Phase transitions and vibrational spectra of almost commensurate structures

V. L. Pokrovskiĭ and A. L. Talapov

L. D. Landau Theoretical Physics Institute, USSR Academy of Sciences
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The simplest one-dimensional model of an incommensurate structure, viz., a chain of atoms in a one-dimensional periodic potential, is considered. In the case when the periods are almost commensurate, the problem of the ground state and spectrum of such a system reduces to a continuum problem. It is shown that, within the framework of the model considered, the phase transitions are continuous and the spectrum contains one acoustic and one optical band. The discreteness leads to the appearance of a large number of phase transitions and to a more complicated spectrum. The limits of applicability of the classical approach, which always fails in the immediate vicinity of a phase-transition point, are discussed.

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Recently, incommensurate crystal structures have been discovered in monolayers of atoms adsorbed on the surface of metals[1] and graphite,[2] in crystals with charge-density waves,[3] and in the three-dimensional crystal $Hg_{2.86}AsF_6$ (Ref. 4). The simplest model of an incommensurate structure—a crystal placed in a periodic field—was considered in Refs. 5 and 6. It was shown that in a sufficiently weak periodic field the state of the incommensurate crystal is invariant under the group of quasi-translations, the operations of which consist of a parallel translation of the atoms and a subsequent displacement of each atom in accordance with the phase of the periodic potential. A consequence of the quasi-translational invariance is the existence of acoustic modes of small oscillations. In Ref. 6 it was shown that incommensurate structures are unstable in a sufficiently strong periodic field, but the character of the transition was not established.

In this paper we consider a one-dimensional model of a crystal with weak incommensurability. It is shown that the model can be reduced to a continuum model of a string in a periodic potential. The phase transition in the latter model is investigated exactly. We succeed in obtaining an analytic expression for the spectrum of the small oscillations of such a system.

The original model is described by the Hamiltonian

$$H=\sum_n\left[\frac{m}{2}\left(\frac{du_n}{dt}\right)^2+\frac{\varkappa}{2}(u_{n+1}-u_n)^2+V\cos\frac{2\pi}{b}(na+u_n)\right]. \tag{1}$$

The first two terms are the kinetic energy and elastic energy of the chain, and the third is the interaction of the chain with the potential. We shall consider first the case when the periods a and b are almost equal: $a=b(1+\delta)$, where δ is a small number. In this case the argument of the cosine in (1) can be replaced by $\varphi_n=2\pi\delta n+2\pi u_n/b$. For small δ the argument varies slowly as a function of n, if the u_n are also slowly varying functions of n. It is reasonable to introduce $2\pi\delta n\equiv x$ as the new argument and $\varphi(x)\equiv\varphi_n$ as the new function. In the new variables the Hamiltonian (1) takes the form

$$H=\int\left[\frac{\rho_0}{2}\left(\frac{\partial\varphi}{\partial t}\right)^2+\frac{\varkappa\delta^2b^2}{2}\left(\frac{\partial\varphi}{\partial x}-1\right)^2+V\cos\varphi\right]\frac{dx}{2\pi\delta}. \tag{2}$$

Obvious changes of variables bring (2) to the standard form

$$H=\text{const}\int\left[\frac{1}{2}\left(\frac{\partial\varphi}{\partial t}\right)^2+\frac{1}{2}\left(\frac{\partial\varphi}{\partial x}-h\right)^2+\cos\varphi\right]\frac{dx}{2\pi\delta}, \tag{3}$$

which depends on one parameter $h=(\varkappa b^2\delta^2/V)^{1/2}$

We consider now the situation $a/b=1/2+\delta$ ($\delta\ll1$). In this case the potential energy U corresponding to the Hamiltonian (1) can be represented in the form

$$U=\frac{\varkappa b^2}{2(2\pi)^2}\sum_n\left[(\varphi_n-\psi_n+\varepsilon)^2+(\varphi_n-\psi_{n-1}-\varepsilon)^2+V(\cos\varphi_n-\cos\psi_n)\right], \tag{4}$$

where

$$\varphi_n=2\pi\delta(2n)+2\pi u_{2n}/b,$$

$$\psi_n=2\pi\delta(2n+1)+\frac{2\pi u_{2n+1}}{b},\quad \varepsilon=2\pi\delta. \tag{5}$$

The quantities φ_n and ψ_n are slow functions of n. We denote $\gamma_n=\varphi_n-\psi_n$ and $\Phi_n=(\varphi_n+\psi_n)/2$. To within small quantities of the next order we find

$$U=\text{const}\int\left[\frac{1}{2}(\gamma+\varepsilon)^2+\frac{1}{2}\left(\gamma-\varepsilon+2\varepsilon\frac{d\Phi}{dx}\right)^2-\frac{4\pi^2V}{\varkappa b^2}\sin\Phi\right]dx. \tag{6}$$

Here it has been taken into account that γ is a small quantity. Minimizing (6) with respect to γ we find

$$\gamma=\frac{2\pi^2V}{\varkappa b^2}\sin\Phi-\varepsilon\frac{d\Phi}{dx}. \tag{7}$$

Substituting (7) into (6), after straightforward transformations we obtain the potential energy of the field Φ:

$$U=\text{const}\int\left[\frac{1}{2}\left(\frac{d\Phi}{dx}-1\right)^2+\left(\frac{\pi V}{2\varkappa b^2\delta}\right)^2\cos2\Phi\right]dx. \tag{8}$$

In the general case ($a/b=M/N+\delta$), analogous though extremely cumbersome calculations lead to a potential energy of the form

$$U=\text{const}\int\left[\frac{1}{2}\left(\frac{d\varphi}{dx}-1\right)^2+\lambda\cos N\varphi\right]dx, \tag{9}$$

where $\lambda\propto V^N/\delta^2$. The quantity φ can be defined as the phase averaged over N successive particles. Thus, the problem of the behavior of weakly incommensurate systems reduces in all cases to a Hamiltonian of the form (3). Minimization of the potential energy from (3) leads to the following equilibrium form φ_0:

$$\varphi_0=2am(x/k+\xi), \tag{10}$$

where am denotes the elliptic amplitude, k is the modulus of the elliptic functions, which is connected

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with h by the relation

$$h=4E(k)/\pi k, \tag{11}$$

and ξ is an arbitrary constant, corresponding to the quasi-translations. The solution (10) exists in the region $h>h_c$, where $h_c=4/\pi$. For $h<h_c$ the minimum of the potential energy corresponds to the constant value $\varphi=\pi(2m+1)$. In the language of the original atomic coordinates $x_n=na+u_n$, constancy of φ implies that the periods of the lattice and the potential coincide (for the case $a/b=1+\delta$) or are commensurate (in cases when $a/b=M/N+\delta$). Thus, at the point $h=h_c$ a phase transition occurs from a commensurate phase (I) to an incommensurate phase (II).

A measure of the incommensurability, determining the difference of the periods of the lattice that is established and the potential, is the quantity $\langle\partial\varphi/\partial x\rangle=2\pi/l$, where l is the period of $\cos\varphi_0$ as a function of x. From (10) we find $l=2kK(k)$ and $\langle\partial\varphi/\partial x\rangle=\pi/kK(k)$. As h decreases from ∞ to h_c the period l increases monotonically from 0 to ∞, and $\langle\partial\varphi/\partial x\rangle$ decreases from ∞ to 0.

In the approximation adopted, phase transitions occur near any rational value of $a/b=M/N+\delta$ for $\delta\sim V^{N/2}$. In other words, a commensurate phase can be found in any neighborhood of an arbitrarily selected value of a/b. However, the total sum of the regions occupied by commensurate phases is small if V is small (it is proportional to $V^{1/2}$). Of course, any temperature or quantum fluctuations will wash out over-fine details of this picture. For example, at a given temperature T it is impossible to distinguish transitions with $N>\ln(T/\varkappa a^2)/\ln(V/\varkappa a^2)$.

We shall now investigate the spectrum of the small oscillations. We represent $\varphi(x,t)$ in the form of a sum $\varphi_0(x)+\psi(x,t)$. In the approximation linear in ψ we obtain the equation

$$\frac{\partial^2\psi}{\partial t^2}=\frac{\partial^2\psi}{\partial x^2}+\cos\varphi_0\psi. \tag{12}$$

It is clear that in the phase I ($\cos\varphi_0=-1$) the spectrum has the form $\Omega^2=1+q^2$, where q is the wave vector. We now consider the phase II. In this case the equation for monochromatic small vibrations:

$$\frac{d^2\psi}{dx^2}+[\Omega^2+\cos\varphi_0]\psi=0, \tag{13}$$

goes over, after the simple transformation $x=zk$, to the well known Lamé equation

$$\frac{d^2\psi}{dz^2}+[k^2(1+\Omega^2)-2k^2\,\mathrm{sn}^2\,z]\psi=0, \tag{14}$$

where snz is the Jacobi elliptic function. The general solution of Eq. (14) has the form[7]

$$\psi=Ae^{z\zeta(a)}\frac{\sigma(z-\omega'-a)}{\sigma(z-\omega')}+Be^{-z\zeta(a)}\frac{\sigma(z-\omega'+a)}{\sigma(z-\omega')}, \tag{15}$$

where $\sigma(z)$ and $\zeta(z)$ are Weierstrass functions, 2ω and $2\omega'$ are the periods of the elliptic functions, A and B are arbitrary constants, and the constant a is determined by the equation

$$\wp(a)=e_1-k^2\Omega^2, \tag{16}$$

where $\wp(z)$ is the elliptic Weierstrass function, and $e_1=(2-k^2)/3$.

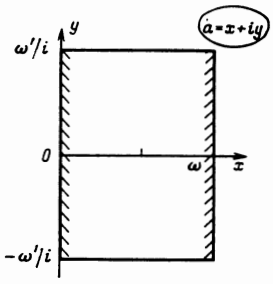

FIG. 1.

Since snz is a periodic function, the solution of Eq. (13) has the form of Bloch waves $\psi(x)=e^{iqx}u(x)$, where $u(x)$ is a periodic function. We are interested only in real values of q. Shifting z by a period and using the properties of $\sigma(z)$,[8] we find the change in the first of the two linearly independent solutions of (15):

$$\psi_1(z+2\omega)=e^{2\omega\zeta(a)-2\eta\omega}\psi_1(z),$$

where $\eta=\zeta(\omega)$. From this we find the quasi-momentum

$$q=\frac{1}{ik}\left[\zeta(a)-\frac{\eta}{\omega}a\right]. \tag{17}$$

The formulas (16) and (17) give the parametric dependence of Ω on q. The condition that q is real determines the set of permissible values of the parameter a. In the parallelogram of the periods this condition consists of the two line segments $a=iy$ and $a=\omega+iy$ with $-\omega'/i<y<\omega'/i$ (see Fig. 1). Corresponding to these two line segments are the two energy bands depicted schematically in Fig. 2. We draw attention to two features of the spectrum. First, only one forbidden region of energies exists. This statement is not absolutely exact. The effects of the discreteness cannot be assumed to be negigibly small when $q\sim 1/\delta$. They lead to the appearance of an infinite number of forbidden bands near $q=2\pi n/\delta+2\pi m/l$, where n and m are arbitrary integers. This implies, in fact, that breaks appear at any point in the spectrum, but the total extent of the forbidden bands is small. A similar picture for the spectrum of the Schrödinger equation has been investigated by Dinaburg and Sinaĭ.[9] The remark about the smearing effect of fluctuations is also fully applicable to the picture of the spectrum considered above. Moreover, in the potential energy (9) we omitted terms of the form $V^N\cos 2N\varphi$, $V^{3N/2}\cos 3N\varphi$, etc., which leads to the appearance of an infinite number of small gaps in the optical band. Secondly, at small q the spectrum is acoustic in character, this being a consequence of the invariance under an arbitrary change of the phase in (10).

From the formulas (16) and (17) it is not difficult to

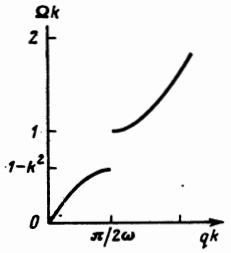

FIG. 2.

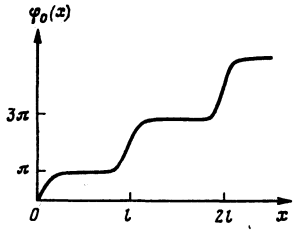

FIG. 3.

find the sound velocity

$$c=(1-k^2)^{1/4}\frac{K(k)}{E(k)}. \tag{18}$$

It is interesting to trace the change in the structure of the ground state and the energy spectrum for values of h close to h_c. The period of the elliptic functions increases like $\sim\ln[1/(h-h_c)]$. The function $\varphi_0(x)$ has the form of a step function. Over the period l the function φ_0 assumes a practically constant value $(2m+1)\,\pi$, and then, over an interval ~ 1, increases by 2π (Fig. 3).

The graph of the function $-\cos\varphi_0$ is shown in Fig. 4. We recall that this is the potential for small oscillations. For oscillations with wavelength $\lambda \ll l$ the periodic character of the potential is unimportant. Therefore, the spectrum of the optical vibrations coincides to within $1/l$ with the vibrational spectrum in the phase I. In addition, the size $2\pi/l$ of the first (acoustic) Brillouin zone decreases like $|\ln(h-h_c)|^{-1}$ as h approaches h_c. The maximum vibrational frequency in the first zone decreases like $(h-h_c)^{1/2}|\ln(h-h_c)|^{-1/2}$. Therefore, the sound velocity tends to zero like $(h-h_c)^{1/2}|\ln(h-h_c)|^{1/2}$. It is not difficult to obtain the same result by direct investigation of formula (18). For large q the vibrational spectrum is again linear: $\Omega \approx q$.

The Hamiltonian (3) has been applied to the description of the phase transitions of helical magnetic structures,[10] a cholesteric liquid crystal in a magnetic field,[11] and the penetration of vortices in a Josephson junction.[12] We shall indicate yet another interpretation, which has been applied in the problem of the movement of a dislocation[13,14]: the quantities x and φ are interpreted as the longitudinal and transverse coordinates of the points of a string situated in a periodic external field. The phase transition in this case is interpreted as the spontaneous breaking of the symmetry with respect to a translation through a period. In the state with broken symmetry the string lies in one valley of the potential contour.

The limits of applicability of the classical approach are determined by the size of the quantum corrections. We shall find them in the framework of the continuum model. We note that the number of independent parameters in the quantum problem is larger than in the classical problem. In fact, we cannot make a change of a scale of φ since this changes the commutation relations of φ and $\dot{\varphi}$. Furthermore, we cannot multiply the Hamiltonian by an arbitrary factor, since this changes the amplitudes of the quantum fluctuations. By changing the scale of the time and coordinates it is possible to put the density and elastic constant equal to unity and bring the Hamiltonian to the following standard form, with three independent constants:

$$H=\int\left[\frac{1}{2}\left(\frac{\partial\varphi}{\partial t}\right)^2+\frac{1}{2}\left(\frac{\partial\varphi}{\partial x}-h\right)^2+V\cos\beta\varphi\right]dx. \tag{19}$$

The ground state of the quantum system described by the Hamiltonian (19) was investigated in a paper by Luther and Pokrovskii.[15] It was shown that for small V the critical value of h coincides with the gap in the excitation spectrum, calculated for $h=0$:

$$h_c=V^{1/(2-\beta^2/4\pi)}Z(\beta,\alpha),$$

where $Z(\beta,\alpha)$ is a slow function of β and of the cutoff parameter (lattice constant) α. The diagram of state in the (h,β^2)-plane is depicted in Fig. 5. The region I corresponds to the commensurate phase and the region II to the incommensurate phase. Near the transition curve, in the region II, the quantity $\langle\partial\varphi/\partial x\rangle$ determining the incommensurability behaves like $(h-h_c)^{1/2}$. At the same time, in the classical picture, $\langle\partial\varphi/\partial x\rangle\propto|\ln(h-h_c)|^{-1}$ for $h\to h_c$. The reason for the contradiction is that the classical treatment is not valid in the immediate vicinity of the transition line. In order to obtain the criterion for applicability of the classical approach we shall consider the mean square fluctuation of the phase difference $\varphi(x)-\varphi(0)$ over a certain characteristic distance x:

$$\langle(\varphi(x)-\varphi(0))^2\rangle \approx\int\frac{dq}{2\pi}(1-e^{iqx})\frac{\hbar}{\rho_0\Omega(q)}. \tag{20}$$

The density ρ_0 can be taken to be unity, but it is necessary to exercise care with Planck's constant. If we wish to use the formulas (16), (17), and (18) for the spectrum of the small oscillations, then in place of the phase φ in the Hamiltonian (19) it is necessary to consider the quantity $\varphi'=\beta\varphi$ and replace t and x by $t'=\beta t$ and $x'=\beta x$. The commutation relation for φ has the form

$$\left[\frac{d\varphi'(x')}{dt'},\varphi'(y')\right]=\beta\left[\frac{d\varphi(x)}{dt},\varphi(y)\right]=\frac{\hbar}{i}\beta\delta(x-y)=\frac{\hbar\beta^2}{i}\delta(x'-y').$$

In order to bring the Hamiltonian (19) to the standard form (3) it is necessary to change the scale of the time and coordinates once more. The constant factor that appears in front of the Hamiltonian is equal to $V^{1/2}$. The product Ht appearing in the S-matrix is invariant

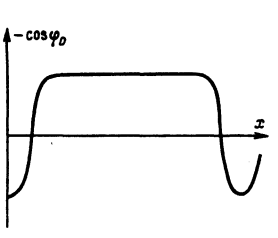

FIG. 4.

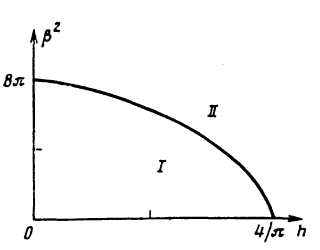

FIG. 5.

in this transformation. Thus, we can use the spectrum obtained earlier and assume the period in φ to be equal to 2π, replacing $\hbar$ by $\hbar\beta^2$. Taking into account what has been said, we shall calculate the fluctuation average (20) for $x \ll l$ ($l = 2kK(k)$ is the period of the incommensurate lattice):

$$\langle(\psi(x)-\psi(0))^2\rangle \approx \frac{\hbar\beta^2}{2\pi}\left(\frac{\pi^2x^2}{2cl^2}+2\ln\frac{l}{\alpha}\right). \quad (21)$$

The two terms in the right-hand side of (21) correspond to the contributions of the acoustic band and optical band. The classical approach is applicable if the quantum phase fluctuations (21) for $x \sim l$ are much smaller then the classical phase difference:

$$\langle(\psi(l)-\psi(0))^2\rangle \ll 4\pi^2.$$

Finally, the criterion for classicality has the form

$$\frac{\hbar\beta^2}{4\pi^2}\left(\frac{1}{c}+\frac{1}{\pi}\ln\frac{l}{\alpha}\right) \ll 1. \quad (22)$$

In order to write this criterion in terms of the "density" ρ_0 and "stiffness" $\varkappa$ (the coefficients of $(\partial\varphi/\partial t)^2$ and $\partial\phi/\partial x)^2$ in the energy density), it is necessary to replace β^2 by the quantity $\beta^2/(\rho_0\varkappa)^{1/2}$. It can be seen from (22) that the region of quasi-classicality corresponds to small β. But, for any fixed β, in a small region $(h-h_c)/h_c \lesssim (\hbar\beta^2/4\pi^2)^2$ about the transition point the quantum fluctuations are large and the classical result is inapplicable. The fact that the region of applicability of the quantum treatment becomes narrower as $\beta \to 0$ is evidently connected with the increase in the number of bound states.

We note that the classical approach becomes meaningless in the limit $\alpha \to 0$. Precisely because of the necessity of a cutoff at short distances, four independent constants (V, h, β, and α) arise in the theory. The mean square fluctuation $\langle\varphi^2\rangle$ diverges, so that the long-range order is destroyed by quantum fluctuations but the fluctuations of $\partial\varphi/\partial x$ are small in the quasiclassical limit, far from the transition point.

The two-dimensional and three-dimensional problems of almost commensurate systems can also be reduced to continuum models. However, even for this simplified problem the exact solution is not known.

When the present work was completed, a preprint by Rice and Theodorou,[16] in which many of the results that we have found are obtained, became known to us. We are grateful to L. P. Gor'kov, who afforded us the opportunity of acquainting ourselves with this preprint.

L. N. Bulaevskiĭ and D. I. Khomskiĭ kindly wrote to us about their paper,[17] in press at the time, in which certain results of the present work were obtained in connection with the problem of charge-density waves in quasi-one-dimensional structures. We are grateful to L. N. Bulaevskiĭ and D. I. Khomskiĭ for this communication and a useful discussion.

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