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LOW-FREQUENCY DYNAMICS OF  
1D QUANTUM LATTICE GAS: THE CASE OF  
LOCAL POTENTIAL WITH DOUBLE WELLS

ЛЬВІВ

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**Низькочастотна динаміка одновимірного ґраткового газу:  
випадок двоямного локального потенціалу**

Р.Я. Стеців, О.Я. Фаренюк

**Анотація.** На основі моделі квантового ґраткового газу досліджено низькочастотну динаміку одновимірних систем (типу атомних ланцюжків з водневими зв'язками) з двомінімунним локальним ангармонічним потенціалом. В моделі враховано короткосяжні кореляції між частинками, а також перенос частинок як на зв'язках в двоямному потенціалі, так і між зв'язками. Методом точної діагоналізації з використанням формалізму функцій Гріна розраховано динамічну дипольну сприйнятливість, що визначає діелектричний відгук системи. Отримано густину коливних станів, аналізується її частотна залежність. Замість стандартної м'якої моди отримано розщеплення найнижчої гілки в спектрі в області переходу до впорядкованого основного стану.

**Low-frequency dynamics of 1D quantum lattice gas: the case of local potential with double wells**

R.Ya. Stetsiv, O.Ya. Farenjuk

**Abstract.** The quantum lattice gas model is used for investigation of low-frequency dynamics of the one-dimensional lattice (an analogue of the H-bonded atomic chain) with the two minima local anharmonic potential. Short-range correlations and particle hopping within potential wells as well as between of them are taken into account. The dynamical dipole susceptibility that determines the dielectric response of the system, is calculated using exact diagonalization procedure on clusters and the Green's function formalism. The density of vibrational states is found, its frequency dependence is analyzed. The splitting of the lowest branch in spectrum in the region of transition to the ordered ground state (instead of the standard soft-mode behaviour) is revealed.

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НИЗЬКОЧАСТОТНА ДИНАМІКА ОДНОВИМІРНОГО ГРАТКОВОГО ГАЗУ:  
ВИПАДОК ДВОЯМНОГО ЛОКАЛЬНОГО ПОТЕНЦІАЛУ

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## 1. Introduction

The lattice gas approach is widely used during many years in the various tasks of the condensed matter theory — from thermodynamics of quantum liquids to description of phase transitions and collective dynamics in intercalated crystalline structures, systems of adsorbed particles on the surface of metals, ionic and superionic conductors. The models of such type, that take into account quantum effects, found recently the application in the theory of optical lattices with ultracold Bose- and Fermi atoms. The processes and characteristics, related to transport of particles on a lattice (such as ionic conductivity, quantum diffusion, as well as the spectra of the single particle excitations) were mainly the subject of researches and calculations. The study of features of corresponding spectral densities in different phases of system (normal, spatially modulated, superfluid, etc.) allows, as was shown, in particular, in [1, 2], to identify separate phases. It can be considered as an additional means at the construction of phase diagrams of equilibrium states. One of examples of objects, where the usage of quantum lattice model appeared to be successful, is the crystalline systems with hydrogen bonds, where the transitions to the states (phases) with superionic conductivity, are possible. In papers [3, 4] based on the so-called orientational-tunneling model [5], the phase transitions to the superionic state in the subsystem of protons were described and the coefficients of proton conductivity were calculated for the group of crystals  $M_3H(XO_4)_2$  where  $M = NH_4, Rb, Cs$  and  $X = S, Se$ . The mentioned model was taken by us as the basis of calculations of the single-particle spectrum and dynamic conductivity of the one-dimensional (1d) ionic conductors [6, 7] by means of exact diagonalization method on finite clusters. Such an approach allowed to establish the existence of different ground-states, to describe the transitions of the crossover type between them at  $T \neq 0$ , and also to investigate the features of collective dynamics that determines the frequency dispersion of conductivity [6, 7]. Ideological basis of our calculations was the hard-core boson approach; it was firstly used by Mahan [8] in description of the quantum particle transport in a lattice.

Approach of exact diagonalization allows, at the same time, to consider other dynamic characteristics that are important in description of the hydrogen bonded systems and are measured experimentally. Low-frequency dielectric response, that for such objects is caused foremost by tunneling motion of protons on hydrogen bonds (except, of course, the standard phonon modes), belongs to them. In normal phases (ferroelectric or paraelectric) of the real 3d systems the soft mode behavior of

the one of the lowest branches of vibrational spectra is known (when in the limit of  $T \rightarrow T_c$  or  $\Omega_0 \rightarrow \Omega_{0c}$ ,  $\omega_i(k=0) \rightarrow 0$ ) [9,10]. In particular, it is characteristics of the known de Gennes model [11], that can be obtained from the orientational-tunneling model when number of protons on each of hydrogen bonds in a lattice is fixed ( $n_i = 1$ ) and the proton hopping between bonds is absent, while their interbond interaction is taken into account. In the random phase approximation (RPA) this result, that relates to behavior of soft mode, can be easily obtained. It is known, however, that RPA (based on the mean field approximation), becomes inapplicable at low dimensions ( $d = 1$  and  $d = 2$ ). Therefore application of procedure of exact diagonalization can be useful in this case.

This work is devoted to the calculation of the frequency dependence of the dynamical susceptibility of the dipole-dipole type of the one-dimensional N-site cluster with the periodical boundary conditions. Numerical calculations are performed at  $N=10$ . The corresponding density of vibrational states is obtained. The vibrational spectra are studied depending on the particles (protons) tunneling frequency on the bond; the influence of transfer of particles between the bonds on these spectra is also investigated.

## 2. The model

Our quantum gas model in the case, when particles obey the Pauli statistics, correspond to hard-core boson limit. If the particles positions are characterized by symmetric local potential possessing two minima on the bond (fig.1), the two stage nature of particle (proton) transport is taken into account via two particle transfer constants ( $\Omega_0$  for intra-bond hopping between two positions  $a$  and  $b$  on each bond as well as  $\Omega_R$  for inter-bond transfer between hydrogen bonds that arises due to orientational motion of ionic groups). Because of that the model is known as orientational-tunneling model [5]. It also includes the correlation between nearest protons caused by the short-range repulsion (the corresponding energies parameter are:  $V$  on the bond and  $w$  for the neighbor bonds).

The Hamiltonian of this model in the case of chain like structure (considered here as an example) can be presented as follows

$$H = (\varepsilon - \mu) \sum_i (n_{ia} + n_{ib}) + V \sum_i n_{ia} n_{ib} + w \sum_i n_{ib} n_{i+1,a} + \Omega_0 \sum_i (c_{ia}^+ c_{ib} + c_{ib}^+ c_{ia}) + \Omega_R \sum_i (c_{ib}^+ c_{i+1,a} + c_{i+1,a}^+ c_{ib}), \quad (1)$$

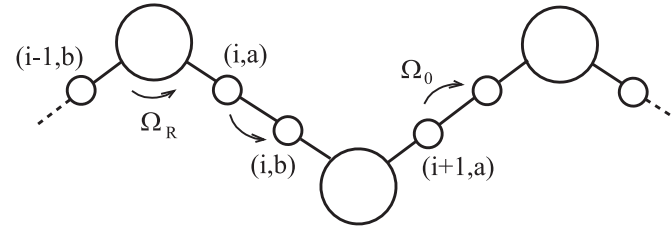


Figure 1. The model of one-dimensional system. The large circles are a heavy motionless ionic groups. The small circles denote two possible positions of particles (protons) on each bond (in particular, hydrogen bond)

In contrast to [5],  $c_{i,\alpha}$  ( $c_{i,\alpha}^+$ ) in our case are the Pauli operators. They describe the process of annihilation (creation) of particle (proton) in position  $i, \alpha$  ( $\alpha = a, b$ ); therefore  $n_{i,\alpha} = c_{i,\alpha}^+ c_{i,\alpha}$  is the occupation number of particles (protons) in this position (see Fig. 1).

## 3. Dielectric susceptibility. Exact diagonalization technique

The Hamiltonian matrix as well as  $c_{i,a}$  and  $c_{i,a}^+$  matrices are constructed on the basis of many-particle states  $|n_{1,a} n_{1,b} \dots n_{N,a} n_{N,b} \rangle$

The diagonalization transformation is applied to Hamiltonian

$$U^{-1} H U = \tilde{H} = \sum_p \lambda_p \tilde{X}^{pp} \quad (2)$$

where  $\lambda_p$  are eigenvalues of the Hamiltonian,  $\tilde{X}^{pp}$  are Hubbard operators. The creation and annihilation operators are presented in the form

$$U^{-1} c_{i,a} U = \sum_{pq} A_{pq}^{ia} \tilde{X}^{pq} \quad , \quad U^{-1} c_{i,a}^+ U = \sum_{rs} A_{rs}^{ia*} \tilde{X}^{sr} \quad (3)$$

where coefficients  $A_{pq}^{ia}$  are the matrix elements of operator  $c_{i,a}$  on the new bases

Dipole moment of the  $i$ -th bond is equal

$$D_i = q_1 d_1 (n_{ib} - n_{ia}) \quad (4)$$

where  $d_1$  is the distance between equilibrium positions of a particle on the bond,  $q_1$  is the charge of the particle. For calculation of dielectric

susceptibility  $\chi_q(\omega)$  we can use the standard relation between such a susceptibility and dipole-dipole two time Green's function

$$\chi_q(\omega) = -\frac{2\pi}{\hbar} \ll D|D \gg_{q,\omega} \quad (5)$$

By means of equation of motion procedure, the following expression for the Green's function in the case of system with Hamiltonian  $\hat{H}$  can be obtained

$$\begin{aligned} \ll D|D \gg_{q,\omega} &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \ll D_i|D_j \gg e^{iq(R_i-R_j)} = \\ &= q_1^2 d_1^2 \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N e^{iq(R_i-R_j)} \ll (n_{ib} - n_{ia})(n_{jb} - n_{ja}) \gg = \\ &= \frac{\hbar}{2\pi} q_1^2 d_1^2 \frac{1}{N^2} \frac{1}{Z} \sum_{i=1}^N \sum_{j=1}^N e^{iq(R_i-R_j)} \sum_{kk_1} \left( \sum_l A_{lk}^{ib*} A_{lk_1}^{ib} \sum_m A_{mk_1}^{jb*} A_{mk}^{jb} + \right. \\ & \left. \sum_l A_{lk}^{ia*} A_{lk_1}^{ia} \sum_m A_{mk_1}^{ja*} A_{mk}^{ja} - \sum_l A_{lk}^{ia*} A_{lk_1}^{ia} \sum_m A_{mk_1}^{jb*} A_{mk}^{jb} - \right. \\ & \left. \sum_l A_{lk}^{ib*} A_{lk_1}^{ib} \sum_m A_{mk_1}^{ja*} A_{mk}^{ja} \right) \frac{e^{-\beta\lambda_k} - e^{-\beta\lambda_{k_1}}}{\hbar\omega - (\lambda_{k_1} - \lambda_k)} \end{aligned} \quad (6)$$

The imaginary part of this Green function determines density of vibrational states

$$\rho_q(\omega) = 2\text{Im} \ll D|D \gg_{q,\omega+i\varepsilon} \quad (7)$$

#### 4. The density of vibrational states

Here, we present the results of numerical calculations of density of vibrational states  $\rho_0(\omega)$  at zero temperature ( $T = 0$ ). Numerical values of model parameters (including  $\hbar\omega$ ) are given in relation to the  $V/6$  energy parameter and are dimensionless. Such a choice corresponds to the values that are characteristics of the chain-like proton conductors and were used in our previous investigation of their equilibrium states [6]. We performed our calculations on the cluster with  $N = 10$  sites and applied the periodical boundary conditions. As usual, having deal with a discrete spectrum, we use the Lorentz distribution to broaden the  $\delta$ -peaks of spectral density.

At large values of transfer constant  $\Omega_0$ , when  $\Omega_0 > 2w$ , we obtained only one peak of the density of vibrational states at the frequency denoted as  $\omega_1$ . At the increase of  $\Omega_0$ ,  $\hbar\omega_1 \rightarrow 2\Omega_0$  (fig.2).

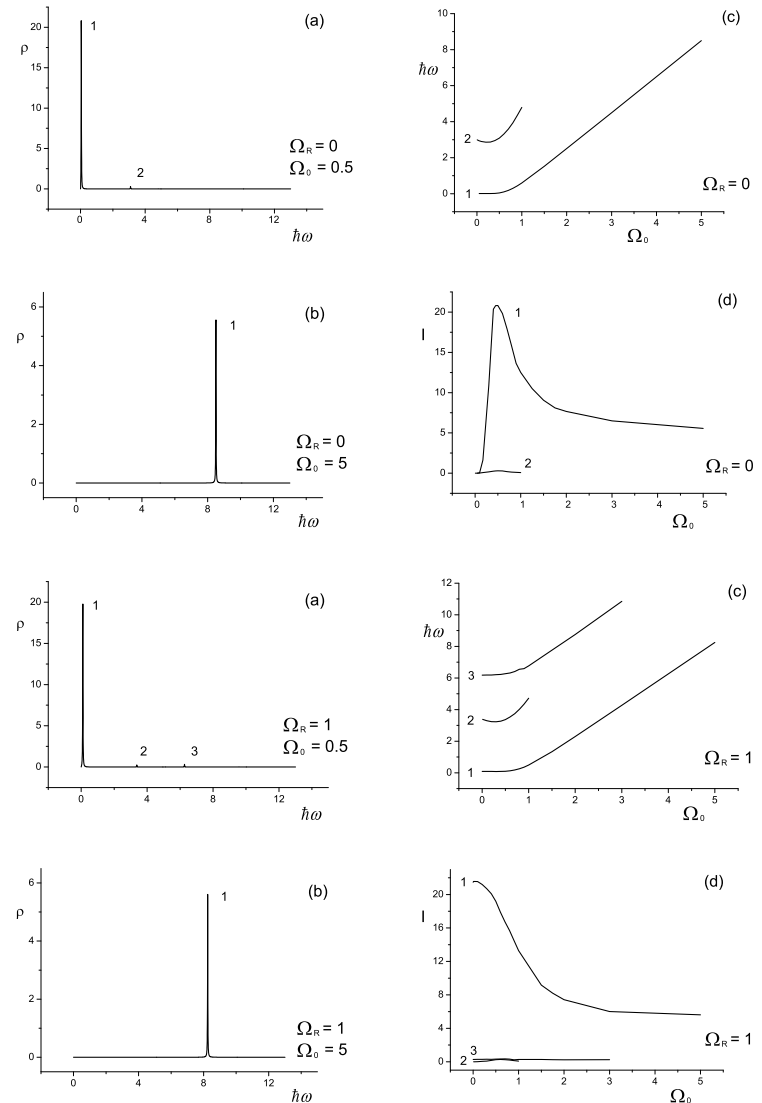


Figure 2. The density of vibrational states (a) and (b) of the one-dimensional system with two-minima local potential for particles (protons). Position (c) and intensity (d) of peaks of the density of states depending on transfer constant  $\Omega_0$ ;  $V = 6, w = 3, n = 1/2, q = 0$  for two cases:  $\Omega_R = 0$  and  $\Omega_R = 1$ .

This peak shifts to the region of lower frequencies  $\Omega_0 < \hbar\omega_1 < 2\Omega_0$  at  $w < \Omega_0 < 2w$ , and its intensity increases monotonously. At the further decrease of  $\Omega_0$  a peak position becomes a fixed one ( $\omega_1 \rightarrow \omega_1^0$ ) and does not change in a relatively wide region of  $\Omega_0$ . At  $\Omega_0 \rightarrow 0$  and  $\Omega_R = 0$  the intensity of  $\omega_1^0$  peak goes to zero ( $I \rightarrow 0$ ). In this region the second peak appears; it is caused by interaction (parameter  $w$ ) between particles on nearest bonds. Its position is  $\hbar\omega_2 \approx w$  at  $\Omega_0 \rightarrow 0$ .

The third peak appears if the transfer of particles between nearest bonds ( $\Omega_R \neq 0$ ) is included. This peak is caused by interaction (parameter  $V$ ) between particles on the same bond. At lowering of  $\Omega_0$  its frequency decreases and if  $\Omega_0 \rightarrow 0$ ,  $\hbar\omega_3 \rightarrow V$ . Peak  $\omega_1^0$  shifts to higher frequencies in the case if the parameter  $\Omega_R$  increases and its intensity grows at  $\Omega_0 \rightarrow 0$ . The position of the  $\omega_2$  peak does not change here. The intensity of  $\omega_1$  peak is of two orders larger than the intensity of peaks  $\omega_2$  and  $\omega_3$ . At  $\Omega_0 = 0.5$  we obtained for  $\Omega_R = 0$ :  $\hbar\omega_1 = 0.043$ ,  $\hbar\omega_2 = 3.09$ ,  $I_1 = 20.82$ ,  $I_2 = 0.294$ ; for  $\Omega_R = 1$ :  $\hbar\omega_1 = 0.098$ ,  $\hbar\omega_2 = 3.37$ ,  $\hbar\omega_3 = 6.27$ ,  $I_1 = 19.22$ ,  $I_2 = 0.250$ ;  $I_3 = 0.320$ . We present the density of states in relative units omitting the multiplier  $\frac{\hbar}{\pi} q_1^2 d_1^2$ .

## 5. Conclusions

The results, obtained in this work illustrate the behaviour of dipole susceptibility and vibrational spectrum of the one-dimensional lattice model (that describes the chain-like hydrogen bonded structure) in the low frequency region. In the absence of hopping of particles between bonds, the existence of mode, frequency of which ( $\omega_1$ ) decreases if tunneling parameter approaches to the region of values, that in the case of a 3d system could correspond to the transition to the ordered (FE) phase, is revealed. In our 1d case we see, however, the absence of behaviour of the soft mode type. Instead of that, the new ( $\omega_2$ ) branch appears; its frequency is determined by energy of repulsion ( $w$ ) of protons residing on nearest bonds.

Additional complication of spectrum arises due to the transfer of particles (protons) between bonds (in this case the model describes the proton 1d conductor). Another branch appears in this case with frequency  $\omega_3$ ; its value is determined by energy of interaction  $V$  of particles on nearest positions (the case of two protons on hydrogen bond). Such splitting of spectrum can be considered as manifestation of appearance of the collective transport of particles along a chain. It should be reminded that we present here the results of calculations at  $T = 0$ . At unzero temperatures there is additional splitting of spectrum (the broadening of the

mentioned peaks on the density of vibrational states takes place, and the new peaks appear)

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