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1990 J. Phys.: Condens. Matter 2 9025

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Phonon modes at the reconstructed surface of a cubic lattice

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Received 1 March 1990

Abstract. We consider the $(\sqrt{2} \times \sqrt{2})R45^\circ$ -reconstruction on the (001) surface of a simple cubic lattice with interaction forces acting between nearest neighbours according to Hooke's law. Using Feynman's complex-time path integral we find the energy of the surface, which provides the usual T^2 law for specific heat. We come to the conclusion that the energy of zero point vibrations at the surface, which can be compared to the Casimir energy, could influence the phenomenon of reconstruction at low temperatures.

1. Introduction

The key point about the reconstruction is that the periodicities of the crystal's surface and bulk are coordinated. It should be noted that the topmost layer of atoms forming the reconstructed surface cannot be obtained by simply terminating the crystal's bulk lattice at a plane. In this paper, in accord with the classical Gibbs approach, we shall consider the topmost layers of the crystal's atoms forming its surface to be a separate system interacting with its bulk in such a way that there is a relation between their periodicities.

In what follows we shall assume that the crystal and its surface are in thermal equilibrium with a reservoir at temperature θ , so that the canonical partition function of the whole reads

$$Z = \text{Tr}(e^{-\beta H}).$$

Here H is the Hamiltonian of the system comprised of the surface and the bulk, and $\beta = \theta^{-1}$.

To separate thermal properties of the bulk and the surface we shall write the canonical partition function as the product

$$Z = Z_s Z_b \tag{1}$$

where Z_s is assigned to the surface and Z_b to the bulk (see the discussion of this procedure by Dash 1975, ch IV).

Feynman's complex-time path integral provides a means of obtaining the factorization. Let us assume that the crystal's dynamics are described by a Lagrangian L , then the canonical partition function is given by the path integral (see Feynman 1972)

$$Z = \int D x \exp\left(\frac{i}{\hbar} S\right) \quad (2)$$

where S is the complex-time action, x are displacements of atoms from equilibrium positions, and

$$S = \int_0^{-i\beta\hbar} L(x, \dot{x}) dt. \quad (3)$$

Following the idea of the paper by Schwinger (1961) on Brownian motion of quantum oscillators, we propose to study thermodynamical properties of the surface lattice by constructing, within the framework of the harmonic approximation and using path-integral technique, an effective Lagrangian that gives the right description of the surface dynamics by accommodating the influence of the bulk on the surface with the help of a Green function. The total Lagrangian of the system is to be resolved as follows:

$$L = L_s^{\text{eff}} + L_b^{\text{eff}}. \quad (4)$$

Here L_b^{eff} is an effective Lagrangian for the bulk. From equations (2–4) we infer that the factorization (1) is to take place.

In studying reconstructed surfaces it is helpful to employ model considerations to obtain results in closed analytic form. In this paper we use the Montroll–Potts model (see Wallis 1959) in which atomic sites in the bulk form a simple cubic lattice, each atom interacting with its nearest neighbours according to Hooke's law. The model is a crude picture of real crystal; for example, it is not rotationally invariant and consequently its predictions may disagree with the theory of elasticity (see Maradudin and Wallis 1966). Nonetheless, its mathematical simplicity provides a means to carry out a fairly complete analysis and, as is generally accepted, it permits one to obtain qualitative information concerning the crystal's dynamics for a wide range of its determining factors, i.e. masses of atoms and force constants.

The Montroll–Potts model has enough structure to mimic reconstruction. In this paper we assume that the crystalline lattice occupies a very large volume in the half space determined by the requirement $z \geq 0$, and the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ -reconstruction (see figures 1, 2) takes place at the (001) face corresponding to $z = 0$ plane in space. Free boundary conditions are imposed on the reconstructed surface. We do not intend to study edge or angle modes of the crystal's vibrations, and in accord with the theorem by Ledermann (1944) we may neglect specifying boundary conditions at faces different from the $z = 0$ one (see section 3).

We take such a spatial scale that the distance between two nearest neighbours in the bulk is equal to one, so that equilibrium positions of atoms in the bulk are given by integer vectors of the form

$$j = (j_1, j_2, j_3) \quad j_1, j_2 = 0, \pm 1, \pm 2, \dots \quad j_3 = 1, 2, \dots$$

The monoatomic layer of the reconstructed surface is formed by atoms of mass M ; their equilibrium positions are:

$$l_1 = \frac{1}{2} + m_1 - m_2 \quad l_2 = m_1 + m_2 \quad l_3 = 0 \quad m_1, m_2 = 0, \pm 1, \pm 2, \dots \quad (5)$$

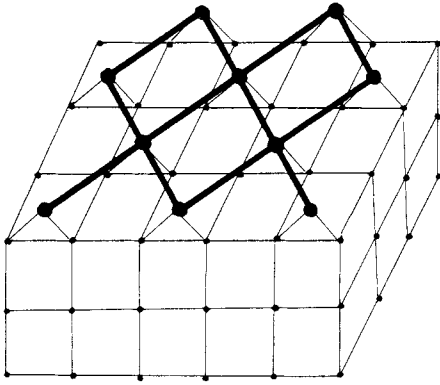


Figure 1. Simple cubic lattice with the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction on the (001) face. Thick lines indicate interaction between surface atoms. Thin lines indicate interaction with atoms in the bulk.

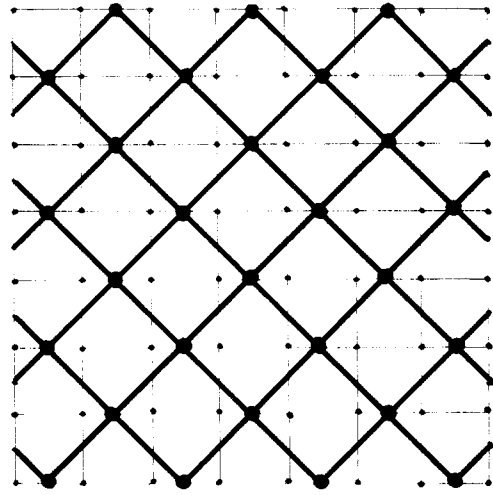


Figure 2. Top view of the reconstructed surface.

We assume that atoms interact according to Hooke's law—each atom in the bulk with its six nearest neighbours, and each atom at the surface with two nearest neighbours in the first layer of the bulk and four nearest neighbours at the surface—so that, on the whole, each atom of the lattice has six bonds (see figures 1 and 2). The ratio M/m , where m is the mass of a bulk atom, is to a certain extent a characteristic of interaction between surface and bulk; for heavy surface atoms, $M \gg m$, we consider it to be small, for $M \ll m$, we consider it large.

We may consider the surface lattice to be the square centred one; in this case both lattices have commensurate periods, 1 and 2. As the surface lattice now has two atoms per elementary cell, we must allow for optical modes as well as acoustic ones. But it is important that until the interaction between the surface and the bulk is neglected, the difference between them is spurious, because it does not involve the existence of a gap that determines a physical optical mode. We shall see that for small enough ratio M/m , optical modes do appear.

2. Symmetry of reconstructed surfaces

As was mentioned, there is a relation between the symmetry of the bulk lattice and that of the surface one, which is seen most clearly with regard to displacements parallel to the surface. Wood (1964) and Fingerland (1972) indicated that the relation may be cast in the form of a requirement that the symmetry group of the surface lattice must be a sub-group of the bulk one. This statement may turn out to be useful for classification of possible surface crystalline structures, or phases. It is important that the symmetry of reconstruction in x, y, z space generates a symmetry in momentum space that establishes a relation between Brillouin zones of the surface and bulk lattices. We shall put forward

our arguments within the framework of the Montroll–Potts model and for the specific case of the reconstruction considered in this paper, but it is obvious that they are of quite general nature.

Since we set the spatial scale equal to one, the Brillouin zone for the bulk lattice is given by the inequalities

$$-\pi \leq q_i \leq +\pi \quad i = 1, 2, 3$$

and for the surface it is two dimensional and given by

$$-\frac{1}{2}\pi \leq k_i \leq +\frac{1}{2}\pi \quad i = 1, 2.$$

Let us consider the cross section B_s of the bulk Brillouin zone given by the constraint $q_3 = 0$; it corresponds to displacements parallel to the surface. This cross section has a special relationship with the surface Brillouin zone. To see this, let us notice that the wave numbers k_i are determined up to summand $\pm\pi$, so that if we have a value of k_i outside the interval $-\pi/2, +\pi/2$ we may reduce it to the necessary size by subtracting or adding π the necessary number of times. Therefore, we obtain the same point of the surface Brillouin zone. But if we make the same subtractions or additions for a point in the bulk Brillouin zone, we obtain a set of transformations given by the following formulae:

$$\begin{aligned} g_1: q_1 &\rightarrow q_1 + \pi & q_2 &\rightarrow q_2 \\ g_2: q_1 &\rightarrow q_1 & q_2 &\rightarrow q_2 + \pi \\ g_3: q_1 &\rightarrow q_1 + \pi & q_2 &\rightarrow q_2 + \pi \end{aligned} \tag{6}$$

and the wave number q_3 remaining the same for all g_i . The transformations given above act on the cross section B_s and, together with the unit transformation g_0 that leaves all the q_i in their places, form a group of the fourth order, i.e. consisting of four elements, which we shall denote R_c . It is important that, if we identify all the points that are transformed into each other by transformations (6), we obtain the Brillouin zone for the surface.

3. Surface interaction with the bulk lattice

The dynamics of the crystal with the reconstructed surface described above can be determined by the Lagrangian L . It is straightforward to write an explicit form for L , and we shall not do it. We aim at finding the effective Lagrangians of equation (4) and to that end we shall write L in the form

$$L = L_s + L_b + L_l$$

where L_s, L_b, L_l are determined as follows.

The Langrangian L_s is given by purely surface terms of L and quadratic terms generated by the interaction, according to Hooke's law, of surface atoms with those in the first layer of the bulk. It reads

$$L_s = \sum_{m_1, 2 = -\infty}^{+\infty} \left(\frac{1}{2} M \dot{x}_l^2 - \sum_{\mu=1}^2 \frac{1}{2} \tau_\mu (x_{l+\mu} - x_l)^2 - \sigma_3 x_l^2 \right). \tag{7}$$

Here x_l are displacements of surface atoms from equilibrium positions l given by equations (5); τ_μ are force constants; μ are vectors given by the equations

$$\mu = (-(-1)^\mu, 1, 0) \quad \mu = 1, 2. \tag{8}$$

σ_3 is the bulk force constant in direction z . Similarly, the bulk term L_b is given by bulk

terms of L and a quadratic term related to the interaction between the bulk and the surface:

$$L_b = \sum_{j_{1,2}=-\infty}^{+\infty} \sum_{j_3=1}^{+\infty} \left(\frac{1}{2} m \dot{x}_j^2 - \sum_{i=1}^3 \frac{1}{2} \sigma_i (x_{j+i} - x_j)^2 - \frac{1}{2} \delta_{j_3,1} \sigma_3 x_j^2 \right). \quad (9)$$

Here x_j are displacements of atoms in the bulk from their equilibrium positions; σ_i , $i = 1, 2, 3$ are force constants; \mathbf{i} are vectors given by the equations

$$\mathbf{i} = (\delta_{i1}, \delta_{i2}, \delta_{i3}).$$

The part L_1 is assembled from terms of L that are not incorporated in either L_s or L_b . It has the meaning of an interaction between the surface and the bulk:

$$L_1 = \sigma_3 \sum_{j_{1,2}=-\infty}^{+\infty} \delta_{j_3,1} \mathbf{x}_j \cdot \mathbf{x}_l. \quad (10)$$

Here \mathbf{l} are given by equations compatible with those of (5):

$$\mathbf{l} = \left(j_1 + \frac{1}{2} (-1)^{j_1+j_2}, j_2, 0 \right). \quad (11)$$

Following Feynman (1972) we shall impose the periodicity constraints in complex time on the displacements

$$\mathbf{x}_j(t) = \mathbf{x}_j(t + i\beta\hbar).$$

So far we have made no requirements concerning boundary conditions on the crystal's faces. The conventional constraint—periodic boundary conditions—is not appropriate in the situation of reconstructed surface. We may assume the free boundary condition at the reconstructed surface, and set the fixed boundary condition (FBC) at other faces of the crystal, which we may visualize as a large cube. Then, as can be inferred from the theorem by Ledermann (1944) (see also Maradudin *et al* 1963, ch II), for a sufficiently large crystal size, the change in density of states (eigenvalues) for either bulk modes, or surface modes of the reconstructed surface, due to the imposition of FBC, is negligible.

Having accepted the FBC, we might use expansions of the displacements in functions that are equal to zero at the boundaries (for example, $\sin x$). But again in the situation of the reconstructed surface this procedure would lead to awkward formulae. We feel that the best approach is to take the cube large enough so that we may perform all expansions as if it occupied half space. Then we may work with the Dirac δ -functions, which turn out to be very helpful in calculations that involve wavevectors from two different Brillouin zones, the surface and the bulk one.

To obtain the factorization formula (1) we need a transformation that splits up the surface and the bulk dynamical variables, and results in formula (4) for the effective Lagrangians. Since our Lagrangian is quadratic, we may use the path integration technique of Popov (1976) and Kleinert (1978).

Let us consider the transformation

$$\mathbf{x}_j \rightarrow \mathbf{x}_j + \boldsymbol{\eta}_j$$

here $\boldsymbol{\eta}_j$ are functions at lattice sites, and we assume that they are equal to zero at sites of the reconstructed surface

$$\boldsymbol{\eta}_j|_{\text{surf}} \equiv 0 \quad (12)$$

so that displacements \mathbf{x}_j of atoms at the surface are not affected by the transformation.

Substituting transformed x_j in the Lagrangian and requiring that terms linear in x_j with $j_3 = 1$ be equal to zero, we get the equation:

$$m\partial_t^2 \boldsymbol{\eta}_j - \sum_{i=1}^3 \sigma_i \Delta_i \boldsymbol{\eta}_j = \sigma_3 \delta_{j_3,1} \mathbf{x}_l \tag{13}$$

$$\Delta_i \boldsymbol{\eta}_j = \boldsymbol{\eta}_{j+i} - 2\boldsymbol{\eta}_j + \boldsymbol{\eta}_{j-i}.$$

Here l are given by equations (11). The Langrangian finally takes on the form (4), in which the effective Lagrangian L_s^{eff} reads:

$$L_s^{\text{eff}} = L_s + \frac{1}{2} \sum_{j_{1,2}=-\infty}^{+\infty} \delta_{j_3,1} \mathbf{x}_l \cdot \mathbf{x}_j. \tag{14}$$

Here L_s is the initial surface Lagrangian given by (7). The last term in equation (14) accommodates the influence of the bulk on the surface.

To get an explicit form for L_s^{eff} we may employ the Green function of equation (13) with zero boundary values at the surface sites, owing to the constraint given by equation (12). Here it should be noticed that the constraint is very important in that it enables us to solve equation (13) in half space, instead of using a sophisticated mesh involved with the reconstructed surface.

To obtain an explicit form for the Green function we use the Fourier transform in complex time defined by

$$f(t) = \sum_{n=-\infty}^{+\infty} f(\omega_n) e^{-i\omega_n t} \tag{15}$$

$$f(\omega_n) = \frac{1}{-i\beta\hbar} \int_0^{-i\beta\hbar} f(t) e^{i\omega_n t} dt \quad \omega_n = \frac{2\pi n}{-i\beta\hbar}$$

and the Fourier transform in the lattice

$$f_q = \sum_{j_{1,2,3}=-\infty}^{+\infty} f_j \exp[i(\mathbf{j} \cdot \mathbf{q})] \quad -\pi \leq q_{1,2,3} \leq +\pi$$

$$f_j = \int_{-\pi}^{+\pi} \frac{d^3 q}{(2\pi)^3} f_q \exp[-i(\mathbf{j} \cdot \mathbf{q})].$$

Using the Fourier transforms indicated above we may cast the Green function in the following form:

$$G(\omega_n, \mathbf{j}, \mathbf{j}^0) = -\frac{1}{-i\beta\hbar} \int_{-\pi}^{+\pi} \frac{d^3 q}{(2\pi)^3} \sin(q_3 j_3) \times \sin(q_3 j_3^0) \exp\left[-i \sum_{i=1}^2 q_i (j_i - j_i^0)\right] / \left(\omega_n^2 m - 4 \sum_{i=1}^3 \sigma_i \sin^2(\frac{1}{2} q_i)\right).$$

It should be taken into account that the Green function equals zero at the surface.

Using the Green function indicated above we cast the solution $\boldsymbol{\eta}_j$ to equation (13) with the boundary condition (12) in the form.

$$\boldsymbol{\eta}_j = \sigma_3 \sum_{j_{1,2,3}^0 = -\infty}^{+\infty} G(\omega_n, \mathbf{j}, \mathbf{j}^0) \delta_{j_3^0, 1} \mathbf{x}_l(\omega_n).$$

Here l are given by equations (11). On substituting the equation given above in equation (13), we obtain the explicit form for L_s^{eff} . Using similar arguments we get L_b^{eff} and, finally, equation (4).

4. Canonical partition function

Thermodynamic functions of a system can be derived from its canonical partition function; for the reconstructed surface considered in this paper, that means from Z_s^{eff} . To obtain an expression for Z_s^{eff} we may use its definition by means of the path integral, which reads:

$$Z_s^{\text{eff}} = \int D\mathbf{x}_l \exp\left(\frac{i}{\hbar} \int_0^{-i\beta\hbar} L_s^{\text{eff}} dt\right). \quad (16)$$

Following Feynman (1972) who applied path integrals to the polaron problem, we shall evaluate equation (16) by using a Fourier transform of the action in the exponent. The point is that we need such a transform that allows for the geometry of the reconstructed surface and reduces evaluations of the path integral to calculating infinite products.

Let us notice that the coordinates of equilibrium sites of the surface can be cast in the form

$$\begin{aligned} l_1 &= \frac{1}{2} + 2p + \mu & l_2 &= 2q + \mu & l_3 &= 0 \\ \mu &= 0, 1 & p, q &= 0, \pm 1, \pm 2 \end{aligned} \quad (17)$$

compatible with those given by (5). In what follows we shall neglect the third, zero, coordinate. The Fourier transform we need reads:

$$U_k^l(t) = \frac{1}{\sqrt{A}} \sum_{p, q = -\infty}^{+\infty} x_l(t) \exp[i(2pk_1 + 2qk_2)] \quad (18)$$

where $l = (l_1, l_2)$; p, q are determined by equation (17) and $\mu = 0, 1$. The wave numbers k_1, k_2 take values in the Brillouin zone of the surface:

$$-\frac{1}{2}\pi \leq k_1, k_2 \leq +\frac{1}{2}\pi.$$

A is the area of the reconstructed surface.

The reasons for putting the factor $1/\sqrt{A}$ into equation (18) are twofold. Firstly, we need to cast our formulae in such a shape that the dependence of thermodynamic functions on area is explicit. Secondly, the series in p, q , generally, does not converge, and we should understand it in the sense of the theory of generalized functions. But, as was stated earlier, the crystal is assumed to occupy a very large cube, so that the surface we consider is a very large square, and series like that in equation (18) are sums with very large limits of summation. Therefore, the factor $1/\sqrt{A}$ in the right-hand side has the meaning of the regularization constant for, generally, a very large sum.

After some computations using the Fourier transform in time (15) and in lattice (18), we cast the effective action in the form

$$S_s^{\text{eff}} = i\beta\hbar \sum_{n=-\infty}^{+\infty} A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} \tilde{W}_k^n \cdot D_k^n W_k^n \tag{19}$$

where W_k^n is the two-vector

$$W_k^n = (U_k^0(\omega_n), U_k^1(\omega_n))$$

and ω_n are the Matsubara frequencies $\omega_n = 2\pi n/(-i\beta\hbar)$. The operator D_k^n has the matrix form

$$D_k^n = \begin{pmatrix} P_k^n & Q_k^n \exp[i(k_1 + k_2)] \\ Q_k^n \exp[-i(k_1 + k_2)] & P_k^n \end{pmatrix}. \tag{20}$$

The operators P_k^n and Q_k^n are given by the equations

$$P_k^n = -M\omega_n^2 + 2\sigma_3 + 2(\tau_1 + \tau_2) + \sigma_3^2 I_A \tag{21}$$

$$Q_k^n = 2\tau_1 \cos(k_1 + k_2) + 2\tau_2 \cos(k_1 - k_2) - \sigma_3^2 I_B. \tag{22}$$

The functions I_A, I_B will be specified below (see equations (26), (27)). It should be noticed that, since the displacements x_i are real, we have the constraint

$$\tilde{W}_k^n = W_{-k}^{-n}. \tag{23}$$

While performing the Fourier transform of the second term in equation (14), we face two different periodicities: that of the surface, equal to two, and of the bulk, equal to one. The latter appeared owing to the Green function we used to solve equation (13). These two different periodicities result in different sizes of the Brillouin zones for surface and bulk (see Section 2) and, quantitatively, generate the symmetry group R_c of the reconstruction. In deriving the off-diagonal terms in equation (14) we have used the formula

$$\sum_{m=-\infty}^{+\infty} e^{imx} = 2\pi \sum_{m=-\infty}^{+\infty} \delta(x - 2\pi m).$$

We may cast the formula for Z_s^{eff} in the form

$$Z_s^{\text{eff}} = \int DW_k^n \exp\left(-\frac{i}{\hbar} \sum_{n=-\infty}^{+\infty} \sum_k \tilde{W}_k^n \cdot D_k^n W_k^n\right).$$

Here we have changed the integration in k for the summation using the general prescription

$$\sum_k = A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2}.$$

The factor $i\beta\hbar$ in the right-hand side of equation (19) is taken into account in the functional integration measure of the equation given above. Employing the technique

of functional integration (see Kleinert 1978) and taking into account constraint (23), we may cast Z_s^{eff} in the form

$$Z_s^{\text{eff}} = J \prod_{n=-\infty}^{+\infty} \left(\det D_k^n \right)^{-1/2}.$$

The normalizing constant J does not depend on dynamical characteristics of the system, i.e. masses and force constants. From the equation given above we infer that the energy reads

$$E_s = -\frac{\partial}{\partial \beta} \ln Z_s^{\text{eff}} = -\frac{\partial}{\partial \beta} \ln J - \frac{1}{\beta} \sum_{n=-\infty}^{+\infty} \left(\frac{X_- + (\beta/2)(\partial/\partial \beta)X_-}{M\omega_n^2 - X_-} + \frac{X_+ + (\beta/2)(\partial/\partial \beta)X_+}{M\omega_n^2 - X_+} \right) \quad (24)$$

with the functions X_{\pm} given by

$$X_- = 4\tau_1 \sin^2[(k_1 + k_2)/2] + 4\tau_2 \sin^2[(k_1 - k_2)/2] + 2\sigma_3 + \sigma_3^2(I_A + I_B)$$

$$X_+ = 4\tau_1 \cos^2[(k_1 + k_2)/2] + 4\tau_2 \cos^2[(k_1 - k_2)/2] + 2\sigma_3 + \sigma_3^2(I_A - I_B).$$

The functions I_A, I_B are defined as follows. Consider the basic integral

$$I = \int_{-\pi}^{+\pi} \frac{dx}{2\pi} \frac{\sin^2 x}{\omega_n^2 m - 4\sum_{i=1}^2 \sigma_i \sin^2 \frac{1}{2}k_i - 4\sigma_3 \sin^2 \frac{1}{2}x}. \quad (25)$$

If we have a function $f(k_1, k_2)$ of the coordinates k_1, k_2 , the group Rc (see Section 2) acts on it:

$${}^g f(k_1, k_2) = f(gk_1, gk_2).$$

Here g is an element of Rc . Using these notations we may write the function I_A in the form

$$I_A = \sum_{g \in Rc} {}^g I \quad (26)$$

of the transforms of integral (25) under the action of elements of Rc . Similarly, we may write I_B in the form

$$I_B = \sum_{g \in Rc} \chi(g) {}^g I. \quad (27)$$

Here $\chi(g)$ is the character of the group Rc , i.e. the function valued in the set $-1, +1$, for which we have

$$\chi(gg') = \chi(g)\chi(g') \quad \chi(g_1) = \chi(g_2) = -1.$$

In what follows we shall also need the analytical continuation for the right-hand side of (24) and functions I_A, I_B . Explicit expressions for them can be obtained using the integral

$$J(z) = \int_{-\pi}^{+\pi} \frac{dx}{2\pi} \frac{\sin^2 x}{z + \cos x} = \begin{cases} z + \sqrt{z^2 - 1}, & z < -1 \\ z - i\sqrt{z^2 - 1}, & -1 < z < +1 \\ z - \sqrt{z^2 - 1}, & 1 < z. \end{cases} \quad (28)$$

To find the analytical continuation given above we take the function determined by the

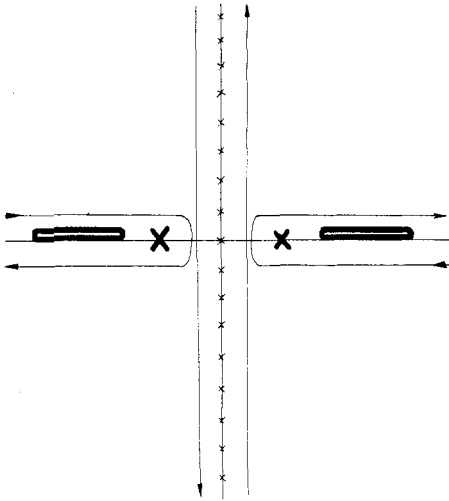


Figure 3. Integration contour in equation (29).

first line in (28) for z real and less than -1 , and perform the analytical continuation in the z plane in such a way that the function obtained by it is equal to the second line of (28) at the upper side of the cut $-1 \leq z \leq +1$. In the same way we obtain the analytical continuation for the functions I_A, I_B as well, but it should be noticed that cuts required for their analytical continuation are different from that indicated above and depend on values of functions generated by the first two terms in the denominator of the integrand in equation (25). The point is that I_A, I_B are constructed from integral (25) with the action of R_c , and therefore are sums of integrals that have the form of integral (28).

Having performed the analytical continuation, we are in a position to use the Sommerfeld–Watson transformation and to cast equation (24) in the form of the contour integral. But firstly it should be noticed that the term with $\ln J$ in equation (24) is to be cancelled out. To see this let us recall that J does not depend on material constants of the system, so that we may evaluate it by setting all bulk characteristics equal to zero. Then the energy E_s is that of 2D lattice and the term with $\ln J$ equal to zero. Finally, we may write the energy of the reconstructed surface in the following form, with the contour C illustrated in figure 3:

$$E_s = -\hbar \sum_k \int_C \frac{dz}{2\pi i} \frac{1}{e^{\beta\hbar z} - 1} \left(\frac{X_- + (z/2) \partial X_- / \partial z}{Mz^2 - X_-} + \frac{X_+ + (z/2) \partial X_+ / \partial z}{Mz^2 - X_+} \right). \quad (29)$$

Concluding this section we would like to point out that the generation of terms in the expression for energy by the action of the symmetry group R_c , and the analytical continuation of basic functions, are the mathematical framework for our study of the thermodynamics of reconstruction.

5. Phonon modes at the reconstructed surface

The key point in studying the phonon modes is that the operators D_k^n defined by equation (20) are Fourier transformed equations of motion for surface displacements. Therefore, by setting the determinant of the operator equal to zero

$$\det \mathbf{D}_k^n = 0 \quad (30)$$

and performing the analytical continuation from the Matsubara frequencies to continuous z , we obtain the equations for surface modes.

For the first time functional determinants were employed for studying elementary excitations in condensed media by Popov (1976), see also Jarunin and Popov (1980).

The equations for the surface modes read as follows:

$$\begin{aligned} z^2 - \omega_s^2 = (m/M) & [z^2 - \cos^2 \frac{1}{2}k_1 \Omega_{00}^2 - \sin^2 \frac{1}{2}k_1 \Omega_{11}^2 \\ & + \cos^2 \frac{1}{2}k_1 \sqrt{(z^2 - \Omega_{00}^2 - \nu^2)^2 - \nu^4} \\ & + \sin^2 \frac{1}{2}k_1 \sqrt{(z^2 - \Omega_{11}^2 - \nu^2)^2 - \nu^4}] \end{aligned} \quad (31)$$

$$\begin{aligned} z^2 - \omega_{s,op}^2 = (m/M) & [z^2 - \cos^2 \frac{1}{2}k_1 \Omega_{01}^2 - \sin^2 \frac{1}{2}k_1 \Omega_{10}^2 \\ & + \cos^2 \frac{1}{2}k_1 \sqrt{(z^2 - \Omega_{01}^2 - \nu^2)^2 - \nu^4} \\ & + \sin^2 \frac{1}{2}k_1 \sqrt{(z^2 - \Omega_{10}^2 - \nu^2)^2 - \nu^4}]. \end{aligned} \quad (32)$$

Here we have used the following notations:

$$\begin{aligned} \omega_s^2 &= 4(\tau_1/M) \sin^2 \frac{1}{2}k_1 + 4(\tau_2/M) \sin^2 \frac{1}{2}k_2 \\ \omega_{s,op}^2 &= 4(\tau_1/M) \cos^2 \frac{1}{2}k_1 + 4(\tau_2/M) \cos^2 \frac{1}{2}k_2 \end{aligned}$$

for the acoustic ω_s^2 and the spurious $\omega_{s,op}^2$ optical phonon mode at the surface, and:

$$\begin{aligned} \Omega_{00}^2 &= 4(\sigma_1/m) \sin^2 \frac{1}{2}k_1 + 4(\sigma_2/m) \sin^2 \frac{1}{2}k_2 \\ \Omega_{11}^2 &= 4(\sigma_1/m) \cos^2 \frac{1}{2}k_1 + 4(\sigma_2/m) \cos^2 \frac{1}{2}k_2 \\ \Omega_{01}^2 &= 4(\sigma_1/m) \sin^2 \frac{1}{2}k_1 + 4(\sigma_2/m) \cos^2 \frac{1}{2}k_2 \\ \Omega_{10}^2 &= 4(\sigma_1/m) \cos^2 \frac{1}{2}k_1 + 4(\sigma_2/m) \sin^2 \frac{1}{2}k_2 \end{aligned}$$

for the bulk frequencies considered in the small Brillouin zone of the surface, and in this respect $\nu = 2\sigma_3/m$ is the bulk frequency for the wavevector $(0, 0, \pm\pi/2)$. Equation (31) is a kind of extension of the equation for surface acoustic modes allowing for the influence of the bulk represented by the terms in the right-hand side, and equation (32) is a similar one for the optical surface mode. It should be noticed that the latter is spurious without the influence of the bulk.

The essential point is that the frequencies given above are transformed into each other by the action of the group Rc. Consequently, equations (31) and (32), which give the two branches of phonon modes at the surface, are transformed into each other by the group Rc. To make the point more clear, let us write equation (31) in the following form:

$$z^2 - \omega_s^2 - (m/M)Y(z, k_1, k_2) = 0. \quad (33)$$

Here $Y(z, k_1, k_2)$ is the right-hand side of (31). Then equation (32) can be cast in the form

$$z^2 - ({}^g\omega_s)^2 - \frac{m}{M} {}^gY(z, k_1, k_2) = 0 \quad (34)$$

here $g = g_1, g_2$ are elements of Rc, defined by equations (6).

In the equations given above the square roots are to be understood in the sense of the analytical continuation introduced earlier. We should take into account that these equations also have complex solutions that correspond to resonant modes lying inside the band of bulk modes.

Here it should be recalled that Dobrzynski and Mills (1969) studied surface phonon modes for the non-reconstructed (001) surface of a simple cubic lattice formed by adatoms of mass M different from mass m in the bulk. They found that there is only one branch of surface modes which, depending on the mass ratio m/M , can be acoustic, resonant (i.e. lying within the band of bulk modes) or optical (i.e. with a gap). In their subsequent paper Dobrzynski and Mills (1973) studied optical phonon modes at the (2×1) reconstructed surface, and found that among these modes those lying low enough may penetrate the band of bulk acoustic modes. The phenomenon is due to the fact that the Brillouin zone of the reconstructed surface is two times smaller than that of the non-reconstructed one, so that a surface optical mode with a wavevector \mathbf{k} may mix with the bulk one displaced in the direction of \mathbf{k} by an appropriate vector of the reciprocal lattice. Our results agree with the conclusions of Dobrzynski and Mills in that the analysis of equations (31) and (32) shows that there are optical modes caused by the reconstruction which can mix with the bulk ones, and acoustic modes become optical when the ratio m/M is large enough. In fact, the gap tends to $\sqrt[3]{(4\sigma_3/m)}$ as m/M goes to infinity.

6. Surface energy

Using equation (29) we may reduce the computation of the surface energy to evaluating the following integral:

$$E_s = -\hbar A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} F(k_1, k_2).$$

The function $F(k_1, k_2)$ is a sum of residues of the integrand in the contour integral of equation (29), and integrals of the imaginary part of the integrand along the cuts made in the process of the analytical continuation for the functions I_A, I_B .

Following the guidelines provided by the dispersion equations (31) and (32), we may cast the equation for the energy in a more explicit form. To that end let us note that the two summands under the integral in (29) can be obtained from each other by the action of the group R_c . Therefore, we may cast the equation for E_s in the following very symmetric form:

$$E_s = -\frac{1}{2} \hbar A \sum_{g \in R_c} \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} \int_C \frac{dz}{2\pi i} \frac{{}^g f(z)}{e^{\beta \hbar z} - 1} \quad (35)$$

with the function $f(z)$ given by

$$f(z) = \frac{X_+ + (z/2)\partial X_+/\partial z}{Mz^2 - X_+}.$$

It is worth noticing that the summation in elements of R_c is in fact an integration over this group, so that we may infer that the expression for the surface energy involves the integration over the group of symmetry of the reconstructed surface.

To see the structure of equation (35) for the surface energy more clearly let us consider the reconstructed surface formed by heavy adatoms, $m/M \ll 1$. Then, as can

be inferred from equations (31) and (32), there are no resonant modes which correspond to complex poles of the functions ${}^g f(z)$. It is also important that the function $X_+(z)$ depends on z^2 , as is seen from equation (25), which determines it. Therefore, for $m/M \ll 1$ we may assume that poles of ${}^g f(z)$ lie on the real axis symmetrically with respect to the origin, and there is the equation for the two poles $w, -w$:

$$[\text{Res } {}^g f(z)]_{(z=w)} = -[\text{Res } {}^g f(z)]_{(z=-w)}.$$

The cuts made above for the analytical continuation are also symmetrical. Consequently, by deforming the contour C as shown in figure 3, and using the equation for the residues at $z = w, -w$, given above, we may split E_s into two parts:

$$E_s = E_{zp} + E_h.$$

The first term, E_{zp} , does not depend on temperature and is the zero point energy:

$$E_{zp} = \frac{1}{2} \hbar A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} \sum_{g \in \text{Rc}} \left(\sum_{w>0} \text{Res}({}^g f(z))_{(z=w)} + \sum_{\text{cut}>0} \int \frac{dz}{\pi} \text{Im}[{}^g f(z)] \right). \quad (36)$$

The second term is temperature-dependent:

$$E_h = \hbar A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} \sum_{g \in \text{Rc}} \left(\sum_{w>0} \frac{\text{Res}({}^g f(z))_{(z=w)}}{e^{\beta \hbar w} - 1} + \sum_{\text{cut}>0} \int \frac{dz}{\pi} \frac{\text{Im}({}^g f(z))}{e^{\beta \hbar z} - 1} \right).$$

Here w are positive poles of the functions ${}^g f(z)$.

The region of low temperatures is worth special attention. Here we may obtain the formula for specific heat by employing expansions in m/M :

$$c = c_{2D} + (m/M) c_{sb}.$$

Here the first term is the same as for the 2D lattice with the dispersion law given by $\omega_s(k)$, the second term, of first order in m/M , corresponds to corrections due to the interaction between the surface and the bulk. The T^2 law for the specific heat described by the formula given above is preserved. The explicit form of the term c_{sb} is rather difficult and we shall not give it here.

For sufficiently large m/M , i.e. strong interaction between the surface and the bulk, we shall have only optical modes and the specific heat changing according to the Einstein law, in the region of high temperatures.

7. Conclusions

The path integral formulation of lattice dynamics provides the systematic approach for taking into account the influence of the bulk lattice on thermodynamic properties of the surface. We feel that non-equilibrium phenomena at the surface could also be treated within the framework of path integrals by using the method of complex-time path integrals worked out by Jensen and Sauls (1986, 1988) for the polaron problem. Particular properties of the model, especially those related to the symmetry of lattice involved, are not crucial; we may consider the interaction not only between nearest neighbours, change the type of reconstruction, and so on. The more important point is the harmonic approximation, because to break its bondage we need to use perturbation theory.

Expansions of thermodynamic properties of the surface in terms of the ratio m/M are very important. For example, let us consider the Peierls instability, according to which at any finite temperature there cannot exist a 2D crystalline lattice because thermodynamical fluctuations in positions of atoms, $\langle x^2 \rangle$, would increase as the logarithm of the size of a lattice. In real life, the 2D lattices have been prepared so far on substrates, so that there is an interaction, though small, between the surface and the bulk systems. To evaluate the fluctuations $\langle x^2 \rangle$ we may employ the surface Green function which can be derived from the canonical partition function given by equation (23). The surface Green function can be cast in the following matrix form:

$$G_s(z, k_1, k_2) = \frac{1}{D} \begin{pmatrix} p(z) & -q(z) e^{i(k_1+k_2)} \\ -q(z) e^{-i(k_1+k_2)} & p(z) \end{pmatrix}$$

$$D = \left(z^2 - \frac{1}{M} X_-(z) \right) \left(z^2 - \frac{1}{M} X_+(z) \right)$$

$$p(z) = z^2 - (2/M)(\tau_1 + \tau_2) - (1/M)\sigma_3(2 + \sigma_3 I_A)$$

$$q(z) = (2/M)\tau_1 \cos(k_1 + k_2) + (2/M)\tau_2 \cos(k_1 - k_2) - (1/M)\sigma_3^2 I_B.$$

The fluctuations $\langle x^2 \rangle$ are proportional to the imaginary part of the Green function in the x representation (see Lifshitz and Pitaevskii 1980), and for the 2D lattice they tend to grow as $\ln R$, where R is the size of the system, owing to the δ -shaped singularities of the Green function. In our case there are no such δ -shaped singularities, because $G_s(z)$ has a finite imaginary part due to imaginary parts of I_A, I_B , caused by equation (28). It is easy to convince oneself that the peak of $G_s(z)$ has a width of order m/M .

We feel that the specific form of the energy of zero-point vibrations of the surface should draw attention to surface effects in general and the reconstruction in particular. To clarify this, let us consider the energy of zero-point vibrations for the specific case of small m/M , i.e. when we have a weak surface bulk interaction. We have the following expansion in m/M :

$$E_{Zp} = A \int_{-\pi/2}^{+\pi/2} \frac{dk_1 dk_2}{\pi^2} \hbar \omega_s(k) + \frac{m}{M} E_r + O\left(\frac{m}{M}\right).$$

The first term in the equation given above is the energy of zero-point vibrations of the surface 2D lattice without taking into account its interaction with the bulk lattice; the second term, of first order in m/M , accommodates the influence of the bulk on the surface; the third designates higher orders in m/M . The explicit form of the second term is rather lengthy and we shall not write it here, particularly as it is straightforward. Its nature is sufficiently clear from equation (36); it is the part of the energy of zero-point vibrations due to the spatial configuration of the lattice's sites at the topmost layers and the influence of the bulk, i.e. its origin lies in the interplay between the zero-point vibrations at the surface and the topology of bonds that hold together the surface and the bulk, and in that it resembles the Casimir energy.

The current concept of the Casimir effect (Casimir 1948) is that it is the polarization of a vacuum caused by either the finite size of a spatial region containing a quantized field, or the topology of space different from the Euclidean one. The familiar example of the effect is the electromagnetic field confined between two metallic planes which experience therefore an attractive force due to a change in the energy of the vacuum, or

zero-point vibrations of the field. Ginzburg (1981) drew attention to the fact that surface vibrations of the field are essential for adequate treatment of the Casimir effect.

Generally forces due to the Casimir effect are rather weak, even though in some realistic situations, for example Van der Waals forces (see Barash 1988), they can be important. The part played by zero-point vibrations in the stability of solids in the case of melting, i.e. in the situations where geometric characteristics required for effecting it are reduced to the simplest one—the volume—was studied a long time ago by Bennewitz and Simon (1927) who indicated that for inert gases it can be of interest. Later Simon (1934) showed that the energy of zero-point motion plays a crucial role for liquid helium for which it cannot be treated as a small correction. The large values of the energy of zero-point motion result in helium only solidifying under considerable external pressure, even at very low temperatures. The two ground states of helium, solid and liquid, are determined by minimizing the total energy which comprises the part caused by intermolecular forces, i.e. the classical potential energy, and the part due to zero-point motion (see the discussion by London 1954). Drawing parallels with the Casimir effect, we may say that the quantized field corresponds to the motion of helium atoms and the imposed restrictions on size to the fixed volume of liquid. It is also worth noticing that the mole volume of liquid helium is considerably larger than one would expect from estimating only the potential energy, because by expanding to a larger volume the liquid lowers its zero-point energy far more than it increases its potential energy.

According to the experimental results of Elgin and Goodstein (1973), the energy of zero-point motion of helium atoms in films on a graphite substrate is large compared to the barrier height between potential adsorption sites on the substrate, even though for a sufficiently dense coverage the substrate potential is able to impose upon a helium monolayer an ordered state of a 2D crystalline lattice commensurate with itself. Also for Xe monolayers De Wette (1985) reports that in-plane vibrations can be considered as 2D motions in that they appear to be independent of the substrate's motion, but it should be noticed that for transversal vibrations there is a strong interaction with the substrate.

On the grounds of the experimental results cited above we suggest that the Casimir effect could be an interesting phenomenon in the physics of surfaces. From the theoretical point of view, the surface even in simplest model configurations has enough topological structure for the lattice's vacuum to change drastically at its vicinity. Therefore, the lattice's energy of zero-point motion could lead to interesting implications for the phenomenon of reconstruction, at least for low temperatures and inert gases.

Acknowledgments

The author is grateful to the Institute of Physics of the Georgian Academy of Sciences for generous help. Fruitful discussions with A F Andreev, Yu A Kosevich, and A M Kosevich are acknowledged.

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