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Unbinding of surface defects under the defect-selective adsorption

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Unbinding of surface topological defects in the presence of the defect-selective adsorption is investigated using a coupled Coulomb Gas – Lattice Gas model. The unbinding temperature increases with the increasing selectivity (and coverage) for both, sign-dependent and sign-independent adsorption. In the latter case, the adsorbates tend to increase the number density of defects. The stability requirement implies that the adsorbate cluster size must be coherent with the screening length of free defects.

Key words: *adsorption, selectivity, defects*

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1. Introduction

It is a great pleasure for me to contribute this paper to the special issue dedicated to the 60-th anniversary of Professor M.F.Holovko.

Surface defects (such as steps, vacancies, dislocations, disclinations, etc) are known to play an important role in controlling the mechanical properties of surfaces as well as their roughening and melting temperatures [1]. Modification of the electronic density around defects leads to different adsorption sites in comparison with the rest of the surface lattice. This aspect has recently raised considerable interest in connection with nanoscale patterns [2,3] and ultrathin heteroepitaxial films [4].

Usually the binding energy at the defect sites is much larger than that at the regular sites [5], because the defects tend to restore broken bonds by means of adsorption. Thus, one may expect a preferential occupation of the defect sites when the surface is in contact with an adsorbate. In this case a defect-defect interaction should be modified by the adparticles [6]. In our previous studies [7,8] we have demonstrated that such an assumption allows one to recover the experimental results on HCl-ice interfaces. Therefore, a defect-selective adsorption could be a promising tool for a fabrication of a new type of protective coverages and a modification of surface properties.

The objective of this paper is to investigate how the interaction between the surface topological defects and their number density is modified due to the defect-selective adsorption. The latter means that the adparticles reside preferentially at the defect sites (e.g., at dislocation or disclination core). This induces additional interactions between the defects affecting their unbinding temperature.

2. The model

Quite often the defects (dislocations [2,3], or disclinations [9]) form regular networks, or even periodic patterns at metal surfaces. For simplicity we ignore the nonideality of real defect patterns and model the network of surface topological defects as a square lattice. Scalar "charge" variables s_i are associated with each site ($s_i = 0$ – regular site; $s_i = \pm 1$ – defect site). Thus, the defect subsystem is described by a general type Coulomb gas (CG) Hamiltonian [10,11]

$$H_{\mathrm{d}} = -J \sum_{ij} \ln(R_{ij}/R_0) s_i s_j + E_{\mathrm{c}} \sum_i s_i^2 \,, \tag{1}$$

where R_0 is the core radius and E_{c} is the core energy of a defect. The latter quantity determines the number density of defects through their chemical potential $\mu_{\mathrm{d}} = -E_{\mathrm{c}}$. The electroneutrality condition

$$\sum_i s_i = 0 \tag{2}$$

is imposed on the system. The logarithmic interaction is directly applicable either to Coulomb gas or to disclinations in the hexatic phase [12]. It is chosen as a prototype which gives a Kosterlitz-Thouless (KT) transition [13] from a "dielectric" (bound $+-$ pairs) to a "conducting" (free charges) state. For a dilute system ($\mu_{\mathrm{d}} \approx 0$) the transition occurs at the temperature $T_{\mathrm{c}}^0 = kT_{\mathrm{c}}/J = 1/4$. The unbinding temperature decreases with the increasing μ_{d}. Following Kosterlitz and Thouless [13] we construct the approximation

$$\frac{1}{T_{\mathrm{c}}} = \frac{1}{T_{\mathrm{c}}^0} \exp\left(\frac{\mu_{\mathrm{d}}}{T_{\mathrm{c}}}\right) \tag{3}$$

which gives a satisfactory description at low defect densities.

Modifying the logarithmic interaction as appropriate for dislocations or disclinations, we could treat the surface melting transition [12]. Performing the duality transformation [14], we can describe the roughening transition. Nevertheless, the KT nature of these transitions is not sensitive to the modifications of the potential.

The adsorbate is described by the lattice gas (LG) Hamiltonian with a charge-dependent chemical potential.

$$H_{\mathrm{a}} \;=\; \frac{W}{2} \sum_{ij} t_i t_j - \sum_i \mu(s_i) t_i \,, \tag{4}$$

$$\mu(s_i) \;=\; \mu_0 + \delta\mu(s_i), \tag{5}$$

where μ_0 corresponds to the adsorption at regular sites, while $\delta\mu(s_i)$ determines the selectivity (that is, an additional adsorption potential due to defects). Here W is a coupling between the adsorbates at the nearest neighbor sites, the occupation numbers $t_i = 0, 1$ control a distribution of adsorbates at the lattice sites. For concreteness, the pair-wise interaction in the adsorbate is assumed to be attractive ($W < 0$).

Therefore, we deal with a coupled CG-LG system, which is in the same universality class as the XY-Ising model [15]. A dual model was extensively investigated [16] by means of Monte Carlo simulation.

3. Perturbation theory

We are mainly interested to determine the effect of the selectivity on the defect unbinding. For this purpose the adsorbate Hamiltonian is split into two parts

$$H_{\mathrm{a}} = H_{\mathrm{a}}^0 - \sum_i \delta\mu(s_i) t_i \,, \tag{6}$$

where H_{a}^0 describes the adsorption without any preferences (regular sites). Treating the selectivity term as a perturbation, we adopt the scheme developed previously [17,18]. The free energy βF is given by

$$\mathrm{e}^{-\beta(F-F_{\mathrm{a}}^0)} = \int (\mathrm{d}R_i) \mathrm{e}^{-\beta H_{\mathrm{d}}} \left\langle \mathrm{e}^{-\beta \sum_i \delta\mu(s_i) t_i} \right\rangle_{t_i} , \tag{7}$$

where $\beta = 1/kT$ is the Boltzmann thermal factor. The average $\langle F(t_i)\rangle_{t_i}$ should be calculated with the reference Hamiltonian

$$\langle F(t_i)\rangle_{t_i} = \frac{\sum_{\{t_i\}} \mathrm{e}^{-\beta H_{\mathrm{a}}^0} F(t_i)}{\sum_{\{t_i\}} \mathrm{e}^{-\beta H_{\mathrm{a}}^0}}.$$

Performing the cumulant expansion and restricting ourselves to the first two cumulants, we get an effective Hamiltonian for the defects.

$$H_{\mathrm{ef}} = H_{\mathrm{d}} - \frac{\beta}{2} \sum_{ij} \chi(R_{ij}) \delta\mu(s_i) \delta\mu(s_j) - \sum_i \Theta \delta\mu(s_i). \tag{8}$$

Thus, we have an additional (adsorbate-induced) interaction governed by the adsorbate correlation function $\chi(R_{ij})$, which can be approximated by its mean-field value [19]

$$\chi(R_{ij}) = \langle t_i t_j\rangle - \langle t_i\rangle\langle t_j\rangle = \sqrt{\frac{\xi}{R_{ij}}} \mathrm{e}^{-R_{ij}/\xi}. \tag{9}$$

In addition we have the one-body term that couples the selectivity to the coverage. Here $\Theta = \langle \sum_i t_i \rangle$ is the coverage and ξ is the correlation length for the adsorbate. Effects induced by these interactions depend on a choice of the selectivity term $\delta\mu(s_i)$.

3.1. Sign-dependent adsorption

When only the same sign defects are preferable for the adsorbates, we choose

$$\delta\mu(s_i) = \mu_1 s_i \,. \tag{10}$$

Then the Hamiltonian becomes

$$H_{\mathrm{ef}} = -\sum_{ij} V_{\mathrm{ef}}(R_{ij}) s_i s_j + E_{\mathrm{c}} \sum_i s_i^2 \,, \tag{11}$$

$$V_{\mathrm{ef}}(R) = J \ln (R/R_0) + \frac{\beta\mu_1^2}{2}\chi(R). \tag{12}$$

The term $\mu_1\Theta\sum_i s_i = 0$ according to the electroneutrality condition (2). Following the standard scheme [13], we develop a mean-field approach for the screened potential $U(R) = V_{\mathrm{ef}}(R)/\varepsilon(R)$ and focus on the behavior of the dielectric function $\varepsilon(R)$. Namely, the number density $n(R)$ of $+-$ pairs with separation R can be estimated from

$$n(R) = C(R_0)\mathrm{e}^{-\beta U(R)} = C(R_0)\mathrm{e}^{-\beta V_{\mathrm{ef}}(R)/\varepsilon(R)}, \tag{13}$$

where $C(R_0)$ is a constant. On the other hand, the dielectric function $\varepsilon(R)$ differs from unity because the bounded pairs are polarized.

$$\varepsilon(R) = 1 + \int_0^R \mathrm{d}\mathbf{R}' P(R') n(R'). \tag{14}$$

The polarization function $P(R)$ can be approximated by its value for noninteracting dipoles with separation R. Therefore, these two relations can be used for elimination of $n(R)$ obtaining a nonlinear differential equation for $\varepsilon(R)$. Based on this we determine the unbinding temperature T_{c} (at which $\epsilon = \varepsilon(\infty)$ jumps from finite values to infinity) as a function of the selectivity parameter μ_1. As expected, T_{c} grows with the increasing selectivity, since the attractive adsorbate-induced interaction tends to pin the defects of a given sign. Then the opposite sign defects are also partially immobilized.

3.2. Sign-independent adsorption

If there is no defect sign preference, then we have

$$\delta\mu(s_i) = \mu_2 s_i^2 \tag{15}$$

and (1) gives

$$H_{\mathrm{ef}} = H_{\mathrm{d}} - \frac{\beta\mu_2^2}{2}\sum_{ij}\chi(R_{ij}) s_i^2 s_j^2 - \mu_2\Theta\sum_i s_i^2 \,. \tag{16}$$

Thus, in contrast to the sign-dependent case, we have an additional charge-independent interaction (attractive for all the defects). For this reason we have to take into account the charge and density fluctuations [20]. The chemical potential is also changed

$$\mu_\mathrm{d} = \mu_2\Theta - E_\mathrm{c} \tag{17}$$

such that the defect number density changes with the coverage.

To determine the role of this additional interaction we first analyze a case of small E_c and $\mu_\mathrm{d} = 0$, such that the defect number density is fixed. Our main focus is on the inverse dielectric function $\epsilon(\mathbf{q})$. The linear response theory gives

$$\frac{1}{\epsilon(\mathbf{q})} = 1 - 2\pi\beta\frac{g(\mathbf{q})}{\mathbf{q}^2}, \tag{18}$$

where $g(\mathbf{q})$ is the Fourier transform of the charge-density correlation function $g(R) = 2[g_{++}(R) - g_{+-}(R)]$. Hence, we deal with the so-called linearly screened potential [10]

$$U_L(\mathbf{q}) = \frac{2\pi}{\mathbf{q}^2\epsilon(\mathbf{q})} = \frac{2\pi}{\mathbf{q}^2}\left(1 - 2\pi\beta\frac{g(\mathbf{q})}{\mathbf{q}^2}\right) \tag{19}$$

what behaves as

$$U_L(\mathbf{q}) = \frac{2\pi}{\mathbf{q}^2 + \lambda^{-2}}, \quad \text{as} \quad q \to 0. \tag{20}$$

Here λ is the temperature-dependent screening length, such that $\lambda = \infty$ in the low-temperature dielectric phase, and $\lambda \neq \infty$ in the high-temperature conducting phase.

Following [10], we may represent $g(R)$ as a combination of effective potentials $U_{++}(R)$ and $U_{+-}(R)$

$$g(R) = 2[\mathrm{e}^{-\beta U_{++}(R)} - \mathrm{e}^{-\beta U_{+-}(R)}]. \tag{21}$$

Since the adsorbate-induced interaction is sign-independent, it should additively contribute to the effective potentials

$$U_{++}(R) \;=\; U^0_{++}(R) - \frac{\beta\mu_2^2}{2}\chi(R), \tag{22}$$

$$U_{+-}(R) \;=\; U^0_{+-}(R) - \frac{\beta\mu_2^2}{2}\chi(R), \tag{23}$$

where $U^0_{++}(R)$ and $U^0_{+-}(R)$ correspond to the purely logarithmic interaction (no adsorption), when $g(R) = g_0(R)$ according to equation (21).

In the presence of adsorption we obtain the defect correlation function

$$g(R) = g_0(R)\mathrm{e}^{\frac{\beta^2\mu_2^2}{2}\chi(R)} \approx g_0(R)\left[1 + \frac{\beta^2\mu_2^2}{2}\chi(R)\right] \tag{24}$$

which can be represented as a convolution in the Fourier space

$$g(q) = g_0(q) + \frac{\beta^2\mu_2^2}{2}g_0(k-q) * \chi(k), \tag{25}$$

where a large-k cutoff $L \approx 2\pi/R_0$ should be introduced. The Fourier transforms of the clean surface and the adsorbate correlation functions are given by

$$g_0(q) = a(\beta)\frac{q^2}{1+q^2\lambda^2}, \tag{26}$$

$$\chi(q) = \frac{\xi^2}{1+q^2\xi^2}. \tag{27}$$

Calculating the convolution we obtain the following small q behavior

$$g(q) = g_0(q) + \varphi_1(\lambda,\xi) + \varphi_2(\lambda,\xi)q^2, \tag{28}$$

where $\varphi_1(\lambda,\xi)$ and $\varphi_2(\lambda,\xi)$ are given functions of the screening and correlation length. The q-independent term $\varphi_1(\lambda,\xi)$ violates the thermodynamic stability, as it follows from equation (18) at $q \to 0$ (in that case $1/\epsilon(0) \to -\infty$). Thus, we have to require $\varphi_1(\lambda,\xi) = 0$. This imposes a constraint on λ and ξ.

In the dielectric phase ($\lambda \to \infty$) our requirement is satisfied automatically: $\varphi_1(\lambda,\xi) \to 0$ as $\lambda \to \infty$. In this case ξ is not restricted. In particular, we may have $\xi \to \infty$ (for example, due to a nucleation of adsorbates around the defect sites [18]). Then, the defect-adsorbate coupling should facilitate the defect nucleation [21].

Near the conducting phase boundary (finite λ) the numerical solution gives a discrete set of ξ for a given λ. Qualitatively this can be expressed as follows

$$\xi = \lambda\left(\frac{n}{m}\right), \tag{29}$$

where n and m are specific integers with $n < m$. Therefore we have an infinite (but discrete) set of ξ, with $\xi < \lambda$. The adsorbate-induced interaction tends to form defect clusters with their average size of the order of ξ. Therefore, the adsorbate cluster size cannot exceed the defect screening length.

It is known [10] that λ is related to the number density n_f of free defects: $\lambda^2 = 1/b(T)n_\mathrm{f}$. Thus, for a given n_f we have a discrete set of adsorbate cluster sizes $\xi^2 = (n^2/m^2)/(b(T)n_\mathrm{f})$, compatible with the thermodynamic stability of the system. Since the adsorbate diffusion coefficient D is inversely proportional to the squared correlation length ξ, $D \propto \Theta(1-\Theta)/\xi^2$, then it is easily seen that D is proportional to the density of free defects $D \propto m^2/n^2\Theta(1-\Theta)b(T)n_\mathrm{f}$. Near the unbinding temperature we can expect a sharp change in n_f and, consequently, in the adsorbate diffusion flux.

Having determined the conditions for $\varphi_1(\lambda,\xi) = 0$, we obtain the correlation function

$$g(q) = a(\beta)\left(1 + \left[\frac{\mu_2}{J}\right]^2 \beta^2\xi^2\right)q^2. \tag{30}$$

The unbinding temperature T_c is determined from the condition[10] $2\pi\beta g(q)/q^2 = 1$, as $q \to 0$. This gives

$$T_\mathrm{c} = T_\mathrm{c}^0\left(1 + \left[\frac{\mu_2}{J}\right]^2 \xi^2/T_\mathrm{c}^2\right). \tag{31}$$

Solving this equation we obtain the unbinding temperature $T_\mathrm{c} = T_\mathrm{c}(\mu_\mathrm{d} = 0)$ as a function of the selectivity μ_2/J. For small μ_2/J the critical temperature T_c grows monotonically, since the adsorbate-induced interaction favors the binding of the defects.

Nevertheless, according to (17), the selectivity parameter μ_2 changes the chemical potential μ_d. In that case we solve (3) to obtain

$$T_\mathrm{c}(\mu_\mathrm{d}) = T_\mathrm{c}(\mu_\mathrm{d} = 0)\frac{-\mu_\mathrm{d}}{W(-\mu_\mathrm{d})}, \tag{32}$$

where $W(a)$ is the so-called Lambert function which is a solution of equation $x/a = \exp(-x)$.

The unbinding temperature is a nonmonotonic function of the selectivity. An initial increase of T_c is due to the adsorbate-induced binding of the defects. A decrease (at larger μ_2/J) is caused by the increasing defect number density. A competition between these effects induces a reentrant unbinding (with respect to μ_2/J). A general tendency to expand the “dielectric” phase is observed, especially, with the increasing of ξ.

4. Conclusion

The defect-selective adsorption is shown to favor the binding between the topological defects, increasing the thermal stability of the surface. This is manifested by a remarkable increase of the unbinding temperature with the coverage and the selectivity. The CG-LG model is dual to the discrete Gaussian-LG model, discussed [17] in application to the adsorbate-induced roughening [22]. Therefore, the increase of the unbinding temperature, found here, is consistent with the decrease of the roughening temperature [17] in the dual model.

The results, obtained here, suggest a possibility for a reentrant unbinding transition (of KT type). The reentrance results from a competition between the adsorbate-induced attractive interaction (which enhances the defect pairing) and the selectivity dependent binding energy, that increases the defect number density. The effect is well pronounced at relatively low selectivity $\mu_2/J < 1/2$, provided that the adsorbate pairwise coupling W is strong enough to result in a nonzero ξ. This could serve as a criterium for a selection of appropriate adspecies. The concentration of defects (e.g., dislocations) is related to a strength of the surface, while the unbinding can be associated with the surface melting. Thus, the mechanism described here, could be an efficient practical tool for controlling the surface properties.

In the bounded (dielectric) state there is no limitation on the adsorbate cluster size, and adsorption is essentially similar to that occurring at usual crystalline lattices. Nevertheless, when the defect lattice is not rigid, we can expect an adsorbate-induced patterning, similar to that reported earlier [6] for regular surfaces. Near the conducting phase boundary only a particular set of adsorbate cluster sizes and defect screening lengths is compatible with the thermodynamic stability. This implies a correlation between the number density of free defects and the adsorbate cluster size. Such a specific size effect modifies the thermodynamic and kinetic properties. In particular, the adsorbate diffusion coefficient is proportional to the density of free defects.

Since the only key ingredients are the selectivity and the KT type transition for the defects, our results are quite general and applicable (with slight modifications) to a broad class of adsorbate-crystal systems (adsorbate-metal interfaces, surface alloys, etc.). Also, the approach, developed here, elucidates some aspects of the two-dimensional Coulombic criticality in the presence of specific interactions (charge and density fluctuations).

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Вивільнення поверхневих дефектів при дефектно-селективній адсорбції

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Досліджується вивільнення поверхневих дефектів при дефектно-селективній адсорбції, використовуючи комбінацію моделей ґраткового газу і кулонівського газу. Температура вивільнення зростає з ростом селективності як для знако-залежної, так і для знако-незалежної адсорбції. В останньому випадку адсорбат збільшує густину дефектів. Вимога стабільності вказує на те, що розмір кластера в адсорбаті має бути співмірним з довжиною екранування вільних дефектів.

Ключові слова: *адсорбція, селективність, дефекти*

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