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THE IMPORTANCE OF INDIRECT INTERACTIONS BETWEEN ADATOMS FOR TEMPERATURE DEPENDENT PROCESSES ON METAL SURFACE*

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The asymptotic form of the indirect pseudopotential interaction of noble metal adatoms on jellium is used to interpret the phenomena arising during thermal treatment of the noble metal submonolayers on W(110). It is shown that the 2D condensation is an activated process. The growth of open clusters needs lower activation energy than the close-packed island formation. Therefore the open clusters should predominate at low temperatures and low coverages, as it is observed experimentally. On the basis of calculation of the total energy of submonolayers as a function of coverage Θ the experimental measurement of desorption energy vs. coverage is discussed.

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1. Introduction

The electronic structure of noble metal adatoms is only slightly changed in the vicinity of a metal substrate. Therefore the main role in lateral adatoms interactions is played by the oscillatory indirect interactions throughout the electron gas of the substrate [1]. In this work we will try to answer the question: Can the oscillatory interactions explain some experimentally observed [2–6] processes on W(110) covered by Cu, Ag and Au?

The submonolayers of the noble metal adatoms on W(110) consist of two phases [2, 3] — a condensed phase and a gaseous phase. It was found that the van der Waals equation with critical temperature T_C and coverage Θ_C gave the best

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fit to the experimentally determined coexistent line between single-phase (gase) region and two-phase region where two-dimensional (2D) close-packed islands are surrounded by 2D gas (Fig. 1). In this paper an attempt has been made to interpret:

a) the character of the increase of thermal desorption energy vs. Θ;
b) the necessity of heating of the adlayers in order to obtain large islands;
c) a physical meaning of T_R — the temperature of sudden decrease of the heat of 2D condensation $\Delta H(T)$.

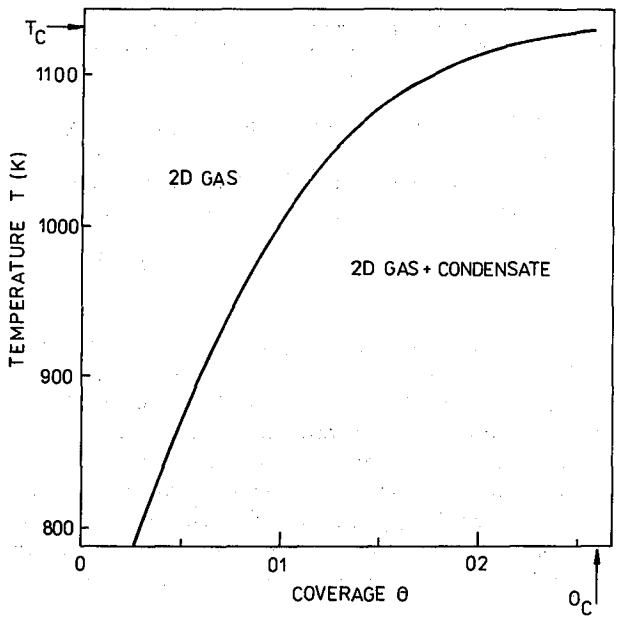

Fig. 1. The van der Waals coexistence curve between single-phase and two-phase region of Au on W(110) [2].

2. The lateral interactions

In a rough approximation the pairwise interactions between adatoms at a distance r consist of van der Waals $V_{\mathrm{VDW}}(r)$, induced dipole–dipole $V_{\mathrm{D-D}}(r)$ and oscillatory $V_{\mathrm{OSC}}(r)$ interactions.

The V_{VDW} and $V_{\mathrm{D-D}}$ may be written as

$$V_{\mathrm{VDW}} = -Cr^{-6}, \tag{1}$$

$$V_{\mathrm{D-D}} = 2\mu^2 r^{-3}, \tag{2}$$

where C is a positive constant [4] and μ is the dipole moment of an adatom [5].

The asymptotic ($k_F r > 1$) form of $V_{OSC}(r)$ was expressed analytically in [1] as

$$V_{OSC}(r) = A(k_F(\langle n(r,d)\rangle))\cos(2k_F r)r^{-3}, \tag{3}$$

where the Fermi momentum k_F represents the mean electron density $\langle n(r,d)\rangle$ in the sphere including two interacting adatoms, being at the distance d from the surface of the metallic background.

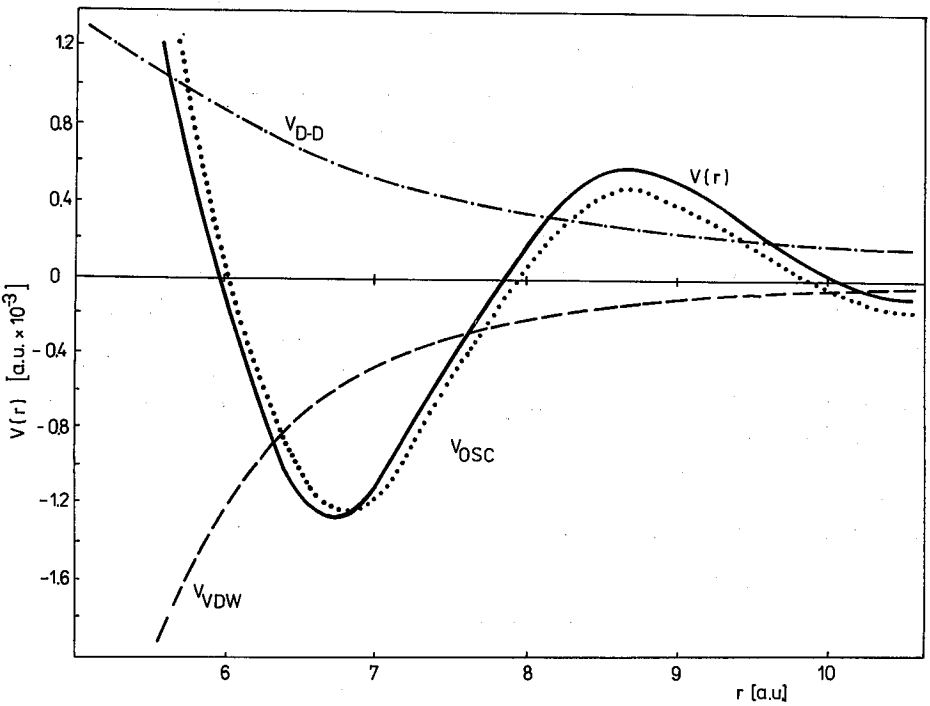

Fig. 2. Comparison of the pairwise interaction energies of Ag adatoms on jellium $k_F = 0.74$. Dashed line — the van der Waals interaction, dotted line — the oscillatory interaction, dashed-dotted line — the induced dipole-dipole interaction, solid line — the sum of V_{VDW}, V_{OSC} and V_{D-D}.

One can see in Fig. 2 that V_{VDW} and V_{D-D} compensate each other almost totally in the region of equilibrium distance between adatoms. Therefore in the further considerations V_{VDW} and V_{D-D} will be neglected because we are particularly interested in the influence of oscillatory character of interactions on the properties of the adlayer.

2.1. 2D gas ($T > T_C$)

The 2D gas is described by a hexagonal submonolayer where the nearest neighbour distance $a(\Theta)$ continuously changes with Θ, $a(\Theta) = a(\Theta = 1)\Theta^{-1/2}$.

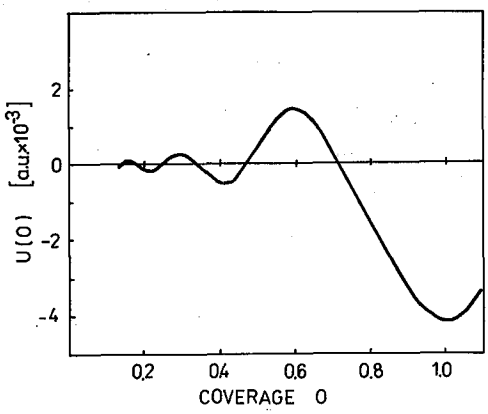

Fig. 3. Total energy of hexagonal submonolayer of Au.

The total energy $U(\Theta)$ of the lateral interactions in the submonolayer is calculated as a sum of pairwise interaction $V_{ij}, U(\Theta) = \Sigma V(r_{ij}(\Theta))$ [1]. As seen in Fig. 3 the continuous distribution of adatoms for certain coverages is particularly energetically unfavourable ($U(\Theta) > 0$). There is little probability that the coverages 0.1, 0.3, 0.6 were accomplished by a quasi-hexagonal uniform distribution. Therefore more energetically favourable structures with lattice constant $a(\Theta \simeq 0.2)$, $a(\Theta \simeq 0.4)$, $a(\Theta \simeq 1)$ would appear locally even at respectively lower coverages. This conclusion is in agreement with thermal desorption spectroscopy (TDS) measurements [6] of desorption energy vs. Θ (see Fig. 4).

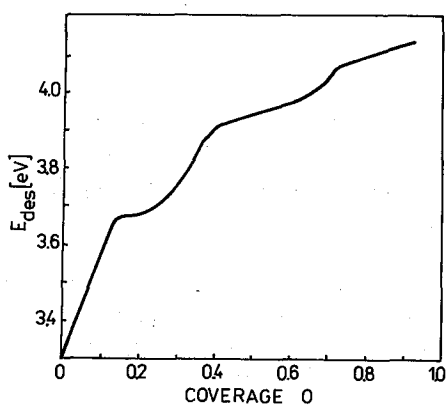

Fig. 4. Desorption energy of Au adatoms on W(110) [6].

Thermal desorption of noble metal adatoms from W(110) occurs at the temperature region close to the critical temperature T_C. It means that during desorption the adsorbate exists in the 2D gaseous phase.

The desorption energy $E_{des}(\Theta)$ increases with Θ (Fig. 4) running through three succesive plateaux at $\Theta = 0.2$, 0.4, and 0.9 which correspond to the minima of the adlayer energy $U(\Theta)$.

2.2. 2D gas + 2D condensate ($T < T_C$)

The 2D condensate was modelled by large clusters (islands) of Cu, Ag and Au with hexagonal symmetry which gives the lowest value of the total cluster energy [1].

The energy $V(z)$ of interaction of an adatom in the 2D gaseous phase with an island has also the oscillatory character. In Fig. 5 the plot of $V(z)$ for the island made of $N = 1140$ adatoms is shown, where z is the distance between the adatom and an edge of island and the temperature is used as a visual measure of energy. The energies V_1, V_1' and V_R, V_R' defined in Fig. 5 correspond to the successive minima and maxima of $V(z)$. They are collected in Table I for Cu, Au and Ag adatoms interacting with island and linear cluster.

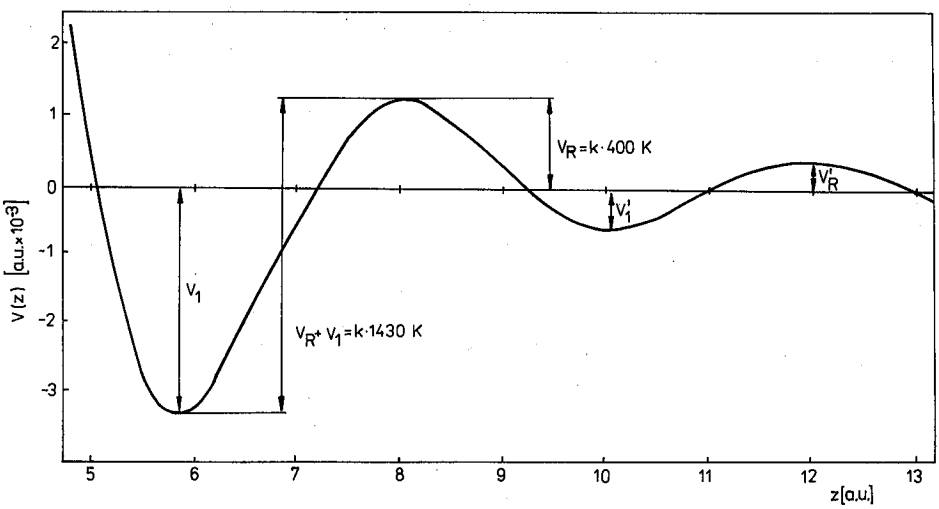

Fig. 5. The interaction energy of Au adatom with close-packed island of $N = 1140$ adatoms. The temperature is used as a visual measure of the energies $V_R + V_1$ and V_R.

The values of $V(z)$ increase very slowly with N and for $N = 7$ (the smallest island with close-packed structure being considered), $V(z)$ is only about 3% lower than for $N = 1140$ (presented in Fig. 5).

TABLE

The values of energies describing adatom–island and adatom–open cluster interaction. The values with asterisk concern $V(r)$ where V_{D-D} and V_{VDW} is considered.

	Adatom + island ($N = 1140$)			Adatom+linear cluster ($N = 200$)		
	Cu	Ag	Au	Cu	Ag	Au
V_1 [au $\times 10^{-3}$]	4.15	2.58	3.33	1.95	1.27	1.64
V_R [au $\times 10^{-3}$]	1.74	1.06	1.26	0.76	0.48	0.57
V_1' [au $\times 10^{-3}$]	0.88	0.53	0.59	0.36	0.26	0.29
V_R' [au $\times 10^{-3}$]	0.52	0.28	0.34	–	–	–
V_R/V_1	0.42	0.41	0.38	0.39	0.38	0.35
V_R/V_1	–	–	–	0.58*	0.45*	0.45*
T_R/T_C [3]	0.53	0.51	0.57	–	–	–

The existence of a repulsive barrier V_R (see Fig. 5) changes radically the mechanism of condensation comparing to the attractive forces we used to consider, since V_R must be understood as an activation energy of condensation what leads to the tendency to lower the nearest neighbours number when $kT < V_R$.

An adatom from 2D gaseous phase needs less energy to join an open cluster than the close-packed island. In the open clusters sketched in Fig. 6 the edge

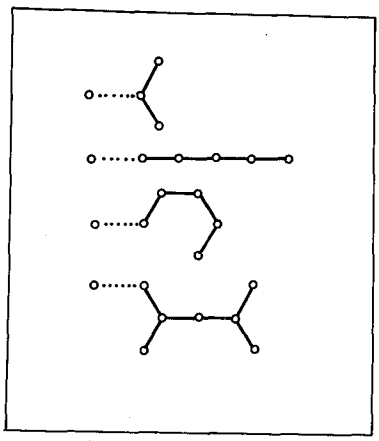

Fig. 6. Some examples of open clusters where the edge adatom has one nearest neighbour.

adatom has only one nearest neighbour and the value of V_R is about two times lower than in the case of condensation near the close-packed island (see Table).

This fact explains why in order to obtain large islands the adsorbate has to

be heated to the temperature much higher than the temperature of migration. For example Au adatoms are mobile at 200 K but close-packed islands bigger than 100 Å can be observed only after heating to 700 K.

The process of condensation for $\Theta < \Theta_C$ could be understood as follows:

Adatoms deposited at 300 K can migrate and build small open clusters for which V_R is smaller. After heating to $T \simeq 700$ K ($k \cdot 700$ K $\simeq V_R$ for large island), the islands begin to grow and are observed by LEED measurements.

If the temperature still increases islands evaporate into the 2D gaseous phase, and at $T \simeq T_C$ (typically about 1000 K, what corresponds to $V_R + V_1$) only 2D gas exists.

When the temperature decreases below T_C the islands grow as long as $kT > V_R$, at lower temperatures only open clusters may grow or adatoms "condense" near edges of large islands in the second minimum of $V(z)$ with energy V_1'.

2.3. The temperature T_R

T_R is the temperature of the sudden increase of the 2D heat of condensation $\Delta H(T)$ during the process of cooling of the sample [3]. From the discussion above, T_R can be interpreted as the temperature at which the island formation is stopped and the growth of the open clusters begins.

The experimentally determined quantities (ΔH, E_{des}, T_C, T_R) cannot be compared with the theory directly, but we can expect that the ratio V_R/V_1 is constant just as T_R/T_C [3]. These values are collected in Table and despite of the simplicity of the presented model we observe very good agreement between theory and experiment.

3. Conclusions

It was shown that the oscillatory interactions play a dominant role in the lateral interactions between noble metal adatoms on metals and can explain some experimental measurements as desorption energy vs. coverage and the sudden decrease of the condensation heat with temperature.

Considering the oscillatory interactions one may conclude that the 2D condensation is an activated process. The growth of open clusters (particularly the linear ones) needs lower activation energy than the close-packed island formation. Therefore the open clusters should predominate at low temperatures and low coverages, as it is observed experimentally.

References

[1] J.M. Rogowska, K.F. Wojciechowski, *Surf. Sci.* **213**, 422 (1989), ibid. 231, 110 (1980) and references therein.

[2] J. Kołaczkiewicz, E. Bauer, *Phys. Rev. Lett.* **53**, 485 (1984).

[3] J. Kołaczkiewicz, E. Bauer, *Surf. Sci.* **155**, 700 (1985).

[4] Yu.S. Barash, *Van der Waals Forces* (in Russ.), Nauka, Moskva 1988.

[5] J. Kołaczkiewicz, E. Bauer, *Surf. Sci.* **160**, 1 (1985).

[6] J. Kołaczkiewicz, E. Bauer, *Surf. Sci.* **175**, 508 (1986).

[7] J.H. de Boer, *The Dynamical Character of Adsorption*, Oxford University Press, Oxford 1968.