Transition to an incommensurate phase on an elastic substrate

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The transition to an incommensurate phase on an elastic substrate at finite temperature is investigated. Allowance for thermal fluctuations reduces to a study of the ground state of the corresponding quantum problem that describes the behavior of solitons in an external field. This makes it possible to determine the behavior of the correlation function of a system of adsorbed atoms.

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In view of improved experimental facilities, interest has increased recently in two-dimensional crystal systems, particularly those adsorbed on sufficiently perfect crystalline surfaces.[1]

In many cases the observed adsorbed-atom crystalline phases were not commensurate with the substrate (examples are Cs layers on molybdenum and tungsten, Kr and Xe on graphite, and others). The phase transition into an incommensurate state is the subject of a large number of theoretical papers (see, e.g., Ref. 2 and the bibliography therein). As a rule, simplest models were considered in whic the substrate was assumed to be ideal and strictly periodic. Such models, however, do not describe adequately the real situation in all cases. For a correct description of the transition into an incommensurate phase it is frequently important to take into account the finite elasticity of the substrate. The effect of substrate elasticity on the behavior of adatoms in the ground state is the subject of Refs. 3–5. In a preceding paper[6] I considered the commensurate-to-incommensurate crystal phase transition on an elastic substrate for the one-dimensional quantum problem. Another formulation of the same problem is that of an incommensurate two-dimensional system at finite temperature.

The present paper deals with the behavior of a two-dimensional system on an elastic substrate at nonzero temperature. Study of the statistical properties of the system by the transfer-matrix method reduces to finding the ground state of a one-dimensional quantum system. It is shown here that the system is unstable to the onset of long-wave periodic displacements of the substate atom. This leads to the appearance of a gap in the spectrum of the single-particle excitations of the quantum system. There occur in the system, however, also collective excitations of the charge-density wave, and these duplicate, at large distances, the power-law behavior of the adatom-system correlation function, a behavior peculiar to inelastic substrates.

In the study of two-dimensional systems it is simplest to consider a situation in which the film atoms are adsorbed on crystal faces with a furrowed potential relief of the W(112) type. The adsorbates can be alkali (Li, Na, K, Cs), alkaline-earth (Ba, Sr), and rare-earth (La) elements. The substrates can be W(112), Mo(112) or Ni(110) faces. The symmetries of these structures can differ.[7,8] We consider the simplest case of a rectangular unit cell near a point at which the basic periods of the film and the substrate coincide. Compression (or dilatation) of such a structure with increasing (decreasing) degree of coverage takes place along the furrows of the potential relief. Such a system can be described by a model in which only displacements along the compression direction are considered.[4] In the case of a primitive unit cell, we write the adatom energy in the form

$$U=\int dx\,dy\left\{\frac{\nu}{2}\left(\frac{\partial u}{\partial x}\right)^2+\frac{\mu}{2}\left(\frac{\partial u}{\partial y}\right)^2+V\cos\frac{2\pi}{b}\,(na+u_n)\right\}, \tag{1}$$

where $x = na$, a and b are the respective periods of the film and the substrate, and $u(x, y) \equiv u_n(y)$ is the displacement of the adatoms along the furrows. We assume here that the x axis is along the furrows and y is perpendicular.

The substitution $2\pi(na + u_n)/b = \varphi_n$ and renormalization of the quantities x, y, and φ yields for U/T (T is the system temperature)

$$\frac{U}{T}=\frac{1}{2}\int dx\,dy\left[\left(\frac{\partial\varphi}{\partial x}\right)^2+\left(\frac{\partial\varphi}{\partial y}\right)^2+\gamma\cos\beta\varphi-h\frac{\partial\varphi}{\partial x}\right], \tag{2}$$

$$\beta=\left(\frac{T^2}{\mu\nu}\right)^{1/4},\quad h=2\delta\left(\frac{\mu\nu}{T^2}\right)^{1/4},\quad \gamma=\frac{V}{T},\quad \delta\sim\frac{a-b}{b}. \tag{3}$$

We investigate the statistical properties of the system at finite temperature by studying, using the transition-matrix method[9] the ground state of a one-dimensional quantum system described by the Hamiltonian[10]:

$$\hat{H}=\frac{1}{2}\int dx\left\{\pi^2(x)+\left(\frac{\partial\varphi}{\partial x}\right)^2+\gamma\cos\beta\varphi-h\frac{\partial\varphi}{\partial x}\right\}, \tag{4}$$

where $\pi(x)$ is the field momentum conjugate to the field $\varphi(x)$.

We take the substrate elasticity into account by assuming that long-wave displacements of the atoms were produced in the system. We note directly that account need be taken only of the projections of the displacements $w(x, y)$ on the x axis (i.e., along the furrows). Displacements of the substrate atoms in the perpendicular direction lead to a like displacement of the adatoms (deep potential relief in this direction) that is negligibly small, by virtue of the rigidity of the substrate, compared with the "resonant" [2] displacement of the adatoms in the x direction.

In expression (1) for the energy, the term that describes the interaction of the adatoms with the substrate should be rewritten in the form

$$V\cos\left[\frac{2\pi}{b}\,(na+u_n-w_{m(n)})\right], \tag{5}$$

where $w_{m(n)}$ is the displacement of the substrate upper-layer

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atom m closest to the adatom numbered n (see Ref. 3 for details).

We illustrate first how instability to formation of long-wave displacements in the elastic substrate appears in the system. To this end we assume that a long displacement wave was produced in the substrate in the x direction:

$$w(x, y) = A \sin \alpha x, \quad \alpha \ll 1.$$

We assume here that the rigidity of the substrate is very high ($\varkappa w^2 \gg T$), so that the fluctuations of the atom displacements w can be disregarded. The Hamiltonian (4) is then transformed into

$$\hat{H} = \frac{1}{2} \int \left[\pi^2(x) + \left(\frac{\partial \varphi}{\partial x} - h + h_1 \cos \alpha x \right)^2 + \gamma \cos \beta \varphi \right] dx. \quad (6)$$

The behavior of a one-dimensional quantum system with such a Hamiltonian in the vicinity of the value of the parameter $\beta^2 = 4\pi$ was investigated in Ref. 6 and is briefly restated here.

The classical ground state of an incommensurate phase can be treated as statistical periodically repeating solitions. At nonzero temperature the solitons begin to bend. In a one-dimensional quantum problem the solitons can be regarded as particles that obey Fermi statistics. The transformation to the solition representation is by constructing the fermion operators[11]:

$$\Psi_{1,2} = \frac{1}{(2\pi a)^{1/2}} : \exp \left\{ -\frac{2\pi}{\beta} \int_{-\infty}^{x} \dot{\varphi}(\xi)\, d\xi \pm i \frac{\beta}{2} \varphi \right\} :.$$

In the case $\beta^2 = 4\pi$, i.e., at a fixed value $T = 4\pi(\mu\nu)^{1/2}$ of the temperature, the solitons do not interact with one another. The incommensurability h plays the role of the chemical potential of these particles: $\zeta = h/\beta$. When ζ exceeds the size m of the gap, particles begin to predominate over antiparticles in the soliton spectrum, meaning a transition to the incommensurate phase.[12] The term proportional to h_1 in the Hamiltonian (6) leads to the appearance in the soliton system of an external periodic field that produces a gap in the soliton spectrum. Let $h = h_0 > m\beta$. We denote the solition momentum corresponding to this energy in the spectrum by $p_F = (\zeta^2 - m^2)^{1/2}$. A Peierls instability appears in the spectrum: conditions become favorable for a displacement wave $w(x, y) = A \sin \alpha x$ with wave vector $\alpha = 2p_F$ modulated in the x direction to appear in the system. This produces in the soliton system a field with a wave vector $2p_F = 2(\zeta^2 - m^2)^{1/2}$ and this in turn leads to formation in the spectrum of a gap in the spectrum at $p = p_F$, and the process becomes energetically preferred. We have thus shown that the system is unstable to formation, in an elastic substrate, of a deformation wave modulated in the x direction and having a wave vector $2p_F = (\zeta^2 - m^2)^{1/2}$, with $\zeta = 2\delta(\mu\nu)^{1/2}T$ and $|\zeta - m| \ll 1$ at a value $T = 4\pi(\mu\nu)^{1/2}$. The solition spectrum is then separated from the ground state by a gap.

To study the correlation properties of adatoms in such a system it is necessary to solve the problem more systematically by considering the long-wave displacements in the substrate. This makes it necessary to consider in the fermion problem not only static external fields but also time-dependent ones.

We shall assume that the upper layer of the substrate interacts with the adsorbed film more strongly than with the remaining layers, so that the latter interaction can be neglected. An equivalent situation (wherein the substrate is simulated by a single layer) arises in the case of a very thin substrate. The qualitative result obtained under these assumptions is generalized to the case of a substrate of arbitrary thickness.

We shall find it convenient to introduce in place of the Hamiltonian (4) the Lagrangian of the system in the form

$$\mathcal{L} = \frac{1}{2} \int dx\, dt \left[\left(\frac{\partial \varphi}{\partial t} \right)^2 - \left(\frac{\partial \varphi}{\partial x} \right)^2 + h \frac{\partial \varphi}{\partial x} - \gamma \cos \beta (\varphi - w_1) \right], \quad (7)$$

where $w_1 = w/\beta$. By an obvious change of variables this expression can be rewritten in the form

$$\mathcal{L} = \frac{1}{2} \int dx\, dt \left[\left(\frac{\partial \varphi}{\partial t} \right)^2 + 2 \frac{\partial w_1}{\partial t} \frac{\partial \varphi}{\partial t} - \left(\frac{\partial \varphi}{\partial x} \right)^2 - 2 \frac{\partial w_1}{\partial x} \frac{\partial \varphi}{\partial x} + h \frac{\partial \varphi}{\partial x} - \gamma \cos \beta \varphi \right]. \quad (8)$$

Transforming to the fermion representation, we obtain for the solitons the Lagrangian

$$\mathcal{L} = \int dx\, dt \left\{ \bar{\Psi} \gamma_0 \left[i\partial_0 + \frac{1}{\beta} \left(2 \frac{\partial w_1}{\partial x} - h \right) \right] \Psi + \bar{\Psi} \gamma_1 \left[i\partial_1 + \frac{2}{\beta} \frac{\partial w_1}{\partial t} \right] \Psi - m \bar{\Psi} \Psi - \frac{1}{2} g j_\mu j^\mu \right\}, \quad (9)$$

which describes a fermion system of relativistic solitions in an external one-dimensional "electromagnetic" field. As before, we assume here that $\beta^2 = 4\pi$, which corresponds to $g = 0$.

We carry out the gauge transformation

$$\begin{aligned} \Psi(x) &\to \Psi'(x) = e^{if(x)} \Psi(x), \\ \Psi^*(x) &\to \Psi^{*\prime}(x) = e^{-if(x)} \Psi^*(x), \\ A_i(x) &\to A_i'(x) = A_i(x) + \frac{\partial f}{\partial x_i}, \end{aligned} \quad (10)$$

where

$$A_0 = \frac{2}{\beta} \frac{\partial w_1}{\partial x}, \quad A_1 = \frac{2}{\beta} \frac{\partial w_1}{\partial t}.$$

After choosing the appropriate gauge we obtain then an expression containing only one vector-potential component:

$$\mathcal{L} = \int dx\, dt [\bar{\Psi} \gamma_1 i\partial_1 \Psi + \bar{\Psi} \gamma_0 (i\partial_0 - U(x, t) - h/\beta) \Psi - m \bar{\Psi} \Psi] dx, \quad (11)$$

where

$$U(x, t) = \frac{2}{\beta} \left(\frac{\partial w_1}{\partial x} - \frac{\partial^2}{\partial t^2} \int_0^x w_1(\xi, t)\, d\xi \right), \quad m = 2\pi^2 \gamma.$$

We discuss now the conditions imposed on the soliton system by the closest-approach requirement, which we use from the very outset when writing the expressions for the adatom energy. The closest-approach condition is equivalent to the requirement $\partial u/\partial x \ll 1$, which by virtue of the relation $\langle n \rangle = (\beta/2\pi)\langle 2\varphi/\partial x \rangle$, which relates the solition density to the phase gradient, is equivalent to the requirement that $\langle n \rangle$ be small. It is easy to show that this condition

is valid when the relation $|\zeta - m| \ll 1$ holds, where $\zeta = h/\beta$, this condition is equivalent to the requirement $p_F^2 \ll 1$ (p_F is the solition momentum corresponding to the energy ζ, i.e., the maximum solition momentum). In the case when the substrate potential relief is not very small, so that $m \sim 1$, we obtain $p_F \ll m$, meaning that the fermion system is nonrelativistic. To describe the behavior of the solitions in the considered region of the transition into the incommensurate phase we can therefore use the Schrödinger equation in place of the relativistic Dirac equation. For our case it takes the form

$$i\frac{\partial\varphi}{\partial t} = \left[\frac{1}{2m}\hat{p}^2 + U(x,t)\right]\varphi, \tag{12}$$

where $\varphi = (\Psi_1 + \Psi_2)/\sqrt{2}$, $\Psi_1 \approx \Psi_2$. If the potential relief of the substrate is small, so that $m \ll 1$, the nonrelativistic approximation is valid in a narrower region of the phase transition than called for by the continuity condition.

Thus, the behavior of the adatoms on an elastic substrate is described in the considered vicinity by the Schrödinger equation for nonrelativistic solitions in the "deformation potential" $U(x, t)$.

To take into acount the thermodynamic fluctuations of the substrate-atoms displacement field (fluctuations neglected up to now), it is necessary to quantize the deformation potential $U(x, t)$ in the fermion problem. The energy connected with the substrate deformation is quadratic in the field $w(x, y)$, meaning also in $v(x, y)$, the latter connected with $U(x, t)$ by the relation $\partial v(x, t)/\partial x = U(x, t)$. Consequently, after expanding the field $v(x, t)$ in plane waves, the Hamiltonian of the "phonon" field of the substrate takes the standard form

$$\hat{H}_1 = \sum_q \omega_q b_q^+ b_q,$$

and the total Hamiltonian of the system of nonrelativistic fermions interacting with the phonons takes in the second-quantization representation the form of the Frölich Hamiltonian

$$\hat{H} = \sum_k \varepsilon_k a_k^+ a_k + \sum_q \omega_q b_q^+ b_q + \sum_{k,q} g_q (b_q a_{k+q}^+ a_k - b_{-q}^+ a_k^+ a_{k+q}). \tag{13}$$

At small q the quantity g_q is also small by virtue of its proportionality to q. We shall hereafter neglect the dependence of g_q on q and regard it to be a small consant equal to g_Q, since all the expressions used will contain the quantity g_q and q close or equal to A. The perturbation-theory expansion will be in powers of this constant.

The spectrum of the single-particle excitations of such an "electronic" system is separated, owing to the interaction with the phonons, by a gap from the ground state. We shall see below, however, that this does not lead to an exponential decrease of the correlation function with distance, since there exist in the system collective excitations due to the onset of a charge-density wave with wave vector $Q = 2p_F$.[13] In the calculation of the correlation function, the contribution that determines its behavior comes from the collective mode.

The correlation function

$$\mathcal{K}(\mathbf{x}-\mathbf{x}') = \langle \exp\,[ik(u(\mathbf{x}) - u(\mathbf{x}')]\rangle,$$

in which the averaging is over the thermodynamic fluctuations of the system and k is the basis reciprocal-lattice vector along the x axis, in view of the fact that

$$\exp\,[iku(\mathbf{x})] = \exp\,(-i2\pi\delta)\,\exp\,(i\beta\varphi) = \exp\,(-i2\pi\delta x)\,(\Psi_1^+\Psi_2)\,2\pi a,$$

can be written in the form

$$\mathcal{K}(\mathbf{x}-\mathbf{x}') = \langle \Psi_1^+(\mathbf{x})\,\Psi_2(\mathbf{x})\,\Psi_2^+(\mathbf{x}')\,\Psi_1(\mathbf{x}')\rangle. \tag{14}$$

Instead of averaging over the thermal fluctuations we take here the vacuum mean in the fermion system.

In the nonrelativistic approximation used by us, we calculate this mean value by a formalism developed in Ref. 14. Following this reference, we introduce the following electron and phonon Green functions:

$$G_{mn}(\mathbf{k}, t) = i\langle T(c_{\mathbf{k}+mQ/2}(t)\, c^+_{\mathbf{k}+nQ/2}(0))\rangle,$$

$$m, n = \pm, \quad |k| < Q/2.$$

$$D_{mn}(\mathbf{q}, t) = -\frac{i}{\omega_Q}\langle T(b_{mQ+\mathbf{q}}(t)\, b^+_{nQ+\mathbf{q}}(0))\rangle, \quad m, n = \pm.$$

In the self-consistent approximation we have

$$\begin{pmatrix} G_{++}(\mathbf{k},\omega) & G_{+-}(\mathbf{k},\omega) \\ G_{-+}(\mathbf{k},\omega) & G_{--}(\mathbf{k},\omega)\end{pmatrix} = \begin{pmatrix} \omega-\varepsilon_{\mathbf{k}-Q/2} & \Delta \\ \Delta & \omega-\varepsilon_{\mathbf{k}+Q/2}\end{pmatrix}[(\omega-\varepsilon_{\mathbf{k}-Q/2})(\omega-\varepsilon_{\mathbf{k}+Q/2})-\Delta^2]^{-1}, \tag{15}$$

and the rule of bypassing the poles is specified in the usual manner: a positive pole is bypassed in the upper half-plane, and a negative in the lower.

$$A_\pm(\mathbf{q},\omega) = {}^1/_2(D_{++}(\mathbf{q},\omega) \pm D_{+-}(\mathbf{q},\omega)) = (1 - m/m^*)/(\omega_\pm^2 - \omega^2), \tag{16}$$

where

$$\omega_+^2 = \lambda\omega_Q^2 + {}^4/_3\left(\frac{m}{m^*}\right)v_F^2q^2, \quad \omega_-^2 = \left(\frac{m}{m^*}\right)v_F^2q^2,$$

$$\frac{m^*}{m} = 1 + 4\frac{\Delta^2}{\lambda\omega_Q^2}, \quad \lambda = \frac{g^2}{\omega_Q\varepsilon_F}.$$

The contribution of the collective mode to the correlation function is graphically represented by the two diagrams in the figure and leads to a power-law decrease of the correlation function at large distances. In fact, the sum of these two diagrams is described by the expression

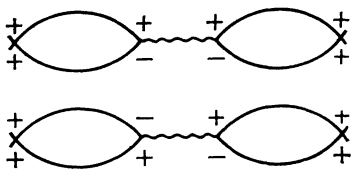

FIG. 1.

$$-\frac{1}{2}g^2\int G_{++}(\mathbf{k},\omega)\,G_{+-}(\mathbf{k}+\mathbf{q},\omega+\nu)\,A_-(\mathbf{q},\nu)$$
$$\times G_{++}(\mathbf{p},\varepsilon)\,G_{+-}(\mathbf{p}-\mathbf{q},\varepsilon-\nu)\,d\omega\,d\varepsilon\,d\mathbf{k}\,d\mathbf{p}. \tag{17}$$

Substituting here the value $A_-(\mathbf{q},\nu)=\frac{1}{2}(D_{++}-D_{+-})$ from (16), we easily find the asymptotic behavior of the Fourier transform of this expression at large distances. As a result we obtain

$$\mathcal{K}(x,y)\infty\frac{x^2-\alpha y^2}{(x^2+\alpha y^2)^2},$$
$$\alpha=\frac{m}{m^*}\frac{\mu}{\nu}v_F^2=\left(1+\frac{4\Delta^2}{\lambda\omega_Q^2}\right)^{-1}\frac{\mu}{\nu}v_F^2, \tag{18}$$

i.e., at large distances the correlation function of the adatoms decreases in power-law fashion.

Our calculations can thus be ended by the deduction that allowance for the finite elasticity of the substrate does not change qualitatively the correlation properties of the atoms adsorbed on it.

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