Національна академія наук України

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СИСТЕМ

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ENERGY SPECTRUM AND THERMODYNAMICS OF
ONE-DIMENSIONAL PROTON CONDUCTOR

ЛЬВІВ

Енергетичний спектр і термодинаміка одномірного протонного провідника

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Анотація. В роботі досліджується енергетичний спектр і термодинаміка протонної підсистеми одномірного молекулярного ланцюжка з водневими зв'язками. За базис для опису системи взято орієнтаційно-тунельну модель протонного транспорту, що базується на механізмі Гроттхуса. Для розрахунку енергетичного спектру використовується метод кластерних розкладів в теорії функцій Гріна. Розрахований в наближенні незалежних підзон спектр складається з восьми енергетичних зон, краї яких є функціями протонної концентрації. Вивчення поведінки хімічного потенціалу показало, що існують області, де хімічний потенціал є спадною функцією концентрації, що вказує на можливість розшарування в системі. Також розглядається вплив додаткового асиметризуючого поля.

Energy spectrum and thermodynamics of one-dimensional proton conductor

I.V.Stasyuk, O.A. Vorobyov

Abstract. Energy spectrum and thermodynamics of the proton subsystem of the one-dimensional hydrogen-bonded molecular chain is investigated. The consideration is based on orientational-tunneling model which includes two types of proton transfer according to Grotthuss mechanism. The method of cluster expansions in the theory of Greens' functions is used to calculate the energy spectrum. In the independent subband approximation the spectrum consists of eight energy bands which edges are functions of proton concentration. The investigation of chemical potential behaviour shows that there exist regions where chemical potential is the decreasing function of proton concentration which points out to the possibility of separation. The influence of additional asymmetry field is also investigated.

1. Introduction

Due to the widening of experimental investigations of the ion (proton) conductivity phenomena in crystalline and molecular systems and the discovery of new materials (superionic crystals with hydrogen bonds, systems with crystallization water, quasi-one-dimensional proton conductors), the problem of search and investigations of the physical mechanism of the proton transport, analysis of features of thermodynamics and energy spectrum of such objects becomes actual. Along with the traditional concepts of formation and motion of ionic and orientational defects there exist some approaches explicitly taking into account the dynamics of proton jumps (which can have two-stage nature (Grotthuss mechanism)), as well as the short-range and long-range proton-proton interactions. These interactions can lead to the proton ordering and corresponding phase transitions. At the same time the strong short-range correlations can significantly rebuild the proton energy spectrum when the values of parameters of such interactions exceed the proton transfer energies. This fact has to be taken into account when investigating the mechanism of formation of proton transport activation energy in the above-mentioned systems.

The aim of the present work is to analyze the influence of short-range interactions on the proton energy spectrum in the one-dimensional case, when one considers molecular chain with the ionic groups consequtively connected by the hydrogen bonds. We take into account the possibility of the dynamical proton jumps which can be directly included in the Hamiltonian of the system. We use the basic approach where the strong short-range interactions are taken into account exactly in the zero approximation. The calculations of proton spectrum at different average proton concentrations are performed and statistics of the proton distribution is also investigated. The influence of proton correlations on the activation energy of proton transport is analyzed.

2. The model

Investigation of the energy spectrum and thermodynamics of the proton subsystem of the molecular hydrogen-bonded chain is based on the orientational-tunneling model. This model was introduced in [1] (see also [2]) to describe molecular complexes with hydrogen bonds. Later it was used for description of the proton transport and calculation of conductivity coefficient in the $Me_3H(XO_4)_3$ (Me=Cs,Rb,NH$_4$; X=S,Se) group of superionic crystals [3,4]. It includes two types of transfer according to Grotthuss mechanism: tunneling on the bond Ω_0 and reorientational hopping Ω_R. Short-range interactions caused by the differences between the energies of the proton configurations near ionic groups and additional interactions, which determine the energies of formation of D- an L-defects, are taken into account.
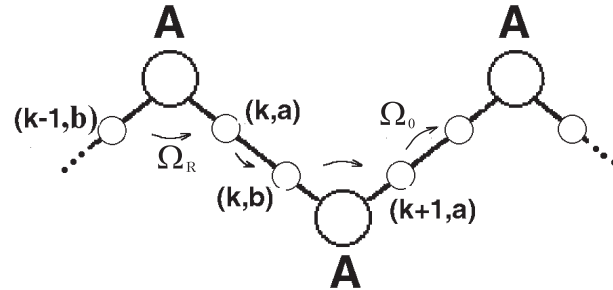

Figure 1. Proton conductor model. Large circles correspond to the ion groups (A), small ones to the possible positions of protons.

We consider one-dimensional proton conductor which consists of ionic groups connected by hydrogen bonds (Fig. 1). Two equilibrium positions (i, a) and (i, b) on each bond (i - is a consequtive number of the bond) are taken into account. The Hamiltonian of such system in the second quantization representation has the following form:

$$H = H_c + H_t + H_d - \mu N, \tag{1}$$

where

$$\hat{H}_c = \sum_i [\varepsilon(1 - n_{ib})n_{i+1,a} + \varepsilon n_{ib}(1 - n_{i+1,a}) + wn_{ib}n_{i+1,a} +$$
$$+ \ w'(1 - n_{ib})(1 - n_{i+1,a})]$$

$$\hat{H}_t = \sum_i \left[\Omega_0(c_{ia}^+ c_{ib} + c_{ib}^+ c_{ia}) + \Omega_R(c_{ib}^+ c_{i+1,a} + c_{i+1,a}^+ c_{ib})\right]$$

$$\hat{H}_d = \sum_i [Un_{ia}n_{ib} + V(1 - n_{ia})(1 - n_{ib})] \tag{2}$$

$$\hat{N} = \sum_i (n_{ia} + n_{ib})$$

Here $n_{i\alpha}(\alpha = a, b)$ is the occupation number in α position; U and V are energies of formation of D- (two protons on the bond) and L-
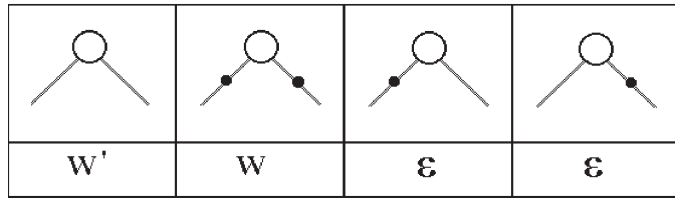
Figure 2. Energies of proton configurations.

(a broken bond) defects correspondingly; w, ε, w' are the energies of configurations with two, one or no protons near the ionic group (Fig. 2).

The model (1) is the one of the fermionic lattice models with transfer. Its spectrum has a band character and its structure is determined by the ratio of the effective transfer parameter Ω_{ef} to the energy of short range interaction (U_{ef}). When $\Omega_{ef} \gg U_{ef}$ interaction between protons can be taken into account in the framework of mean field approximation (MFA), and it only shifts the proton energy band (such approach was utilized in [4] when obtaining dispersion laws $E(\vec{k})$ in proton bands, which describe the motion of protons in quasi-two-dimensional layers of hydrogen bonds in $(NH_4)_3H(SeO_4)_2$). Otherwise (when $\Omega_{ef} \ll U_{ef}$) correlation leads to the additional splitting in spectra. These results are well-known for Hubbard model and the similar ones [5] . Corresponding theoretical investigation cannot be performed in the frames of MFA, it has to be based on the allowance for the short-range interactions in the zero approximation. The cluster approximation and its generalization are used for the purpose in the present work.

We utilize the perturbation theory to obtain proton energy spectrum, considering the operator

$$\hat{H}_0 = \hat{H}_c + \hat{H}_d - \mu\hat{N} \tag{3}$$

as the zero-order Hamiltonian and making the expansion in terms of $\hat{H}_t$. Calculation of the energy spectrum at different average concentration of the protons are performed using the Green's function method.

3. Perturbation theory (expansion in terms of H_t)

The proton Green's function

$$G_{i\alpha,j\beta}(\tau - \tau') = -\langle T_\tau \tilde{c}_{i\alpha}(\tau)\tilde{c}_{j\beta}^+(\tau')\rangle, \tag{4}$$

is constructed of the proton creation and annihilation operators given in the Heisenberg representation ($0 \le \tau, \tau' \le \beta = \frac{1}{kT}$). Imaginary part of the Fourier-component of the function (4) characterizes the density of the proton states

$$g_{i\alpha}(E) = -\frac{2}{\pi}Im\, G_{i\alpha,i\alpha}(i\omega_n)|_{i\omega_n \to E+i\varepsilon}. \tag{5}$$

Let's utilize thermodynamical perturbation theory [6], treating the part H_t of the Hamiltonian as a perturbation. In the interaction representation

$$G_{i\alpha,j\beta}(\tau - \tau') = -\langle T_\tau c_{i\alpha}(\tau)c_{j\beta}^+(\tau')\sigma(\beta)\rangle_0^c, \tag{6}$$

$$\sigma(\beta) = T_\tau \exp\left\{-\int_0^\beta H_t(\tau)d\tau\right\}, \tag{7}$$

where the average values are calculated with the help of the statistical distribution with Hamiltonian H_0. Expansion in terms of H_t leads to series

$$G_{i\alpha,j\beta}(\tau - \tau') = -\langle T_\tau c_{i\alpha}(\tau)c_{j\beta}^+(\tau')\rangle_0 +$$

$$+ \sum_{\substack{k\,l\\\gamma\delta}} t_{k\gamma,l\delta}\langle T_\tau c_{i\alpha}(\tau)c_{j\beta}^+(\tau')\int_0^\beta d\tau_1 c_{k\gamma}^+(\tau_1)c_{l\delta}(\tau_1)\rangle_0^c -$$

$$- \frac{1}{2}\sum_{\substack{klm\\n}}\sum_{\gamma\delta\nu\mu} t_{k\gamma,l\delta}t_{m\nu,n\mu}\langle T_\tau c_{i\alpha}(\tau)c_{j\beta}^+(\tau')\int_0^\beta d\tau_1 c_{\nu\gamma}^+(\tau_1)c_{l\delta}(\tau_1) \cdot$$

$$\cdot \int_0^\beta d\tau_2 c_{m\nu}^+(\tau_2)c_{n\mu}(\tau_2)\rangle_0^c + \ldots \tag{8}$$

where we introduced the transfer matrix

$$t_{ia,ib} = \Omega_0; \qquad t_{ib,i+1a} = \Omega_R. \tag{9}$$

Since the Hamiltonian H_0 includes the terms which describe interaction between protons, application of the Wick's theorem in its usual form for calculation of the average values of products of Fermi operators is impossible. To avoid additional expansion in terms of interaction parameters, we use the method similar to the one used in [7] for the Hubbard type systems, introducing the irreducible many-particle Green's

functions in the following way. Let us define the single particle proton Green's function as

$$-\langle T_\tau c_{i\alpha}(\tau) c_{j\beta}^+(\tau')\rangle_0 = g_{i\alpha,j\beta}^0(\tau-\tau') \equiv \delta_{ij}\delta_{\alpha\beta} g_\alpha^0(\tau-\tau') \qquad (10)$$

or in a shorthand notation:

$$-\langle T c_1 c_2^+\rangle_0 = g_{12}^0;$$

thus

$$
\begin{aligned}
\langle T c_1 c_2^+ c_3^+ c_4\rangle_0^c &= -g_{12}^0 g_{43}^0 + g_{13}^0 g_{42}^0 - \Gamma_{12,34}^{(2)} \\
-\langle T c_1 c_2^+ c_3^+ c_4 c_5^+ c_6\rangle_0^c &= \\
&= -g_{12}^0 g_{63}^0 g_{45}^0 - g_{13}^0 g_{62}^0 g_{45}^0 + \Gamma_{42,56}^{(2)} g_{13}^0 + ... + \Gamma_{12,34,56}^{(3)} (11)
\end{aligned}
$$

where

$$
\begin{aligned}
\Gamma_{i\alpha,j\beta;k\gamma,l\delta}^{(2)} &= -\langle T_\tau a_{i\alpha}(\tau) a_{j\beta}^+(\tau') a_{k\gamma}^+(\tau_1) a_{l\delta}(\tau_1)\rangle_0^{ir} \\
\Gamma_{i\alpha,j\beta,k\gamma,l\delta;m\nu,n\mu}^{(3)} &= \\
&= -\langle T_\tau a_{i\alpha}(\tau) a_{j\beta}^+(\tau') a_{k\gamma}^+(\tau_1) a_{l\delta}(\tau_1) a_{m\nu}^+(\tau_2) a_{n\mu}(\tau_2)\rangle_0^{ir}. \quad (12)
\end{aligned}
$$

are the irreducible parts.

The series for the function G obtained by this procedure can be formally presented as the infinite sum

$$G = \Sigma + \Sigma t\Sigma + \Sigma t\Sigma t\Sigma + ... \qquad (13)$$

This corresponds to the Larkin equation

$$G = \Sigma + \Sigma t G, \qquad (14)$$

where Σ is the irreduciable self-energy part.

Contributions to Σ can be presented as a cumulant expansion:

$$
\begin{aligned}
\Sigma_{i\alpha,j\beta}(\tau-\tau') &= g_{i\alpha,j\beta}^0(\tau-\tau') - \int_0^\beta d\tau_1 \sum_{k\gamma,l\delta} \tilde{t}_{k\gamma,l\delta} \cdot \\
&\quad \cdot \Gamma_{i\alpha,j\beta,k\gamma l\delta}^{(2)}(\tau\tau';\tau_1\tau_1) + ... , \qquad (15)
\end{aligned}
$$

where

$$\tilde{t} = t + tg^0 t + tg^0 tg^0 t + ... \qquad (16)$$

Let us restrict ourselves to the simplest approximation for Σ, taking $\Sigma = g^0$. This corresponds to the approximation, where the scattering processes are not taken into account when calculating energy spectrum as it can be seen from the farther consideration. This approach is analogous to the well-known Hubbard-I approximation for the strongly correlated electron systems [8].

Equation $G = g^0 + g^0 tG$ after Fourier transformation takes the form

$$G_{\alpha\beta}(k) = g^0\delta_{\alpha\beta} + \sum_\gamma g^0 t_{\alpha\gamma}(k) G_{\gamma\beta}(k), \qquad (17)$$

where

$$t_{\alpha\gamma}(k) = \sum_{i-j} t_{i\alpha,j\gamma} e^{ik(R_i-R_j)} \qquad (18)$$

is the Fourier component of the transfer matrix. Summation over the nearest proton positions leads to the following result

$$
\begin{aligned}
t_{ab}(k) &= \Omega_0 e^{-ik\delta} + \Omega_R e^{ik\Delta} \\
t_{ba}(k) &= \Omega_0 e^{ik\delta} + \Omega_R e^{-ik\Delta} \\
t_{aa}(k) &= t_{bb}(k) = 0
\end{aligned}
\qquad (19)
$$

(δ is the distance (along the chain) between the equilibrium positions of the proton on the bond; Δ - the distance that corresponds of the Ω_R transfer).

One can obtain the expression for the full Green's function solving the equation (17)

$$G_{aa}(k) = \frac{g_a^0}{1 - (g_a^0)^2 |t_{ab}(k)|^2}, \qquad (20)$$

where

$$|t_{ab}(k)|^2 = \Omega_0^2 + \Omega_R^2 + 2\Omega_0\Omega_R \cos ka, \qquad (21)$$

$a = \delta + \Delta$ is the period of the chain structure.

The band energy spectrum of protons can be obtained from the expression (20), if the zero-order function g^0 is known, by substituting $i\omega_n \to E$.

4. The zero-order Green's function

The Green's function g^0 is the one-site function and, as a consequence of the Hamiltonian additivity, is determined by its part related to the

cluster which includes the given site (position) and two nearest neighbouring positions (such is the cluster $[(i-1,b),(ia),(ib)]$ for the function g_{ia}^0). The energy of proton on the central site of the cluster depends on the occupation of the extreme positions. There are four possible configurations:

$$
\begin{aligned}
\alpha &= 1: & n_{i-1,b} &= 0, & n_{ib} &= 0 \\
\alpha &= 2: & n_{i-1,b} &= 0, & n_{ib} &= 1 \\
\alpha &= 3: & n_{i-1,b} &= 1, & n_{ib} &= 0 \\
\alpha &= 4: & n_{i-1,b} &= 1, & n_{ib} &= 1.
\end{aligned}
\tag{22}
$$

Corresponding transition energies are:

$$
\begin{aligned}
\varepsilon_1 &= \varepsilon - w' - V; & \varepsilon_2 &= \varepsilon - w' + U \\
\varepsilon_3 &= -\varepsilon + w - V; & \varepsilon_4 &= -\varepsilon + w + U.
\end{aligned}
\tag{23}
$$

After performing the standard calculations (for example using the method of equations of motion) we obtain

$$
g_a^0 = \sum_{\alpha=1}^{4} \frac{C_\alpha}{E - \varepsilon_\alpha + \mu}
\tag{24}
$$

where

$$
\begin{aligned}
C_1 &= \langle (1 - n_{i-1,b})(1 - n_{ib}) \rangle; & C_2 &= \langle (1 - n_{i-1,b}) n_{ib} \rangle \\
C_3 &= \langle n_{i-1,b}(1 - n_{ib}) \rangle; & C_4 &= \langle n_{i-1,b} n_{ib} \rangle
\end{aligned}
\tag{25}
$$

are statistical weights of the corresponding transitions.

There are two ways to calculate the correlation functions C_α. Exact results can be obtained using the transfer-matrix method, but first we shall see what can be obtained in the simple approximation which neglects the correlations between the next nearest neighbours (the mean field approximation):

$$
\langle n_{i-1,b} n_{ib} \rangle = \langle n_{i-1,b} \rangle \langle n_{ib} \rangle = n^2/4
\tag{26}
$$

Here we introduced a notation for the mean number of protons on the band

$$
n = \sum_\alpha \langle n_{i\alpha} \rangle; \quad \langle n_{ia} \rangle = \langle n_{ib} \rangle = n/2.
\tag{27}
$$

In this case

$$
\begin{aligned}
C_1 &= 1 - n + n^2/4; & C_2 &= n/2 - n^2/4 \\
C_3 &= n/2 - n^2/4; & C_4 &= n^2/4,
\end{aligned}
\tag{28}
$$

and C_α are temperature independent constants at a given concentration of protons.

Transfer-matrix method for the infinite chain leads to the following expressions (see Appendix):

$$
\begin{aligned}
C_1 &= \frac{(2-n)^2}{4} + \frac{n(2-n)}{4} \cdot \frac{\lambda_2}{\lambda_1}; \quad C_2 = C_3 = \frac{n(2-n)}{4}\left(1 - \frac{\lambda_2}{\lambda_1}\right); \\
C_4 &= \frac{n^2}{4} + \frac{n(2-n)}{4} \cdot \frac{\lambda_2}{\lambda_1},
\end{aligned}
\tag{29}
$$

where

$$
\lambda_{1,2} = \frac{a+b}{2} \pm \sqrt{\left(\frac{a-b}{2}\right)^2 + cd}
\tag{30}
$$

$$
\begin{aligned}
a &= e^{\frac{\beta}{4}(2\varepsilon - 3w + w' - 3U + V) + \beta\mu} + e^{\frac{\beta}{4}(U + V + J)} \\
b &= e^{\frac{\beta}{4}(2\varepsilon + w - 3w' + U - 3V) - \beta\mu} + e^{\frac{\beta}{4}(U + V + J)} \\
c &= 2\mathrm{ch}\left[\frac{\beta}{2}(\varepsilon - w' + U - \mu)\right] \\
d &= 2\mathrm{ch}\left[\frac{\beta}{2}(w - \varepsilon - V - \mu)\right]
\end{aligned}
\tag{31}
$$

and $J = w + w' - 2\varepsilon$.

Parameters C_α are temperature dependent in this case and are also functions of chemical potential μ. At a zero transfer μ and n are connected by the following equation

$$
\langle n_{ia} \rangle = \frac{n}{2} = \left[1 - \frac{(\lambda_1 - a)(\lambda_2 - a)}{cd}\right]^{-1}
\tag{32}
$$

Parameters C_α as a functions of proton concentration can be obtained by excluding the chemical potential from (32). At non-zero temperatures this can be done numerically and at $T = 0$ one can obtain the analytical expressions

$$
C_1 = \frac{2 - 3n + \frac{3}{2}n^2}{2 - n}; \quad C_2 = C_3 = \frac{n(1-n)}{2-n}; \quad C_4 = \frac{n^2}{2(2-n)}
\tag{33}
$$

when $0 \leq n \leq 1$ and

$$
C_1 = \frac{2 - 2n + \frac{1}{2}n^2}{n}; C_2 = C_3 = \frac{3n - n^2 - 2}{n}; C_4 = \frac{2 - 3n + \frac{3}{2}n^2}{n}
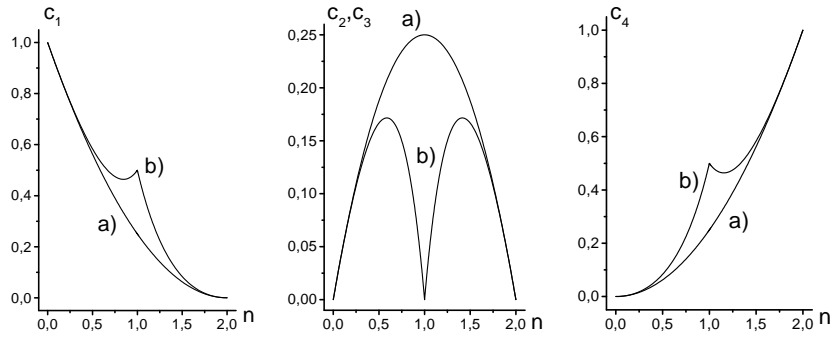\tag{34}
$$

Figure 3. Dependences of correlation functions on proton concentration: a) - in the mean field approximation, b) - calculated via transfer matrix method.

when $1 \leq n \leq 2$.

The plots of the functions (33), (34) are given in Fig. 3. There are also shown dependences of $C_\alpha(n)$ obtained in the mean field approximation (28). The difference between exact and approximated dependences is the most essential at intermediate occupation of proton positions (when the number of protons per bond is close to unity).

5. Band proton spectrum

Four poles of the one site Green's function (24) according to (20) lead to the eight poles of the full Green's function and thus to the formation of eight energy bands. It's hard to obtain this spectrum analytically, but in the case of $\Omega_0, \Omega_R \ll w, w', U, V$ we can utilize the independent subband approximation:

$$
\begin{aligned}
G_{aa}(k) &= \frac{1}{2}\left(\frac{g_a^0}{1 - g_a^0 |t_{ab}(k)|} + \frac{g_a^0}{1 + g_a^0 |t_{ab}(k)|}\right) \approx \\
&\approx \frac{1}{2}\sum_{\alpha=1}^{4}\left(\frac{C_\alpha}{E - E_\alpha^+(k)} + \frac{C_\alpha}{E - E_\alpha^-(k)}\right),
\end{aligned} \tag{35}
$$

where

$$
E_\alpha^\pm(k) = \varepsilon_\alpha - \mu \pm C_\alpha[\Omega_0^2 + \Omega_R^2 + 2\Omega_0\Omega_R \cos ka]^{1/2}. \tag{36}
$$

Bands $E_\alpha^\pm(k)$ are grouped into four pairs; the distance between the bands in the pair $\Delta E_\alpha = 2C_\alpha|\Omega_R - \Omega_0|$ is small compared with the distance between the pairs (Fig. 4) that is of the same order as the transition energies ε_α in cluster ($\varepsilon_3 - \varepsilon_1 = \varepsilon_4 - \varepsilon_2 = J$; $\varepsilon_2 - \varepsilon_1 = \varepsilon_4 - \varepsilon_3 = U + V$; $\varepsilon_4 - \varepsilon_4 = U + V + J$; $\varepsilon_2 - \varepsilon_3 = U + V - J$). The width of the subband in the pair is $2C_\alpha\Omega_0$ when $\Omega_R > \Omega_0$ or $2C_\alpha\Omega_R$ when $\Omega_0 > \Omega_R$.

The position of the chemical potential in relation to the obtained band scheme can be found using equation (27). Calculation of the average value $\langle n_{ia}\rangle$, with the function $G_{aa}(k)$ and use the spectral theorem, lead to the result

$$
n = \sum_{\alpha=1}^{4}\frac{1}{N}\sum_k\left[\frac{\alpha}{e^{\beta E_\alpha^+(k)} + 1} + \frac{\alpha}{e^{\beta E_\alpha^-(k)} + 1}\right] \tag{37}
$$

This relation is the equation for μ.

The solution of (37) can be found analytically at $T = 0$. In this case

$$
\begin{aligned}
&\frac{1}{N}\sum_k \frac{1}{e^{\beta(\varepsilon_\alpha - \mu \pm_\alpha |t_{ab}(k)|)} + 1} = \\
&\frac{1}{2} \pm \frac{1}{2} \mp \frac{1}{\pi}\arccos\left[\left(\frac{(\varepsilon_\alpha - \mu)^2}{\frac{2}{\alpha}} - \Omega_R^2 - \Omega_0^2\right)\frac{1}{2\Omega_0\Omega_R}\right] \tag{38}
\end{aligned}
$$

There exists a possibility to determine the behaviour of the chemical potential as a function of n in each band. Obtained results are presented in Fig. 4 (here $J > U + V > 0$. All the farther numerical calculations were performed at $U = 3280 cm^{-1}, V = 3130 cm^{-1}, w - \varepsilon = 10000 cm^{-1}, J = w + w' - 2\varepsilon = 9400 cm^{-1}$ [1]). One can see that the chemical potential as a function of n jumps three times: at $n = 1 - \frac{1}{\sqrt{5}}$ between the $E_4^\pm$ subbands, at $n = 1$ - between E_4^+ and E_1^- subbsnds and at $n = 1 + \frac{1}{\sqrt{5}}$ - between $E_1^\pm$ subbands. At these critical concentrations the lower subbands $E_\alpha^\pm(k)$) are completely occupied and higher ones are empty at $T = 0$. This situation is similar to the one in the dielectric or semi-conductor. Thus proton conductivity is in this case of a semi-conductor type with activation energies $E_a = 2(1 - 1/\sqrt{5})(\Omega_R - \Omega_0)$ for $n^* = 1 \pm \frac{1}{\sqrt{5}}$ and $E_a = U + V + J - (\Omega_R + \Omega_0)$ for $n^* = 1$. The charge carriers in the case $n^* = 1$ are proton "couples" and "holes" − D- and L-defects. At intermediate values of n the band that holds the chemical potential is partially occupied; conductivity in this case is similar to the metallic one (we have to admit here that interaction between protons and phonons can lead to the formation of proton polarons; their contribution to conductivity has the activation character [3] even in quasi-metallic state).

The next important feature of the obtained dependences of μ on n is the existence of the regions where $d\mu/dn < 0$. This feature takes place
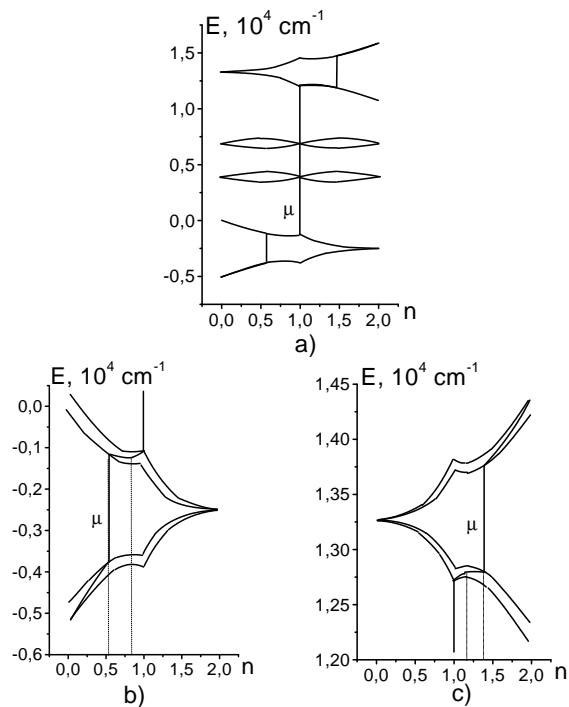
Figure 4. Energy spectrum and chemical potential of the system as a function of n: a) the whole spectrum; b) two lowest subbands; c) two highest subbands. $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 2500\ cm^{-1}$, T=0 K

at the certain proton concentrations, and when the transfer parameters considerably differ one from another ($\Omega_0/\Omega_R \ll 1$ or $\Omega_R/\Omega_0 \ll 1$) that corresponds to the small widths of the bands. This fact points out to the instability of the state with the uniform distribution of protons. It can result in the some kind of separation in the system.

At non-zero temperatures the $\mu(n)$ dependence becomes smooth (Fig. 5). With the increasing of T the region with $d\mu/dn < 0$ quickly disappears and uniform distribution of protons becomes thermodynamically stable. Fig. 6 also shows the function $\mu(n)$ in the case when correlation functions C_α are calculated approximately (28). In this case the band spectrum also includes four pairs of subbands. The character of their dependence on n is different, especially in the vicinity of value $n = 1$. In this case the chemical potential makes more jumps, but not all of them, as it was seen from the former analysis, are left when one goes to the
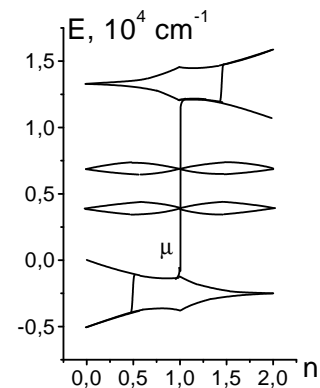

Figure 5. Energy spectrum and chemical potential of the system as a function of n for non zero temperature. Correlation functions are obtained via the transfer matrix method. $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 2500\ cm^{-1}$, T=100 K

more accurate solution.

We have to emphasize here, that application of the mean field approximation to the initial Hamiltonian leads to completely different results for the proton energy spectrum. There are only two subbands in this case

$$E^\pm(\vec{k}) = \tilde{\varepsilon} - \mu \pm [\Omega_0^2 + \Omega_R^2 + 2\Omega_0\Omega_R \cos ka]^{1/2},$$
$$\tilde{\varepsilon} = \varepsilon - w' - V + \frac{n}{2}(J + U + V). \tag{39}$$

Their positions are shifted depending on n due to the influence of the mean field. Splitting in the spectra can only appear in the case of proton ordering [4]. Mechanism of formation of the activation energy of conductivity differs from the one, that takes place in the case of correlation splitting of the bands.

6. Additional asymmetry field

As it is shown by the recent experimental investigations, the transition to the superionic phase in many superionic conductors is accompanied with the so-called percursor effect, when conductivity starts to increase considerably at the temperatures lower than the temperature of superionic phase transition [9–11]. It means that in this temperature range (which can be about 30-40 K) a large number of protons are distributed
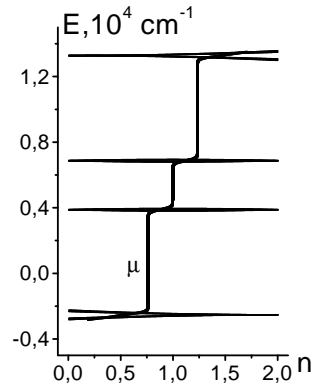
Figure 6. Energy spectrum and chemical potential of the system as a function of n. Correlation functions are obtained in the mean field approximation. $\Omega_0 = 100 \; cm^{-1}$, $\Omega_R = 250 \; cm^{-1}$, T=100 K

randomly with some probability among the possible positions, like in superionic phase.

One of those crystals is $CsDSO_4$ [12,13]. When this crystal is in ordered state, hydrogen bonds form the chain structures SO_4-D-SO_4-D-SO_4-... Inside the chain deuterons occupy only a (or b) positions, which is the consequence of existing of the internal ordering field. The mentioned precursor effect taking place before the superionic phase transitions is connected with the partial rupture of the bonds (A-positions) and occupation of the new B-positions, disposed in transverse directions between SO_4 groups, by the deuterons. Here we will consider this effect on the basis of one-dimensional model described above.

Let's start with the initial Hamiltonian (1) with the additional term

$$\hat{H}_a = \sum_i h(n_{ia} - n_{ib}) \tag{40}$$

which describes the influence of the ordering asymmetry field. Applying the scheme described in the previous sections we can obtain the energy spectrum in this case. First we have to calculate the zero approximation Green's function for both a and b sublattices:

$$g_\beta^0 = \sum_{\alpha=1}^4 \frac{C_{\alpha,\beta}}{E - \varepsilon_{\alpha,\beta} + \mu}$$
$$\alpha = 1, 2, 3, 4 \quad ; \quad \beta = a, b \tag{41}$$

where corresponding energies are:

$$\begin{aligned} \varepsilon_{1,a} &= \varepsilon - w' - V + h; \quad \varepsilon_{2,a} = \varepsilon - w' + U + h \\ \varepsilon_{3,a} &= -\varepsilon + w - V + h; \quad \varepsilon_{4,a} = -\varepsilon + w + U + h. \end{aligned} \tag{42}$$

for a sublattice and

$$\begin{aligned} \varepsilon_{1,b} &= \varepsilon - w' - V - h; \quad \varepsilon_{2,b} = \varepsilon - w' + U - h \\ \varepsilon_{3,b} &= -\varepsilon + w - V - h; \quad \varepsilon_{4,b} = -\varepsilon + w + U - h. \end{aligned} \tag{43}$$

for b sublattice. As the nearest neighbours for site a are sites b, the correlation functions for g_a^0 are calculated on b sublattice:

$$\begin{aligned} C_{1,a} &= \langle (1 - n_{i-1,b})(1 - n_{ib}) \rangle; \quad C_{2,a} = \langle (1 - n_{i-1,b})n_{ib} \rangle \\ C_{3,a} &= \langle n_{i-1,b}(1 - n_{ib}) \rangle; \quad\quad\quad C_{4,a} = \langle n_{i-1,b}n_{ib} \rangle \end{aligned} \tag{44}$$

Respectively the correlation functions for g_b^0 are calculated on a sublattice:

$$\begin{aligned} C_{1,b} &= \langle (1 - n_{ia})(1 - n_{i+1,b}) \rangle; \quad C_{2,b} = \langle (1 - n_{ia})n_{i+1,b} \rangle \\ C_{3,b} &= \langle n_{ia}(1 - n_{i+1,a}) \rangle; \quad\quad\quad C_{4,b} = \langle n_{i,a}n_{i+1,a} \rangle \end{aligned} \tag{45}$$

Using the transfer-matrix method we obtain an expressions which are equivalent to (29):

$$\begin{aligned} C_{1,\beta} &= (1 - n_\beta)^2 - (n_\beta^2 - n_\beta)\frac{\lambda_{2,\beta}}{\lambda_{1,\beta}} \\ C_{2,\beta} &= C_{3,\beta} = n_\beta(1 - n_\beta) + (n_\beta^2 - n_\beta)\frac{\lambda_{2,\beta}}{\lambda_{1,\beta}} \\ C_{4,\beta} &= n_\beta^2 - (n_\beta^2 - n_\beta)\frac{\lambda_{2,\beta}}{\lambda_{1,\beta}} \end{aligned} \tag{46}$$

where

$$\lambda_{1,\beta} = \frac{a_\beta + b_\beta}{2} + \sqrt{\left(\frac{a_\beta - b_\beta}{2}\right)^2 + c_\beta d_\beta}$$

$$\lambda_{2,\beta} = \frac{a_\beta + b_\beta}{2} - \sqrt{\left(\frac{a_\beta - b_\beta}{2}\right)^2 + c_\beta d_\beta} \tag{47}$$

and

$$a_a = e^{\frac{\beta}{4}(w' - 3w - 3U + V + 2\varepsilon) + \beta\mu} + e^{\frac{\beta}{4}(J + U + V) + \beta h}$$

$$b_a = e^{\frac{\beta}{4}(w-3w'+U-3V+2\varepsilon)-\beta\mu} + e^{\frac{\beta}{4}(J+U+V)-\beta h}$$

$$c_a = 2ch\left[\frac{\beta}{2}(\varepsilon-w+V-h+\mu)\right]$$

$$d_a = 2ch\left[\frac{\beta}{2}(w'-\varepsilon-U-h+\mu)\right]$$

$$a_b = e^{\frac{\beta}{4}(w'-3w-3U+V+2\varepsilon)+\beta\mu} + e^{\frac{\beta}{4}(J+U+V)-\beta h} \qquad (48)$$

$$b_b = e^{\frac{\beta}{4}(w-3w'+U-3V+2\varepsilon)-\beta\mu} + e^{\frac{\beta}{4}(J+U+V)+\beta h}$$

$$c_b = 2ch\left[\frac{\beta}{2}(w'-\varepsilon-U+h+\mu)\right]$$

$$d_b = 2ch\left[\frac{\beta}{2}(\varepsilon-w+V+h+\mu)\right]$$

The full Green's function in the independent subband approximation is given by the following expression

$$G_{\beta\beta}(k) = \frac{1}{2}\sum_{\alpha=1}^{4}\left(\frac{S_\alpha^{\beta,-}}{E-E_\alpha^-(k)} + \frac{S_\alpha^{\beta,+}}{E-E_\alpha^+(k)}\right) \qquad (49)$$

where the poles of Green's functions are

$$E_\alpha^\pm(k) = \varepsilon_\alpha \pm \sqrt{h^2 + C_\alpha^a C_\alpha^b|t_{ab}|^2} - \mu \qquad (50)$$

Corresponding statistical weights are not just correlation functions as it was in the case of the absence of the asymmetry field. They are given by the following expressions

$$S_\alpha^{\beta,\pm} = \left(1 \pm \frac{h}{\sqrt{h^2 + C_\alpha^a C_\alpha^b|t_{ab}|^2}}\right)C_\alpha^\beta \qquad (51)$$

Using the method described in section 5 we can obtain the equation

$$n = \sum_{\alpha=1}^{4}\frac{1}{N}\sum_k\left[\frac{P_\alpha^+}{e^{\beta E_\alpha^+(k)}+1} + \frac{P_\alpha^-}{e^{\beta E_\alpha^-(k)}+1}\right]$$

$$P_\alpha^+ = S_\alpha^{a,-} + S_\alpha^{b,+} \quad ; \quad P_\alpha^- = S_\alpha^{a,+} + S_\alpha^{b,-} \qquad (52)$$

To obtain the zero-order dependences of $S_\alpha^{\beta,\pm}$ on μ we shall consider the low temperature region to get rid of the terms with considerably large energies in their exponents. Thus considering the expressions for correlation functions (47) in the vicinity of the points where chemical
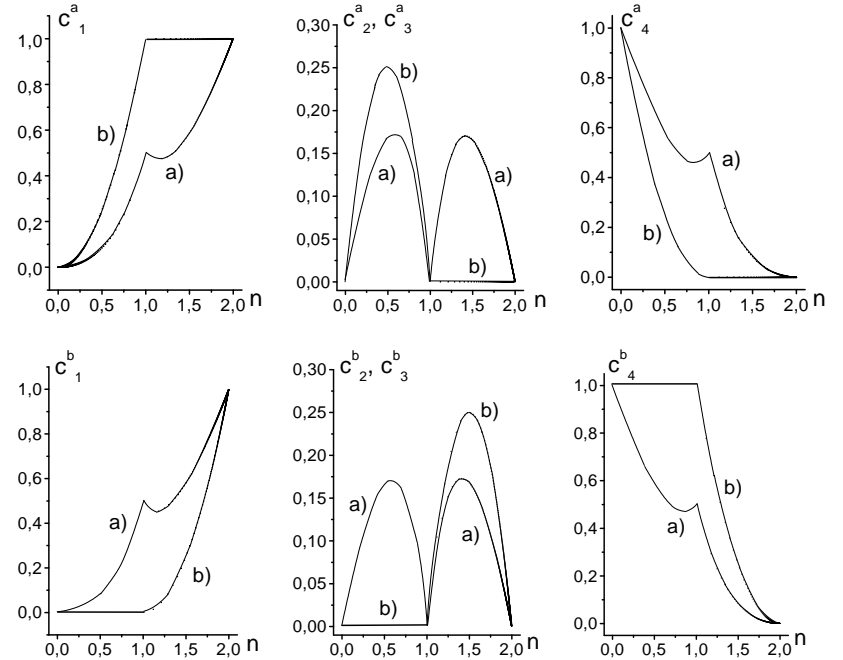

Figure 7. Dependences of correlation functions on proton concentration for a and b sublattice: a) in the absence of the asymmetry field h; b) in the case of $h = 40\ cm^{-1}$.

potential jumps, we obtain the following expressions for parameters in (47):

$$\frac{\lambda_{2,\beta}}{\lambda_{1,\beta}} = \frac{n_\beta - 1 + n_\beta(z+\rho_\beta)}{n_\beta + (n_\beta-1)(z+n_\beta)} \qquad . \qquad (53)$$

Here

$$n_\beta = \frac{1}{2} + \frac{1-z-\rho_\beta}{2\sqrt{(1-z-\rho_\beta)^2+4z}}$$

$$\rho_a = e^{-2\beta h} \quad ; \quad \rho_b = e^{2\beta h} \quad ; \quad z = e^{\beta(-w'+\varepsilon-V-h-\mu)} \qquad (54)$$

for $0 \le n < 1$ and

$$n_\beta = \frac{1}{2} + \frac{z+\rho_\beta-1}{2\sqrt{(z+\rho_\beta-1)^2+4z}}$$

$$\rho_a = e^{2\beta h} \quad ; \quad \rho_b = e^{-2\beta h} \quad ; \quad z = e^{\beta(w-\varepsilon+U+h-\mu)} \qquad (55)$$

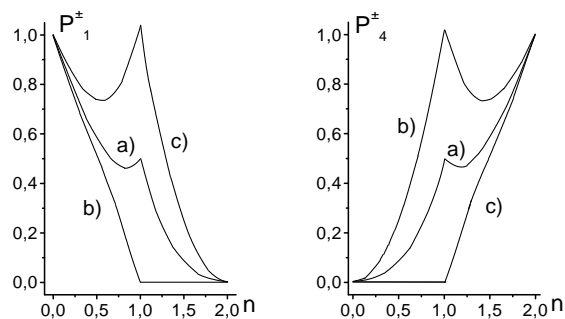Figure 8. $P_\beta^\pm$ as a function of n at $h = 40\ cm^{-1}$, $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 250\ cm^{-1}$. a) the case of $h = 0$; b) P_1^+ and P_4^+, $h = 40\ cm^{-1}$; c) P_1^- and P_4^-, $h = 40\ cm^{-1}$;

for $1 \le n < 2$.

These expressions are valid when $e^{-\beta U} \ll 1$, $e^{-\beta V} \ll 1$, $e^{-\beta(w-\varepsilon)} \ll 1$, $e^{-\beta(\varepsilon - w')} \ll 1$. Corresponding dependences of $C_{\alpha,\beta}$ on n ($n = n_a + n_b$) can be seen in Fig. 7.

Thus one can determine the dependences of parameters $P_\alpha^\pm$ on n (Fig. 8) which determine the behaviour of chemical potential with the change of n.

In Fig. 9 the results obtained by solving the equation (52) in low-temperature limit are presented.

Comparing this results with the ones for the case of $h = 0$ one can see that at the increase of h the point of the chemical potential jump shifts towards the value $n = 1$. At intermediate values of h ($h < \sim 20\ cm^{-1}$ for $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 250\ cm^{-1}$) the concentration range where $\partial\mu/\partial n < 0$ increases with the increasing of h due to the change in the bands' shape (Fig. 9). But farther increasing of h leads to the situation that the statistical weight of the upper of the lowest subbands (Fig. 10 a) becomes much smaller then the weight of the lower one. In this case the chemical potential jumps at $n = 1$ from the lowest subband directly to the highest one (Fig. 10 b) and the region with $\partial\mu/\partial n < 0$ first starts to decrease ($\sim 20\ cm^{-1} < h < \sim 40\ cm^{-1}$) and then disappears ($h > \sim 40\ cm^{-1}$ for the taken values of Ω_0 and Ω_R). Thus the possibility of separation into the regions with different values of n exists only at small values of h (in the range from zero to some critical value).

We considered h as additional parameter of the model. More correct consideration should take into account the fact that h is temperature dependent quantity which can be determined in a self-consistent way.
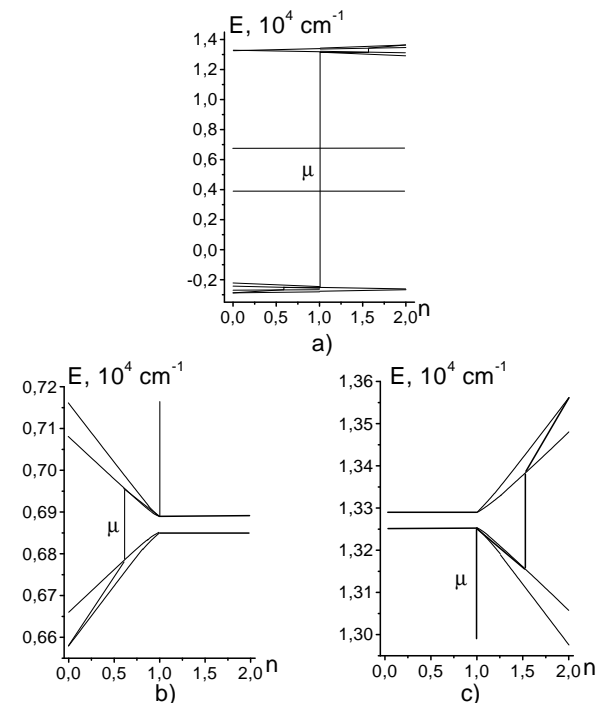

Figure 9. Energy spectrum and chemical potential of the system as a function of n at $h = 20\ cm^{-1}$, $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 250\ cm^{-1}$. a) shows the whole spectrum, b) - two lowest subbands, c) - two highest subbands.

If we consider h as proportional to the order parameter (describing the ordering of protons in the chains) (Fig. 11) we can obtain the explicit temperature dependence of parameter $\rho = e^{-2\beta h}$ (Fig. 12). The region with $\partial\mu/\partial n < 0$ exists when $0.98 < \rho < 1$ (for $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 2500\ cm^{-1}$). Parameter ρ starts to exceed the critical value $\rho^* = 0.98$ (Fig. 11) at a certain temperature which is lower then the temperature of superionic phase transition τ_c^*. Thus there is a possibility of coexistence of two phases with different proton concentrations.

7. Conclusions

The method of cluster expansions in the theory of Greens' functions was used for investigation of the proton spectrum and the behaviour
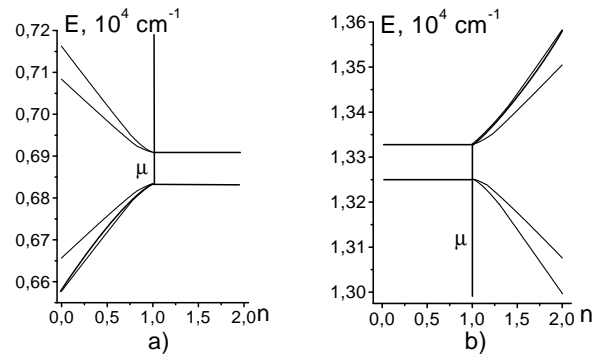
Figure 10. Energy spectrum and chemical potential of the system as a function of n at $h = 40\ cm^{-1}$, $\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 250\ cm^{-1}$. a) shows two lowest subbands, b) - two highest subbands.

of chemical potential of one-dimensional proton conductor. The most important results are:

1) Short range proton correlations lead to the splitting in proton energy spectrum which has a band character. The edges of the bands depend on proton concentration;

2) The occupancy of proton subbands can have a quasi-metallic (1) or dielectric (semi-conductor) (2) character depending on the proton concentration. This determines the proton conductivity activation energy (quasipolaronic conductivity in the case (1) or defect one in the case (2));

3) Possibility of the decreasing dependence $\mu(n)$ $(\partial\mu/\partial n < 0)$ when $n \le 1$, points out to the instability of the state with the uniform proton distribution along the chain. This effect appears when the internal ordering field decreases, which takes place at the increase of temperature. This results in the fact that protons (deuterons) partially occupy the positions outside the chain;

4) In the case of $CsDSO_4$ crystal the above mentioned instability can be one of the reasons for transition of some number of deuterons into B positions (placed between the chains formed by SO_4 groups and A hydrogen positions), which causes the so-called percursor effect observed in the wide temperature range below T_s - the superionic phase transition point.
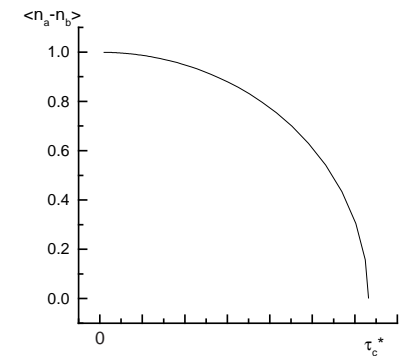

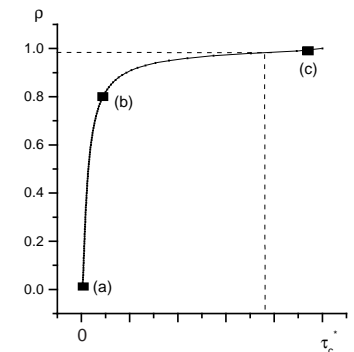Figure 11. Temperature dependence of the order parameter of the system ($\tau = T/T_c$).

Figure 12. Temperature dependence of ρ ($\Omega_0 = 100\ cm^{-1}$, $\Omega_R = 2500$ cm^{-1}). a) $h = \infty$ or $\tau = 0$; b) finite values of h, $\partial\mu/\partial n > 0$; c) small values of h, the region of n with $\partial\mu/\partial n < 0$ exists at $\rho > \rho^* = 0.98$.

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Енергетичний спектр і термодинаміка одномірного протонного провідника