. Electron emission from metal island films under the action of CO_2 laser radiation. *Fiz. Tverd. Tela* **26**, 1519 (1984) (in Russian).
67. A.A. Benditskii, L.V. Viduta, Yu.A. Kulyupin, A.P. Ostranitsa, P.M. Tomchuk, R.D. Fedorovich, V.A. Yakovlev. Interaction of laser radiation with island metal films. *Izv. Akad. Nauk SSSR Ser. Fiz.* **50**, 1634 (1986) (in Russian).
68. P.M. Tomchuk. "Hot" electrons in metal island films. *Poverkhnost'* **5**, 49 (1989) (in Russian).
69. E.D. Belotskii, P.M. Tomchuk. Hot electrons in island metallic films. *Int. J. Electron.* **69**, 173 (1990).
70. R.D. Fedorovich, A.G. Naumovets, P.M. Tomchuk. Electronic properties of island thin films caused by surface scattering of electrons. *Prog. Surf. Sci.* **42**, 189 (1993).
71. E.D. Belotskii, P.M. Tomchuk. An anomaly of electron-lattice energy exchange in small metal particles. *Ukr. J. Phys.* **34**, 1050 (1989) (in Ukrainian).
72. E.D. Belotskii, P.M. Tomchuk. Electron–lattice exchange in metal island films. *Int. J. Electron.* **69**, 169 (1990).

73. E.D. Belotskii, P.M. Tomchuk. Surface electron-phonon energy exchange in small metallic particles. *Int. J. Electron.* **73**, 955 (1992).
74. E.D. Belotskiĭ, S.P. Luk'yanets, P.M. Tomchuk. Theory of hot electrons in island metal films. *Sov. Phys. JETP* **74**, 88 (1992).
75. S.A. Gorban', S.A. Nepijko, P.M. Tomchuk. Electron–phonon interaction in small metal islands deposited on an insulating substrate. *Int. J. Electron.* **70**, 485 (1991).
76. A. Gloskovskii, D.A. Valdaitsev, M. Cinchetti, S.A. Nepijko, J. Lange, M. Aeschlimann, M. Bauer, M. Klimenkov, L.V. Viduta, P.M. Tomchuk, G. Schönhense. Electron emission from films of Ag and Au nanoparticles excited by a femtosecond pump-probe laser. *Phys. Rev. B* **77**, 195427 (2008).
77. Y. Bilotsky, N.I. Grigorchuk, P.M. Tomchuk. Hot electrons and laser optoacoustics in metal nanoparticles. *Surf. Sci.* **603**, 3267 (2009).
78. P.M. Tomchuk, N.I. Grigorchuk, D.V. Butenko. Generation of sound by metal nanoclusters in a dielectric matrix. *Ukr. J. Phys.* **55**, 440 (2010).
79. N.I. Grigorchuk, P.M. Tomchuk. Sound generation by spheroidal metallic nanoclusters embedded in transparent matrix under the action of laser pulses. *Eur. Phys. J. B* **80**, 371 (2011).
80. H. Raether. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* (Springer, 1988).
81. Y. Bilotsky, P.M. Tomchuk. Size effect in electron-lattice energy exchange in small metal particles. *Surf. Sci.* **600**, 4702 (2006).
82. Y. Bilotsky, P.M. Tomchuk. Peculiarities of electron–phonon energy exchange in metal nanoparticles and thin films. *Surf. Sci.* **602**, 383 (2008).
83. P. Tomchuk, Y. Bilotsky. New peculiarity in the temperature and size dependence of electron-lattice energy exchange in metal nanoparticles. *Int. J. Mod. Phys. B* **28**, 1450220 (2014).
84. P.M. Tomchuk, V.N. Starkov. Electron-lattice energy exchange and hot electrons in metal island films. *Ukr. J. Phys.* **65**, 979 (2020).
85. K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz. The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment. *J. Phys. Chem.* **107**, 668 (2003).
86. S.A. Maier. *Plasmonics: Fundamentals and Applications* (Springer, 2007).
87. G. Mie. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Ann. Phys.* **25**, 377 (1908).
88. P. Tomchuk. Peculiarities of optical emission and absorption in island metal films. *Int. J. Electron.* **76**, 903 (1994).
89. P.M. Tomchuk, N.I. Grigorchuk. Peculiarities of the absorption of ultrashort laser pulses by asymmetric metallic nanoparticles. *Ukr. J. Phys.* **52**, 888 (2007).
90. N.I. Grigorchuk, P.M. Tomchuk. Theory for absorption of ultrashort laser pulses by spheroidal metallic nanoparticles. *Phys. Rev. B* **80**, 155456 (2009).
91. P.M. Tomchuk, D. Butenko. Single and double ultrashort laser pulse scattering by spheroidal metallic nanoparticles. *J. Nanophotonics* **10**, 016018 (2016).
92. P.M. Tomchuk. Dependence of light scattering cross-section by metal nanoparticles on their shape. *Ukr. J. Phys.* **57**, 552 (2012).
93. P.M. Tomchuk, D.V. Butenko. The nanoparticle shape's effect on the light scattering cross-section. *Surf. Sci.* **606**, 1892 (2012).
94. P.M. Tomchuk, D. Butenko. Nonlocal effects in metallic nanoparticles: the kinetic approach outlook. *Int. J. Mod. Phys. B* **31**, 1750029 (2017).
95. P.M. Tomchuk, V.N. Starkov, D.V. Butenko. Integral equations in the general theory of light absorption and scattering. *Ukr. J. Phys.* **62**, 705 (2017).
96. P.M. Tomchuk, V.N. Starkov. Influence of shape spread in an ensemble of metal nanoparticles on their optical properties. *Ukr. J. Phys.* **63**, 204 (2018).
97. P.M. Tomchuk, V.N. Starkov. Averaged optical characteristics of an ensemble of metal nanoparticles. *Int. J. Mod. Phys. B* **33**, 1950188 (2019).
98. D.V. Butenko, P.M. Tomchuk. Influence of the magnetic dipole moment of a metal nanoellipsoid on the scattering of electromagnetic waves. *Ukr. J. Phys.* **61**, 255 (2016).
99. P.M. Tomchuk, V.N. Starkov. Magnetic absorption of metal nanoparticles. *Ukr. J. Phys.* **63**, 906 (2018).
100. V.V. Kulish, P.M. Tomchuk. Optical properties of metal nanotubes and metal nanoshells. *Surf. Sci.* **602**, 1045 (2008).
101. S.S. Rozhkov. Liquid crystals. In *Solid State Physics: Encyclopedic Dictionary, Vol. 1.* Edited by V.G. Baryakhtar *et al.* (Naukova Dumka, 1996) (in Russian).
102. B.I. Lev, O.M. Tovkach, S.B. Chernyshuk. *Liquid Crystal Colloids: Some Aspects of the Theory* (Naukova Dumka, 2018) (in Ukrainian).
103. J. Planer. Notiz über das Cholesterin. *Annal. Chemie Pharmacie* **118**, 25 (1861).
104. J. Planer. Note about cholesterol. *Condens. Matter Phys.* **13**, 37001 (2010).
105. F. Reinitzer. Beiträge zur Kenrniss des Cholesterins. *Monatsh. Chem.* **9**, 421 (1888).
106. O. Lehmann. Über fliessende Krystalle. *Z. Phys. Chem.* **4**, 462 (1889).
107. O. Lehmann. Die Struktur krystallinischer Flüssigkeiten. *Z. Phys. Chem.* **5**, 427 (1890).
108. A. Trokhymchuk. On Julius Planer's 1861 paper "Notiz über das Cholestearin" in Annalen der Chemie und Pharmacie. *Condens. Matter Phys.* **13**, 37002 (2010).
109. V.A. Shenderovskyi, A.D. Trokhymchuk, L.N. Lisetski, B.V. Kozhushko, I.A. Gvozdovskyy. Julius Planer. A pioneer in the study of liquid crystals. *J. Mol. Liq.* **267**, 560 (2018).

110. J.A. Castellano. *Liquid Gold: The Story of Liquid Crystal Displays and the Creation of an Industry* (World Scientific Publishing, 2005).
111. A.M. Donald, A.H. Windle, S. Hanna. *Liquid Crystalline Polymers* (Cambridge University Press, 2006).
112. M. Kuryk. An example of individual longevity of a person. In *The Life Credo is Science: To the 80th Anniversary of the Birth of Petro Mykhailovych Tomchuk*. Edited by I. Gandzha, V. Shenderovskyi (Prostir Publishing House, 2014) (in Ukrainian).
113. F.C. Frank. I. Liquid crystals. On the theory of liquid crystals. *Discuss. Faraday Soc.* **25**, 19 (1958).
114. C.W. Oseen. The theory of liquid crystals. *Trans. Faraday Soc.* **29**, 883 (1933).
115. O.D. Lavrentovich, V.M. Pergamenshchik. Patterns in thin liquid crystal films and the divergence ("surfacelike") elasticity. *Int. J. Mod. Phys. B* **9**, 2389 (1995).
116. E.D. Belotskii, B.I. Lev, P.M. Tomchuk. Effective mass and mobility of ions in a nematic liquid crystal. *Ukr. J. Phys.* **26**, 625 (1981) (in Russian).
117. E.D. Belotskii, B.I. Lev, P.M. Tomchuk. Effective mass of a charge carrier in nematic liquid crystals. *Mol. Christ. Liq. Cryst.* **213**, 99 (1992).
118. R. Williams. Liquid crystals in an electric field. *Nature* **199**, 273 (1963).
119. R. Williams. Domains in liquid crystals. *J. Chem. Phys.* **39**, 384 (1963).
120. M. Lowe, J.P. Gollub, T.C. Lubensky. Commensurate and incommensurate structures in a nonequilibrium system. *Phys. Rev. Lett.* **51**, 786 (1983).
121. E.D. Belotskii, N.G. Migranov, P.M. Tomchuk. Formation of two-dimentional incommensurate structures in the system of Williams domains. *Liq. Cryst.* **3**, 1327 (1988).
122. E.D. Belotskii, N.G. Migranov, P.M. Tomchuk. Construction of generalized thermodynamic potentials using Lie algebra methods. *Teor. Mat. Fiz.* **81**, 239 (1989) (in Russian).
123. Ye.D. Bilotsky, P.M. Tomchuk. Theory of high-frequency dissipative structures in nematic liquid crystas. *Ukr. J. Phys.* **37**, 860 (1992) (in Ukrainian).
124. B.I. Lev, V.G. Nazarenko, A.B. Nych, P.M. Tomchuk. Deformation and instability of nematic drops in an external electric field. *JETP Lett.* **71**, 262 (2000).
125. B.I. Lev, V.G. Nazarenko, A.B. Nych, D. Schur, P.M. Tomchuk, J. Yamamoto, H. Yokoyama. Deformation of liquid crystal droplets under the action of an external ac electric field. *Phys. Rev. E.* **64**, 021706 (2001).
126. B.I. Lev, K.M. Aoki, P.M. Tomchuk, H. Yokoyama. Structure formation of colloids in nematic liquid crystals. *Condens. Matter Phys.* **6**, 169 (2003).
127. B.I. Lev, H. Yokoyama, S.B. Chernyshuk, P.M. Tomchuk. Symmetry breaking, elastic interaction and structures in nematic colloids. *Mol. Cryst. Liq. Cryst.* **409**, 99 (2004).
128. J.D. Jackson. *Classical Electrodynamics, 3rd edition* (John Wiley ans Sons, 1998).
129. L. Glasser. Proton conduction and injection in solids. *Chem. Rev.* **75**, 21 (1975).
130. S.F. Fischer, G.L. Hofacker, M.A. Ratner. Spectral behavior of hydrogen-bonded systems: Quasiparticle model. *J. Chem. Phys.* **52**, 1934 (1970).
131. H.J. Morowitz. Proton semiconductors and energy transduction in biological systems. *Am. J. Physiol.* **235**, R99 (1978).
132. J.F. Nagle, S. Tristman-Nagle. Hydrogen bonded chain mechanism for proton conduction and proton pumping. *J. Membrane Biol.* **74,** 1 (1983).
133. L. Onsager. Thermodynamics and some molecular aspects of biology. In: *The Neurosciences*. Edited by F.O. Schmitt (Rockefeller University Press, 1967), p. 75.
134. L. Onsager. Thermodynamics and some molecular aspects of biology. In: *The Collected Works of Lars Onsager: With Commentary*. Edited by P.C. Hemmer *et al.* (World Scientific, 1996), p. 899.
135. S.I. Pekar. Local quantum states of an electron in an ideal ionic crystal. *Zh. Èksp. Teor. Fiz.* **16**, 341 (1946) (in Russian).
136. V.L. Vinetsky. Polaron. In *Solid State Physics: Encyclopedic Diction*ary, Vol. 2. Edited by V.G. Baryakhtar *et al.* (Naukova Dumka, 1998) (in Russian).
137. T. Holstein. Studies of polaron motion. Part II. The "small" polaron. *Ann. Phys.* **8,** 343 (1959).
138. A.S. Davydov, N.I. Kislukha. Solitons in one-dimensional molecular chains. *Phys. Status Solidi B* **75,** 735 (1976).
139. V.V. Krasnogolovets, P.M. Tomchuk. The anharmonicity influence on the proton conductivity of an hydrogen-bonded chain. *Phys. Status Solidi B* **131,** 865 (1985).
140. V.V. Krasnogolovets, P.M. Tomchuk. The Coulomb correlations and the electric field local heterogeneities on the proton conductivity of hydrogen bonded chains. *Phys. Status Solidi B* **130**, 807 (1985).
141. V.V. Krasnogolovets, P.M. Tomchuk. The influence of external effects on the proton conductivity of an hydrogen-bonded chain. *Phys. Status Solidi B* **138**, 727 (1986).
142. V.V. Krasnogolovets, N.A. Protsenko, P.M. Tomchuk, V.S. Guriev. The mechanism of bacteriorhodopsin functioning. I. The light-induced proton throw-over by retinal. *Int. J. Quantum Chem.* **33**, 327 (1988).
143. V.V. Krasnogolovets, N.A. Protsenko, P.M. Tomchuk. The mechanism of bacteriorhodopsin functioning. II. Ejection and injection of proton. *Int. J. Quantum Chem.* **33**, 349 (1988).
144. V.V. Krasnogholovets, V.B. Taranenko, P.M. Tomchuk, M.A. Protsenko. Molecular mechanism of light-induced proton transport in bacteriorhodopsin. *J. Mol. Struct.* **355**, 219 (1995).
145. R. Müller, H. Pagnia. Water-influenced switching in discontinuous Au film diodes. *Mater. Lett.* **2**, 283 (1984).

146. V.V. Krasnogolovets, P.M. Tomchuk. On the theory of the phenomenon of water-dependent current switching in continuous metal films. *Ukr. J. Phys.* **36**, 1392 (1991) (in Russian).

147. P.M. Tomchuk, S.P. Luk'yanets. Coherent tunnel repolarization of a hydrogen bonded chain. *Condens. Matter Phys.* **14**, 203 (1998).

148. P.M. Tomchuk, S.P. Luk'yanets. Coherent tunnel repolarization of a short hydrogen-bonded chain. *J. Mol. Struct.* **513**, 35 (1999).

149. P.M. Tomchuk, S.P. Lukyanets. Coherent proton tunneling in a short hydrogen bonded chain. *Phys. Status Solidi B* **218**, 291 (2000).

150. A. Braun, Q. Chen. Experimental neutron scattering evidence for proton polaron in hydrated metal oxide proton conductors. *Nat. Commun.* **8**, 15830 (2017).

151. V. Mohaček-Grošev, J. Grdadolnik, D. Hadži. Evidence of polaron excitations in low temperature Raman spectra of oxalic acid dihydrate. *J. Phys. Chem. A* **120**, 2789 (2016).

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НАУКОВИЙ СПАДОК ПЕТРА ТОМЧУКА В ГАЛУЗІ ТЕОРЕТИЧНОЇ ФІЗИКИ І ФІЗИКИ КОНДЕНСОВАНОГО СТАНУ

У роботі розглянуто основні наукові результати видатного українського фізика-теоретика Петра Михайловича Томчука (2.01.1934–7.10.2024). Петро Томчук працював у багатьох напрямах фізики конденсованого стану, таких як фізика напівпровідників, фізика металів, фізика м'якої речовини, нанофізика. У цій оглядовій статті про науковий спадок Петра Томчука головну увагу приділено його дослідженням кінетичних і оптичних явищ у напівпровідниках, транспорту носіїв у напівпровідникових структурах, електрон-ґраткового енергообміну і гарячих електронів у напівпровідниках та острівцевих металевих плівках, оптичних властивостей металевих наночастинок і їхніх ансамблів, рідинних кристалів і колоїдів, а також молекулярних структур з водневими зв'язками.

Ключові слова: теоретична фізика, фізика конденсованого стану, фізика твердого тіла, нанофізика, напівпровідники, гарячі електрони, рідинні кристали, водневі зв'язки, полярон, протонна провідність.