

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

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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 the 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.

Keywords: *hard-core boson model, double-well local potential, dynamical susceptibility, vibrational spectrum.*

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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. The full description of vibrational spectrum and dynamics should be based on the allowance for all degrees of freedom including both tunneling motion of protons on hydrogen bonds and phonon modes. At the same time, the so-called soft mode (the branch with minimal frequency) is formed by coupled proton-lattice vibrations (according to the known idea of Kobayashi [9]). Having not an intention to investigate the full spectrum, we can apply our simplified model considering only this lowest mode. The corresponding local normal coordinates, that are connected with hydrogen bonds and their nearest environment, can be presented in form of pseudospins taking into account the two lowest quantum states of proton on H-bond. In particular, it is characteristics of the known de Gennes model [10], that formally 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.

Respective local dipole moments are formed by protons together with nearest ions (at the bond creation the part of the hydrogen electronic charge is transferred to them [11]). In this case the effective dipole moments can be ascribed to hydrogen bonds and considered as parameters of model description. Such an approach corresponds to the proton ordering model that was successfully used in description of ferroelectric phase transitions in a set of H-bonded ferroelectrics (see [12]).

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 $\Omega_0 \rightarrow \Omega_0^c$, $\omega_i(k=0) \rightarrow 0$) [13, 14]. 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 transport (proton) is taken into account via

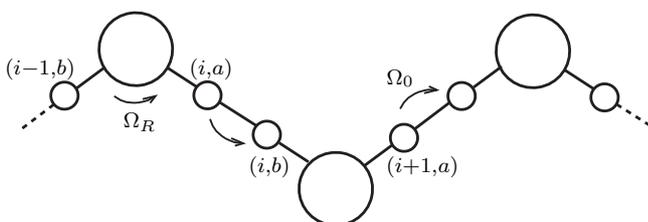


Fig. 1. The model of one-dimensional system. The large circles are a heavy motionless ionic groups. The small circles denote two possible positions of particles (protons) on each bond (in particular, hydrogen bond).

two particle transfer constants (Ω_0 for intra-bond hopping between two positions a and b on each bond as well as Ω_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

$$\begin{aligned}
 H = & (\varepsilon - \mu) \sum_i (n_{ia} + n_{ib}) + V \sum_i n_{ia}n_{ib} + w \sum_i n_{ib}n_{i+1,a} + \Omega_0 \sum_i (c_{ia}^+c_{ib} + c_{ib}^+c_{ia}) \\
 & + \Omega_R \sum_i (c_{ib}^+c_{i+1,a} + c_{i+1,a}^+c_{ib}).
 \end{aligned}
 \tag{1}$$

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, α ($\alpha = a, b$); therefore $n_{i,\alpha} = c_{i,\alpha}^+c_{i,\alpha}$ is the occupation number of particles (protons) in this position, see Fig. 1 (here the eigenvalues of $n_{i,a}$ and $n_{i,b}$ are equal to 0 or 1 independently, contrary to the case of de Gennes model). The problem is solved within the grand canonical ensemble approach. It gives a possibility to consider the cases with a different average number of particles by introducing their chemical potential. A case is examined in this work, when the mean value of filling of hydrogen bond is equal to 1 (on the average, one particle (proton) per bond).

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

$$U^{-1}HU = \tilde{H} = \sum_p \lambda_p \tilde{X}^{pp},
 \tag{2}$$

where λ_p are eigenvalues of the Hamiltonian, \tilde{X}^{pp} are Hubbard operators (in general, $\tilde{X}^{pq} = |p\rangle\langle q|$). The creation and annihilation operators are presented in the form

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

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

$$D_i = \mu_{ef}(n_{ib} - n_{ia}),
 \tag{4}$$

where μ_{ef} is effective local dipole moment connected with hydrogen bond and its environment. 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

$$\chi_q(\omega) = -\frac{2\pi}{\hbar} \langle\langle D|D \rangle\rangle_{q,\omega}.
 \tag{5}$$

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

$$\begin{aligned}
 \langle\langle D|D \rangle\rangle_{q,\omega} &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \langle\langle D_i|D_j \rangle\rangle e^{iq(R_i - R_j)} \\
 &= \mu_{ef}^2 \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N e^{iq(R_i - R_j)} \langle\langle (n_{ib} - n_{ia})|(n_{jb} - n_{ja}) \rangle\rangle
 \end{aligned}$$

$$\begin{aligned}
&= \frac{\hbar}{2\pi} \mu_{ef}^2 \frac{1}{N^2} \frac{1}{Z} \sum_{i=1}^N \sum_{j=1}^N e^{iq(R_i - R_j)} \sum_{kk_1} \left(\sum_l A_{lk}^{ib*} A_{lk_1}^{ib} \sum_m A_{mk_1}^{jb*} A_{mk}^{jb} \right. \\
&+ \sum_l A_{lk}^{ia*} A_{lk_1}^{ia} \sum_m A_{mk_1}^{ja*} A_{mk}^{ja} - \sum_l A_{lk}^{ia*} A_{lk_1}^{ia} \sum_m A_{mk_1}^{jb*} A_{mk}^{jb} \\
&\left. - \sum_l A_{lk}^{ib*} A_{lk_1}^{ib} \sum_m A_{mk_1}^{ja*} A_{mk}^{ja} \right) \frac{e^{-\beta\lambda_k} - e^{-\beta\lambda_{k_1}}}{\hbar\omega - (\lambda_{k_1} - \lambda_k)}, \tag{6}
\end{aligned}$$

here q is the component of wave vector directed along the H -bonded chain, R_i coordinate of i -th bond, $\beta = 1/(kT)$.

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

$$\rho_q(\omega) = 2 \operatorname{Im} \langle \langle D | D \rangle \rangle_{q, \omega + i\varepsilon}. \tag{7}$$

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 w energy parameter and are dimensionless (usually w is of order of 0.02 – 0.04 eV, such an estimate follows from the experimental data for T_c in the case of H -bonded ferroelectrics). Our choice of values of another parameters corresponds to the ones that are characteristics of the chain-like proton conductors (see e.g. [15, 16]) 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 δ -peaks of spectral density.

At large values of transfer constant Ω_0 , when $\Omega_0 > 2w$, we obtained only one peak of the density of vibrational states at the frequency denoted as ω_1 . At the increase of Ω_0 , $\hbar\omega_1 \rightarrow 2\Omega_0$ (Fig. 2).

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 Ω_0 a peak position becomes a fixed one ($\omega_1 \rightarrow \omega_1^0$) and does not change in a relatively wide region of Ω_0 . At $\Omega_0 \rightarrow 0$ and $\Omega_R = 0$ the intensity of ω_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 Ω_0 its frequency decreases and if $\Omega_0 \rightarrow 0$, $\hbar\omega_3 \rightarrow V$. Peak ω_1^0 shifts to higher frequencies in the case if the parameter Ω_R increases and its intensity grows at $\Omega_0 \rightarrow 0$. The position of the ω_2 peak does not change here. The intensity of ω_1 peak is of two orders larger than the intensity of peaks ω_2 and ω_3 . At $\Omega_0 = 0.167$ we obtained for $\Omega_R = 0$: $\hbar\omega_1 = 0.014$, $\hbar\omega_2 = 1.03$, $I_1 = 20.82$, $I_2 = 0.294$; for $\Omega_R = 0.33$: $\hbar\omega_1 = 0.033$, $\hbar\omega_2 = 1.12$, $\hbar\omega_3 = 2.09$, $I_1 = 19.22$, $I_2 = 0.250$; $I_3 = 0.320$. We present the density of states in relative units omitting the multiplier $\frac{\hbar}{\pi} \mu_{ef}^2$.

One can explain the appearance of additional branches $\hbar\omega_1$ and $\hbar\omega_2$ in spectrum taking into account that in the $\Omega_0 < \Omega_0^c$ case (where Ω_0^c is certain ‘‘critical’’ value; in our case $\Omega_0^c = 0.33$), the ordered state of protons analogous to the ferroelectric phase with the dominant occupation of ‘‘a’’ (or ‘‘b’’) positions is set up. Tunneling of protons within the bonds is connected in this case with the excitation energy w , while at the hopping between bonds the doubly occupied bonds can appear, and, respectively, the energy of excitation is equal to V . Degree of proton ordering increases at the decrease of Ω_0 ; as a result, the spectral weight of such excitations becomes higher.

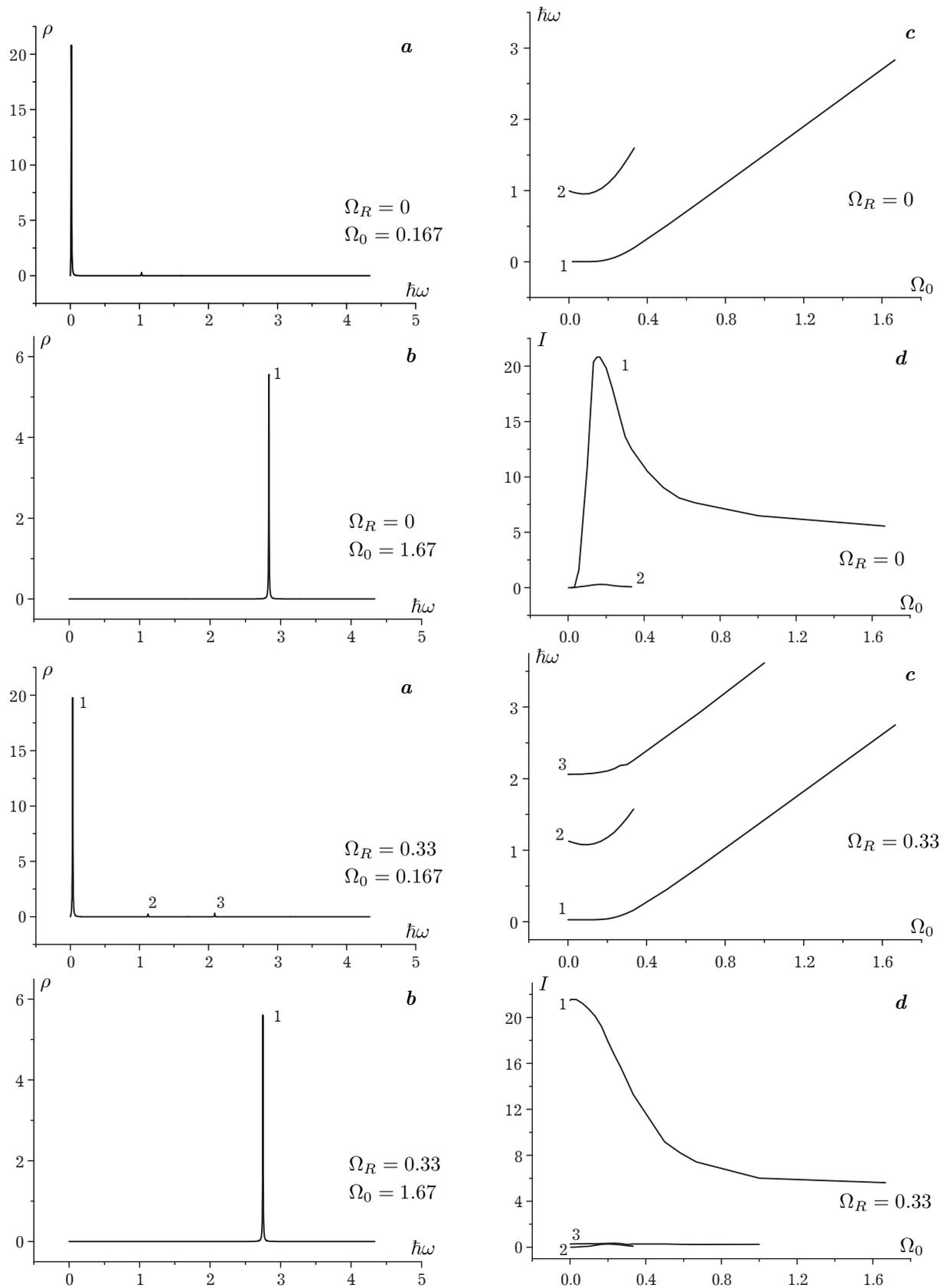


Fig. 2. The density of vibrational states (a) and (b) of the one-dimensional system with two-minima local potential for particles (protons). Position (c) and intensity (d) of peaks of the density of states depending on transfer constant Ω_0 at $T = 0$; $V = 2$, $w = 1$, $q = 0$ for two cases: $\Omega_R = 0$ and $\Omega_R = 0.33$. All energetic quantities are given in relation to w ; the ρ function and peak intensities are presented in the $\frac{\hbar}{\pi} \mu_{ef}^2$ units.

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 (ω_1) decreases if tunneling parameter approaches the region of values, that in the case of a 3d system could correspond to the transition to the ordered (FE) phase, is revealed. It should be noted that in this case, if the system is described by the pseudospin de Gennes model with Hamiltonian $\hat{H} = \Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z$, the ferroelectric phase transition temperature T_c , that is given in the mean field approximation by the expression $kT_c = \Omega [2\text{Arth } 2\Omega/J(0)]^{1/2}$ (where $J(0) = J(\mathbf{q} = 0) = \sum_j J_{ij}$ [13, 14]), goes to zero at $\Omega \rightarrow J(0)/2 \equiv \Omega^*$. At this point, the quantum phase transition takes place at $T = 0$ in the 3d case in the decrease of the tunneling parameter Ω . The corresponding proton soft mode frequency $\hbar\omega_{q=0} = [\Omega^2 - \frac{1}{2}\Omega J(0)th\Omega/2kT]^{1/2}$ [13, 14] can be presented in the $T = 0$ limit in the form $\hbar\omega_{q=0} = (\Omega^2 - \Omega\Omega^*)^{1/2}$. This expression certifies the existence of the soft mode in this limit (it is true for 3d system and remains valid independently on the used approach). In our 1d case we see, however, the absence of behaviour of the soft mode type. Instead of that, the new (ω_2) branch appears; its frequency is determined by energy of repulsion (w) of protons residing on the nearest bonds. In our model, the interaction constant w is an analogue of the $\frac{1}{2}J(0)$ parameter in the de Gennes model (it can be shown passing to pseudospins by means of relations $n_{ib} = \frac{1}{2} + S_i^z$ and $n_{ia} = \frac{1}{2} - S_i^z$ that are valid in the case of fixed number of protons on the bond, $n_i = 1$), and just the value of w determines the position of effective border of paraelectric phase on the Ω axis.

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 the frequency ω_3 ; its value is determined by energy of interaction V of particles in the 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. Such a result correlates in the case of half-filling with the calculation data for dynamical conductivity of linear ionic conductor, where a position of the first low-frequency peak is determined by the short-range interaction constant analogous to V [7]. Besides, the similar behaviour was observed for dynamical susceptibility of the optical lattice with ultra-cold bosonic atoms when the low-frequency modulation of the lattice potential profile is applied [17]; the effect was explained [18] within the Bose-Hubbard model, that is reduced to our one in the limit of hard-core bosons (position of the above mentioned peak is determined here by the repulsion energy of bosons occupying the same potential well). It should be reminded that we present here the results of calculations at $T = 0$. In nonzero temperatures there is additional splitting of the spectrum (the broadening of the mentioned peaks on the density of vibrational states takes place, and the new peaks appear)

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Низькочастотна динаміка одновимірного квантового ґраткового газу: випадок двоямного локального потенціалу

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На основі моделі квантового ґраткового газу досліджено низькочастотну динаміку одновимірних систем (типу атомних ланцюжків з водневими зв'язками) з двомінімним локальним ангармонічним потенціалом. В моделі враховано короткосяжні кореляції між частинками, а також перенесення 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, проаналізовано її частотну залежність. Замість стандартної м'якої моди отримано розщеплення найнижчої гілки в спектрі в області переходу до впорядкованого основного стану.

Ключові слова: *модель жорстких бозонів, двоямний локальний потенціал, динамічна сприйнятливість, коливний спектр.*

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