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Localization of a Gaussian polymer in a weak periodic surface potential disturbed by a single defect

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Abstract. Using the results of the recently studied problem of adsorption of a Gaussian polymer in a weak periodic surface potential we study the influence of a single rod like defect on the polymer being localized in the periodic surface potential. We have found that the polymer will be localized at the defect under condition $u > u_c$, where u_c is the localization threshold in the periodic potential, for any infinitesimal strength of the interaction with defect. We predict that the concentration of monomers of the localized polymer decays exponentially as a function of the distance to the defect and is modulated with the period of the surface potential.

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1 Introduction

Adsorption of polymers at surfaces and interfaces is of large interest in different topics of science and technology and has been investigated extensively in recent years [1–4] (and citations therein). The effects of surface heterogeneities, which is of wide interest for different applications such as pattern recognition, technological and biological applications etc., have been studied in [5–14]. Recently, we have considered the problem of adsorption of a Gaussian polymer in a weak periodic surface potential [15]. We present here the details of these calculations and apply the method we used in [15] to study the localization of a Gaussian polymer in the periodic surface potential disturbed by a single defect.

The problem of the behaviour of a Gaussian polymer in an external potential is equivalent to the problem of the behaviour of a quantum mechanical particle in an external potential [1,2]. According to this mapping our results for polymer adsorption are valid for localization of a quantum mechanical particle in the periodic external potential. In the case of polymer the periodic surface potential can be realized by the surface of a microphase separated diblock copolymer melt (see for example [16,17] and references therein), while in the quantum mechanical counterpart of the problem in context of semiconductor superlattices [18] (and references therein).

The paper is organized as follow. After brief introduction to the model and the Green's function method in Section 2, we consider in details the problem of adsorption of a polymer chain in a weak periodic surface potential. In Section 3 we study the effect of a single defect on the polymer being localized in the periodic surface potential.

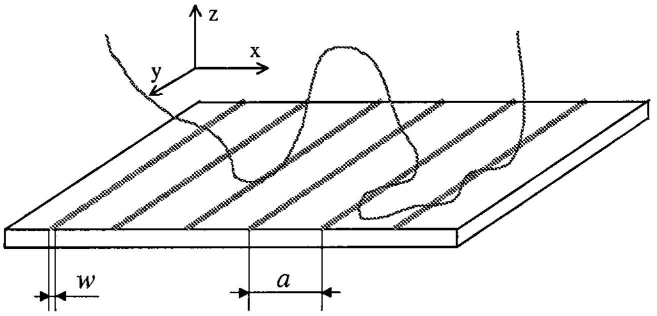

Fig. 1. The periodic surface, which is modelled by the potential in equation (1).

2 Adsorption of a polymer in the periodic surface potential

The periodic surface potential can be described by

$$V(x,y,z) = -u\delta(z-z_0)\sum_{n=-\infty}^{\infty}\delta(x-na), \qquad (1)$$

where u, a, z_0 are assumed to be positive, and $\delta(x)$ is the Dirac's delta-function. The potential models rods which are parallel to the y axis with the distance a along the x axis between the next neighbors (see Fig. 1). The size of the rods w, which is suppressed in (1), is however a relevant quantity as it will be shown below. Due to the impenetrability of the wall at $z = 0$ the distance of the

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potential well to the surface is chosen as z_0. As it is well-know from Quantum Mechanics [19] the delta-function potential corresponds to the shallow potential well. The limit to the homogeneously attracting surface can be obtained from (1) by $a \to 0$ and $u/a \to \text{const}$ (see below).

The Green's function of a polymer in an external potential, which gives the relative number of conformations of the chain with the ends fixed at $\mathbf{r}$ and $\mathbf{r}'$, obeys the following equation

$$\frac{\partial}{\partial N}G(\mathbf{r},N;\mathbf{r}') - D\nabla^2 G(x,z,N;x',z') + \frac{V(\mathbf{r})}{k_BT}G = 0 \tag{2}$$

with condition $G(\mathbf{r},0;\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$. Here N is the polymerization degree of the ideal chain and $D = l^2/6$, where l is the statistical segment length of the chain. The equation (2) can be written as an integral equation as follows

$$\begin{aligned} G(x,z,N;x',z') &= G_0(x,z,N;x',z') \\ &- \int_0^N \mathrm{d}s \int_{-\infty}^{\infty} \mathrm{d}x_1 \int_0^{\infty} \mathrm{d}z_1 G_0(x,z,N-s;x_1,z_1) \\ &\times \frac{V(x_1,z_1)}{k_BT} G(x_1,z_1,s;x',z'), \end{aligned} \tag{3}$$

where

$$\begin{aligned} G_0(x,z,N;x',z') &= \frac{1}{4\pi DN}\exp\left(-\frac{(x-x')^2}{4DN}\right) \\ &\times \left[\exp\left(-\frac{(z-z')^2}{4DN}\right) - \exp\left(-\frac{(z+z')^2}{4DN}\right)\right] \end{aligned} \tag{4}$$

for $N \geq 0$ and is zero for $N < 0$. Equation (2) is related to the Schrödinger equation by using the replacements: $N = \mathrm{i}t$, $l^2/3k_BT = 1/m$, $k_BT = \hbar$. The bare Green's function $G_0(x,z,N;x',z')$ is the solution of the diffusion equation *i.e.* equation (2) with $V(\mathbf{r}) = 0$ in the half space, $z \geq 0$, with the Dirichlet boundary condition at $z = 0$. The dependence on y in equation (3) is separated while the potential is independent of y. Inserting the potential (1) into (3) and carrying out the Laplace transform with respect to N we arrive at

$$\begin{aligned} G(x,z,p;x',z') &= G_0(x,z,p;x',z') \\ &+ u\sum_{n=-\infty}^{\infty} G_0(x,z,p;an,z_0)G(an,z_0,p;x',z'), \end{aligned} \tag{5}$$

where

$$\begin{aligned} &G_0(x,z,p;x',z') \\ &= \frac{1}{2\pi D}(K_0(\sqrt{(x-x')^2+(z-z')^2}\sqrt{p/D}) \\ &-K_0(\sqrt{(x-x')^2+(z+z')^2}\sqrt{p/D})), \end{aligned} \tag{6}$$

is the Laplace transform of (4), $K_0(x)$ is the modified Bessel function of the second kind. Henceforth u is given in units of k_BT. In the case of adsorption onto an interface only the first term on the right-hand side of (6) appears. Restricting the summation in (5) to only one term gives the problem of localization onto one rod. Neglecting the z-dependence in (5) and using

$$G_0(x,p;x') = 1/\sqrt{4Dp}\exp(-\left|x-x'\right|\sqrt{p/D}) \tag{7}$$

instead of (6) gives the Green's function formulation of the well-known Kronig-Penney model [20]. The Kronig-Penney model was used in [21] to study the behaviour of a polymer in a striped potential.

We now will solve equations (5). Inserting $x = an$, $n = 0, \pm 1, ...$ and $z = z_0$ into (5) we obtain an infinite inhomogeneous system of equations for $G(an,z_0,p;x',z')$

$$\begin{aligned} G(an,z_0,p;x',z') - u\sum_{m=-\infty}^{\infty} G_0(an,z_0,p;am,z_0) \\ \times G(am,z_0,p;x',z') = G_0(an,z_0,p;x',z'). \end{aligned} \tag{8}$$

The periodicity of the potential (1) along the x axis, which entails the Bloch theorem for the wave function [22], permits to solve the system of equations (8) by using the Fourier transformation. Assuming that the system consists of $2M+1$ rods we consider the discrete Fourier transform for each rod-dependent quantity F_n as follows $F_n = \sum_k \mathrm{e}^{\mathrm{i}kan} f_k$, where $k = \frac{2\pi}{a}\frac{j}{(2M+1)}$, $(j = -M, ..., M)$ is the quasimomentum. Substituting $G(an,z_0,p;x',z') = \sum_k \mathrm{e}^{\mathrm{i}kan} g_k$ and $G_0(an,z_0,p;x',z') = \sum_k \mathrm{e}^{\mathrm{i}kan} b_k$ into (8) diagonalizes the latter (in the limit of large M), so that we obtain the solution as

$$g_k = \frac{b_k}{1 - u\sum\limits_{m=-M}^{M} \mathrm{e}^{\mathrm{i}kam} G_0(am,z_0,p;0,z_0)}\cdot \tag{9}$$

The inverse Fourier transform of (9) gives

$$\begin{aligned} G(an,z_0,p;x',z') &= \frac{1}{2M+1}\sum_k \frac{1}{1-uR(k,p)} \\ &\times \left[\sum_{m=-M}^{M} \mathrm{e}^{\mathrm{i}ka(n-m)} G_0(am,z_0,p;x',z')\right], \end{aligned} \tag{10}$$

where we have introduced the function

$$\begin{aligned} R(k,p) &= G_0(0,z_0,p;0,z_0) \\ &+ 2\sum_{m=1}^{\infty}\cos(mka)G_0(am,z_0,p;0,z_0). \end{aligned} \tag{11}$$

Insertion of (10) into (5) gives $G(x,z,p;x',z')$ as

$$\begin{aligned} G(x,z,p;x',z') &= G_0(x,z,p;x',z') \\ &+ \frac{u}{2M+1}\sum_k \sum_{n=-M}^{M}\sum_{m=-M}^{M} \frac{\exp(\mathrm{i}ka(n-m))}{1-uR(k,p)} \\ &\times G_0(x,z,p;an,z_0)G_0(am,z_0,p;x',z'). \end{aligned} \tag{12}$$

In the limit $M \to \infty$ the sum over k should be replaced by the integral in agreement with $\sum_k f(k) \to (2M+1)(a/2\pi)\int \mathrm{d}k f(k)$. The zeros of the denominator of (12) give the main contributions to $G(x,z,N;x',z')$ for large N. Taking into account the latter generates the spectral expansion of the Green's function

$$G(x,z,N;x',z') \simeq \sum_k \mathrm{e}^{p_k N}\psi_k(x,z)\psi_k^*(x',z'), \qquad (13)$$

where $\psi_k(x,z)$ and p_k are eigenfunctions and eigenvalues of the time-independent Schrödinger equation

$$-D\nabla^2\psi_k(x,z) + \frac{V(\mathbf{r})}{k_B T}\psi_k(x,z) = -p_k\psi_k(x,z). \qquad (14)$$

Thus, the zeros of the denominator in equation (12) considered as function of p gives the energy eigenvalues $-p_k$. The comparison of the inverse Laplace transform of equation (12) with (13) gives the following expression for the wave functions

$$\psi_k(x,z) \sim \sum_{n=-\infty}^{\infty} \mathrm{e}^{\mathrm{i}kan} G_0(x,z,p_k;an,z_0). \qquad (15)$$

It is easy to check that (15) fulfils the Bloch theorem. Notice that the exact wave function $\psi_k(x,z)$ is given as the Laplace transform of the bare Green's function.

We now will show how to recover from (12) the case of continuously attracting surface. The first two terms in the denominator of (12) corresponds to the eigenvalue condition for a rod. If a is small, the sum can be replaced by the integral as follows $\sum_{m=1}^{\infty} f(ma) \to a^{-1}\int_0^{\infty}\mathrm{d}x f(x)$. The quantity $u/a = \overline{u}$ is the surface density of the strength of the potential. The integral over x with $f(x) = G_0(x,z_0,p;0,z_0)$ gives

$$\int_0^{\infty}\mathrm{d}x\cos(kx)G_0(x,z_0,p;0,z_0) = 1/(4\sqrt{D}\sqrt{p+Dk^2}) \times(1-\exp(-2z_0/\sqrt{D}\sqrt{p+Dk^2})). \qquad (16)$$

The case of adsorption onto a homogeneously attracting surface will be recovered by taking the limit $u \to 0$, $a \to 0$ and $u/a = \overline{u}$. As it was pointed in [23] for the case of continuously interface the transverse degree of freedom are decoupled to the in-plain degree of freedom, since the latter can be integrated out in the definition of Green's function. The full Green's function can be obtained from the reduced Green's function by replacing the Laplace transform variable p through $p + Dk^2$, where k is the wave vector corresponding to the Fourier transformation with respect to the in-plane coordinates. The term Dk^2 is simply the energy of free motion along the surface. If we are interested in studying the localization at the surface only and do not consider migration of polymer along the surface we can put the quasimomentum $k = 0$. The second term in the denominator of (12) disappears in the limit $u \to 0$, so that the denominator of (12) gives the correct eigenvalue condition, $1 - \frac{\overline{u}}{2\sqrt{pD}}(1-\exp(-2z_0\sqrt{p/D})) = 0$, for adsorption onto a homogeneously attracting surface with the potential $u(z) = -\overline{u}\delta(z-z_0)$.

Equation (12) applies to the Kronig-Penney model if one neglects there the dependences on z. The bare Green's function is then given by equation (7). As a result the denominator in (12) yields

$$\frac{\cos(ka) - \cosh(\sqrt{a^2p/D}) + u/(2\sqrt{Dp})\sinh(\sqrt{a^2p/D})}{\cos(ka)-\cosh(\sqrt{a^2p/D})}. \qquad (17)$$

The numerator of (17) equated to zero gives the well-known energy eigenvalue condition for Kronig-Penney model.

We now will consider the case of the periodic surface potential given by (1). The bare Green's function obeys the Dirichlet boundary condition at $z = 0$ and is given by (4). Its Laplace transform is given by

$$G_0(am,z_0,p;0,z_0) = 1/(2\pi D)(K_0(am\sqrt{p/D}) - K_0(\sqrt{a^2m^2+4z_0^2}\sqrt{p/D})). \qquad (18)$$

The divergence of (18) for $am \to 0$, which is due to modelling the potential by Dirac's delta-function, can be avoided by replacing N in the first term of the expression $G_0(0,z_0,N;0,z_0) = 1/(4\pi DN) - 1/(4\pi DN)\exp(-z_0^2/DN)$ by $N + b$ with b being a microscopic cutoff along the polymer (corresponds to time in QM language), will be related to the size of the potential well w. The necessity of introduction of the cutoff b is due to the following. The interaction potential of one rod is product of two delta functions, *i.e.* the problem is two dimensional. It is well-known from Quantum mechanics [19] that in two dimensional potential well the eigenenergy depends on both the depth and the width of the potential well separately. The comparison of the binding energy in the potential $-u\delta(x)\delta(z-z_0)$ obtained *via* the present method with the energy in a shallow two dimensional potential well [19] gives $b = w^2/4D$, where w is the radius of the potential well. The Laplace transform of $G_0(0,z_0,N;0,z_0)$ is then obtained as

$$G_0(0,z_0,p;0,z_0) = -\frac{\mathrm{e}^{bp}\mathrm{Ei}(-bp)}{4\pi D} - \frac{1}{2\pi D}K_0(2\sqrt{pz_0^2/D}), \qquad (19)$$

where $\mathrm{Ei}(-x) = \int_{-\infty}^{-x}\mathrm{d}t\exp(t)/t$ is the exponential integral. Notice that we can avoid the introduction of a cutoff at intermediate steps of the work by replacing one of delta-functions in equation (1) by the d-dimensional delta-function with $d < 1$ and introducing the cutoff in carrying out the limit $d \to 1$. Using (18) and (19) gives the denominator of (12) as

$$1 + \frac{u}{4\pi D}\exp(bp)\mathrm{Ei}(-bp) + \frac{u}{2\pi D}K_0(2\sqrt{pz_0^2/D}) - \frac{u}{\pi D}\sum_{m=1}^{\infty}\cos(amk)\Big[K_0(am\sqrt{p/D}) - K_0(\sqrt{a^2m^2+4z_0^2}\sqrt{p/D})\Big]. \qquad (20)$$

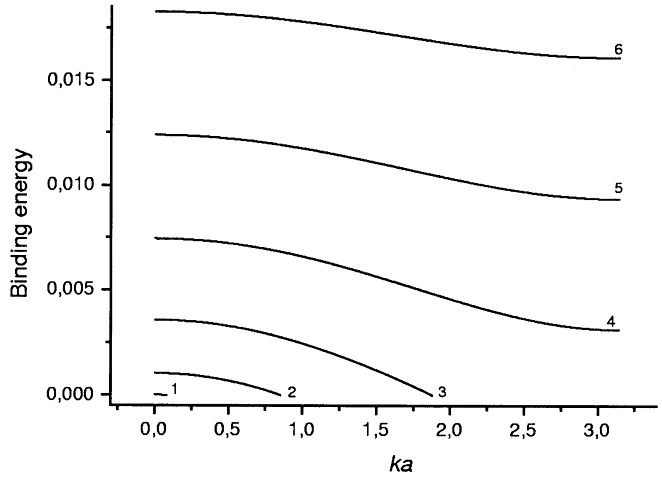

Fig. 2. The localization band for $w = 1$, $z_0 = 2$, $a = 10$ measured in units of l for following strengths of the potential: 1. $u = 0.55$; 2. $u = 0.6$; 3. $u = 0.65$; 4. $u = 0.7$; 5. $u = 0.75$; 6. $u = 0.8$. The localized states appears for $u > u_c$: $u_c = 0.54$. For $u < 0.674$ the quasimomentum of localized states does not exceed the value $k_{max} < \pi/a$, for $u > 0.674$ the localized states exist up to the edge of the Brillouin zone.

Considering (20) as an equation for p gives the spectrum of the problem under consideration. The sum in (20) cannot be performed exactly, so that we have solved equation (20) for p numerically. The localized states appears, if u exceeds some threshold value u_c. Figure 2 shows the binding energy as a function of the quasimomentum k for different strengths u. Figure 2 demonstrates that the localized states in the periodic potential form a band with the width depending on the strength of the potential u. The localized states exist, if the quasimomentum does not exceed the value $k_{\max}$. In contrast to a homogeneously attracting surface, the in-plane degrees of freedom here are coupled to the transversal degree of freedom. We expect that the width of the localization band influences the migration of the localized polymer chain along the surface. Due to the fact that the width is controlled by the temperature, the in-plane migration of the polymer will be controlled by temperature. We expect that also in the quantum mechanical counterpart of the problem the finite width band of surface localized states will affect the in-plane properties (see below).

We now will consider the mean-square distance of one end of the polymer chain to the surface, which has to be computed according to

$$\left\langle z^2(N)\right\rangle = \frac{\int\limits_{-\infty}^{\infty} \mathrm{d}x \int\limits_{0}^{\infty} \mathrm{d}z \int\limits_{0}^{a} \mathrm{d}x' z^2 G(x,z,N;x',0)}{\int\limits_{-\infty}^{\infty} \mathrm{d}x \int\limits_{0}^{\infty} \mathrm{d}z \int\limits_{0}^{a} \mathrm{d}x' G(x,z,N;x',0)}, \quad (21)$$

where the integration over x' is carried for simplicity over the period of potential. To evaluate the (21) we have to perform the inverse Laplace transform of (12). In the limit of large chain lengths $N \to \infty$ the main contribution to the inverse Laplace transform appears from the residues associated with the poles. The computation of $\langle z^2\rangle = \lim_{N\to\infty}\langle z^2(N)\rangle$ is straightforward and results in

$$\left\langle z^2\right\rangle = \frac{2D}{p_0} + \frac{z_0^2}{1-\exp\left(-z_0\sqrt{p_0/D}\right)}, \quad (22)$$

where p_0 is the absolute value of the ground state eigenenergy associated with the quasimomentum $k = 0$. It is surprising that the states with $k > 0$ do not contribute to $\left\langle z^2\right\rangle$. We have checked that the same holds for the mean square-distance of an arbitrary monomer, and for the monomer distribution function $\rho(x,z)$. This is due to the fact that after integrating over x (x') in equation (12) the sum over n (m) gives $\delta(k)$ so that only the ground state contributes to $\left\langle z^2\right\rangle$.

The obtained spectrum allows us to investigate the in-plane behavior of adsorbed polymer. Due to the periodicity of the potential the long polymer chain behaves in plane as free chain endowed with effective statistical segment length l_{eff}^2. To define the effective statistical segment we compute the x-component of the mean-square end-to-end distance of the adsorbed polymer for large N by using equation (12) and find that

$$\left\langle\, (x-x')^2\right\rangle = \frac{1}{3} l_{\text{eff}}^2 N, \quad (23)$$

where the effective statistical segment length

$$l_{\text{eff}}^2 = -3\partial^2 p_k/\partial k^2 \,|_{k=0}$$

can be represented as

$$l_{\text{eff}}^2 = 3\left.\frac{\partial^2 R(k,p)}{\partial k^2}\right|_{\substack{k=0\\ p=p_0}} \left[\left.\frac{\partial R(k,p)}{\partial p}\right|_{\substack{k=0\\ p=p_0}}\right]^{-1}.$$

Notice that l_{eff} defined in (23) relates to the behaviour of the polymer along the x-axes. The numerical evaluation of l_{eff} is shown in Figure 3 for three values of the period of the potential a. At the localization transition l_{eff} is equal to l. It strongly decreases for large p_0 *i.e.* in the regime of strong adsorption. For large strength of the potential well u all pieces of the polymer are localized at the surface, so that in this limit the problem of the localization in the surface periodic potential converts to the Kronig-Penney model. It is well-known that for this model the effective statistical segment is smaller than the bare one [21]. The squeezing of the polymer due to $l_{\text{eff}} < l$ can be explained by the fact that the polymer wins energy while the portions of the polymer make excursions along the attracting rods as it shown in Figure 1. This results in squeezing the polymer along the periodicity direction. Notice that the squeezing of the polymer occurs at the expense of the transversal size of the polymer. The size of the polymer along the y-axes does not change. Figure 3 shows that the decrease of a results in a weaker decrease of l_{eff}. The numerical analysis of the behaviour of l_{eff} in the vicinity of the localization transition for parameters $w = 1$, $z_0 = 2$, $a = 3$ yields that $l_{\text{eff}}/l = 1.0044 > 1$ for $p_0 = 0.002$, *i.e.* l_{eff} has a weak maximum as a function of p_0 (see Fig. 3).

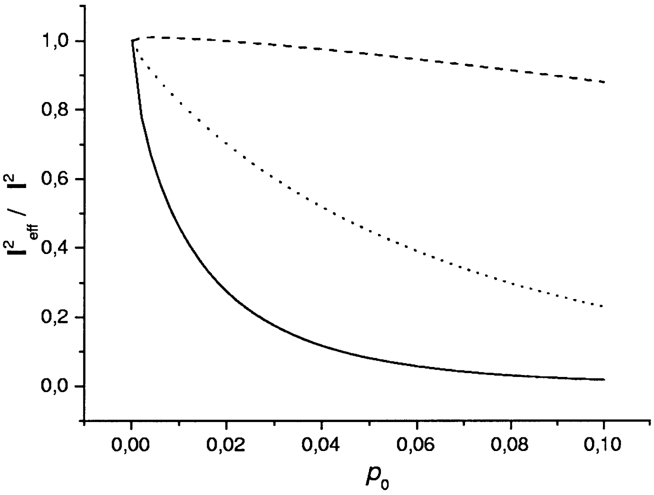

Fig. 3. The effective statistical segment length as a function of the binding energy p_0 for $w = 1$, $z_0 = 2$ measured in units of l. Dashed line: $a = 3$; Dotted line: $a = 6$; Continuous line: $a = 10$.

The latter disappears for larger values of a. The condition $l_{\mathrm{eff}} > l$ means that the polymer stretches along the x-axes. Due to this the polymer wins energy by having contacts with more rods. We expect that the maximum is due to the rigidity of the polymer, which however cannot be described in a more consistent way by the present model.

In context of the behaviour of a quantum particle (for example an electron) in a surface periodic potential the motion of the particle along the surface can be described in terms of the effective mass m^*, which is the counterpart of the statistical segment length and is proportional to l_{eff}^{-2}. Notice, that the above explanation of the inequality $l_{\mathrm{eff}} < l$ in terms of configurations of the polymer chain implicates an explanation of the inequality $m^* > m$ in terms of time-space trajectories of the quantum particle. The increase of the mass is related to the size of the pieces of the trajectory localized at the same rod. Using the well-known formula for electric conductivity in Solid State Physics (see for example [24]) we write the surface electric conductivity as $\sigma = e^2\tau n/m^*$, where m^* is the effective mass, e is the electron charge, τ is the relaxation time, and n is the surface electron density. We expect that this formula is valid for a weakly filled band, while in the opposite case of an almost filled band we have to take into account the effect of the delocalization of electrons due to the external field. According to Figure 3 the effective mass is nearly everywhere larger than the bare mass. It increases with the increase of the strength of the potential, excepting the vicinity of the localization transition, which is in agreement with the prediction for Kronig-Penney model. According to the dependence of σ on m^* we expect that the surface electric conductivity is a decreasing function of the strength of the potential. This is intuitively clear because if the size of the pieces of the trajectory of the particle along one rod is large, the driving field is ineffective to disengage the latter from the rod.

3 Localization at a single surface defect

The real surfaces contain various defects, so that studying their effect on adsorption of polymers is an important question. In this section we consider the localization of the polymer chain in a periodic surface potential disturbed by a single defect. The surface potential in the presence of the extended defect, which can be viewed as the additional rod situated at $x = x_0$, is modeled by the following potential

$$V(\mathbf{r}) = -u\delta(z-z_0)\sum_{n=-\infty}^{\infty}\delta(x-na) - v\delta(x-x_0)\delta(z-z_0), \tag{24}$$

where v is the strength of the defect. The method developed in Section 2 can be used in a straightforward way to study the effect of the defect. For this aim we use the system with the periodic potential (1) as the reference state, where the Green's function $G(x, z, N; x', z')$ in the periodic potential is given by equation (10). Considering the last term in equation (24) as perturbation we rewrite the equation (2) as an integral equation as follows

$$G_d(x, z, N; x', z') = G(x, z, N; x', z') + v\int_0^N \mathrm{d}s G(x, z, N-s; x_0, z_0)G_d(x_0, z_0, s; x', z'). \tag{25}$$

Henceforth the potential of defect v as the strength of the periodic potential u is given in units of k_BT. The explicit expression for $G(x, z, N; x', z')$ appearing in (25) can be derived by using the inverse Laplace transform of (12). Carrying out the Laplace transform of (25) we arrive at the following algebraic equation

$$G_d(x, z, p; x', z') = G(x, z, p; x', z') + vG(x, z, p; x_0, z_0)G_d(x_0, z_0, p; x', z'). \tag{26}$$

To solve this equation we substitute $x = x_0, z = z_0$ and find

$$G_d(x_0, z_0, p; x', z') = \frac{G(x_0, z_0, p; x', z')}{1 - vG(x_0, z_0, p; x_0, z_0)}\cdot \tag{27}$$

Therefore, the Green's function G_d of the problem with potential (24) can be expressed in terms of the Green's function G of the system with the ideal periodic potential as follows

$$G_d(x, z, p; x', z') = G(x, z, p; x', z') + v\frac{G(x, z, p; x_0, z_0)G(x_0, z_0, p; x', z')}{1 - vG(x_0, z_0, p; x_0, z_0)}\cdot \tag{28}$$

The zero of the denominator in the last term of (28) gives the value of the eigenenergy of the state when polymer chain is localized at the defect. The eigenenergy condition

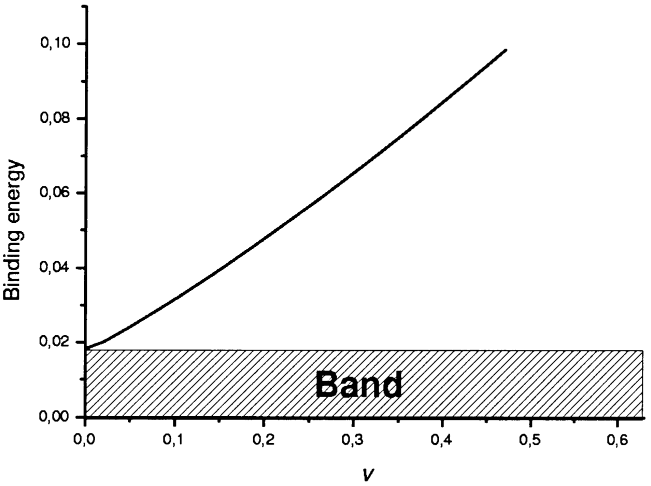

Fig. 4. The binding energy of localized in-plane ground state as function of the defect's potential v for $w = 1$, $a = 10$, $z_0 = 2$, $u = 0.8$. At $v = 0$ the energy coincide with the energy corresponding to the upper edge of the band.

is obtained from (28) as

$$1 - vG_0(x_0, z_0, p; x_0, z_0) - uv\frac{a}{\pi}\int_{-\pi}^{\pi}\frac{\mathrm{d}k}{1 - uR(k,p)} \times \sum_{n,m=-\infty}^{\infty} \mathrm{e}^{\mathrm{i}ka(n-m)} G_0(x_0, z_0, p; an, z_0) \times G_0(am, z_0, p; x_0, z_0) = 0, \tag{29}$$

where we have taken the limit $N \to \infty$. Equation (29) cannot be solved analytically so that we analyzed it numerically. We consider the case of extended adsorbing defect ($v > 0$) which is situated at $x_0 = 0$. This allows us to simplify the equation (29), so that we obtain

$$1 - vG_0(0, z_0, p; 0, z_0) - uv\frac{a}{\pi}\int_{-\pi}^{\pi}\mathrm{d}k\frac{[R(k,p)]^2}{1 - uR(k,p)} = 0. \tag{30}$$

The numerical calculation shows that upon condition $u > u_c$, where u_c is the threshold value of the periodic potential, the equation (30) has a single solution $p_d(v)$ starting at the upper edge of the band $p_d(0) = p_0$ which increases with the strength of the defect v. The typical dependence of p_d on v is shown in Figure 4. Figure 4 shows that the polymer is localized for any infinitesimal potential of the defect v, if there are localized states in the periodic potential. The eigenfunction corresponding to the eigenvalue p_d is obtained from (28) using the spectral expansion of the Green's function (13) as

$$\psi_d \sim G_0(x, z, p_d; 0, z_0) + u\frac{a}{\pi}\int_{-\pi}^{\pi}\mathrm{d}k\frac{R(k,p_d)}{1 - uR(k,p_d)} \times \sum_{m=-\infty}^{\infty}\cos(mka)G_0(x, z, p_d; am, z_0). \tag{31}$$

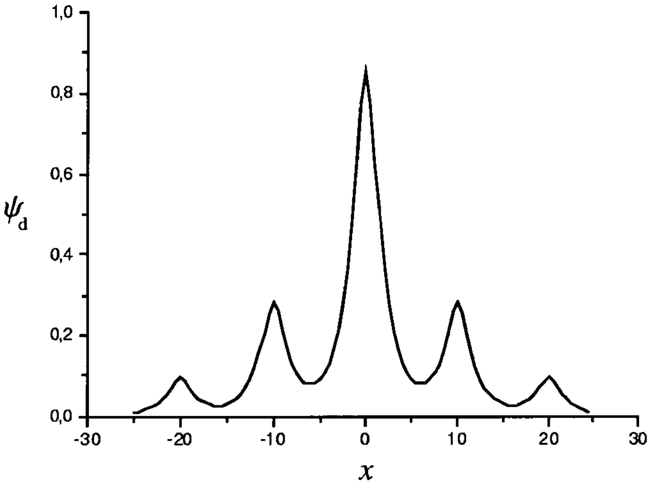

Fig. 5. The profile of wave function $\psi_d(x, z)$ in the plane $z = 3$ for $w = 1$, $a = 10$, $z_0 = 2$, $u = 0.8$, $v = 0.01$.

The function $\psi_d(x, z)$ decays exponentially as function of the distance to the defect and is modulated with the period of the periodic surface potential (see Fig. 5). Due to the gap between the localized state and the band we have the situation of the ground state dominance, if the polymer chain is large enough. The consequence of this is that only the eigenfunction (31) contributes to the Green's function (13). It is well-known that in this case the concentration of monomers is given by $c(r) \sim |\psi_d(r)|^2$ [2], so that the oscillations of $\psi_d(r)$ may be observed experimentally by studying the distribution of polymer chains on the periodic surfaces with defects.

4 Conclusion

We have considered the adsorption of a Gaussian polymer (and of a quantum particle) onto an attracting surface with potential periodic along one direction. We have found that the surface localized states form a band which can be described by the quasimomentum entailed by the periodicity of the surface potential. The width of the localization band depends on the strength of the attracting potential. The binding energy decreases with increase of the quasimomentum and becomes zero at $k = k_{\max}$, where for not to large strengths u of the periodic potential $k_{\max}$ lies within Brillouin zone, *i.e.* $k_{\max} < \pi/a$. For $k_{\max} < k < \pi/a$ no localized states exist. For sufficiently strong potential strengths (when $k_{\max}$ becomes equal to π/a) the polymer is always localized.

We have studied the effect of perturbation of the periodic potential by a single rod-like defect on the adsorption of the polymer. We have found that the defect localizes the polymer for any infinitesimal strength of the defect potential, so that the concentration of monomers decays exponentially with the distance to the defect and undergoes modulation associated with the periodic surface potential. We expect, that this oscillations can be observed experimentally by studying the distribution of polymer chains on the periodic surfaces with defects.

The method used here can be straightforwardly applied to treat more complicated periodic arrangements (ideal or with weak deviations from the periodicity) of attracting wells, for example the infinite periodic set of parallel planes along the z-axes with the potential in each of the plane being periodic along the x- and y-axes.

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