The peculiarities of phase transitions in adsorbed layers

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Abstract

Two-dimensional phase transitions are the most interesting phenomena discovered in the field of physical adsorption. The purpose of the article is to show the main changes that occur in our understanding of the nature of various "two-dimensional" phases recently. The special attention pays here to the results obtained by computer simulation of two classical adsorption systems N_2/graphite and C_6H_6/graphite. Approximation of two-dimensional behaviour, effects of influence of the periodicity of adsorption potential and effects of anisotropy of intermolecular potential on the properties of adsorbed layers are reviewed.

Do we really know how the adsorption layers are built and what is the real nature of the processes in these layers? Even if we give the positive answer to this question we have to remember that our description of adsorption layers (as well as any other complex systems) possible only in the form of model which reflects our current knowledge. It is clear that due to new information accumulation the model of the phenomena become more and more contradictory to available theoretical and experimental data and finally we have to make it more complicated or even change it. All these general considerations completely applicable to the problem of phase state of surface layers and phase transitions occur between these states.

The study of nature of phases of adsorbed substances is the most interesting and fast growing branch of modern science. This can be confirmed by the amount of publications and conferences deal with the problem of phase transitions in surface layers (see for example ref. 1-9). The new possibilities for studying these phenomena appeared due to improvement of traditional adsorption and calorimetry measurements as well as due to improvement of modern surface analysis techniques such as LEED, AES, NMR, X-ray diffraction, neutron scattering and others. It is interesting to mention that a number of fundamental results concerning phase transitions in surface layers on the molecular level were obtained with the help of computer simulations - new and very perspective technique of studying matter.

In this paper we will try to describe the main recent changes that happened in understanding of adsorption phases and phase transitions in surface layers. For this purpose the available literature data as well as our data obtained in intensive computer simulation of classical adsorption systems N_2/graphite (ref. 10-14) and C_6H_6/graphite (ref. 15-17) will be used.

Speaking about models used for the representation of adsorbed layer state it is necessary to mention that adsorbed layers are extremely nonuniform in the direction perpendicular to the surface of adsorbent. This gave the most essential feature usually used for the description of state of an adsorbed layers: their two dimensional nature. This concern first of all layers of molecules adsorbed on the uniform surfaces such as liquids or solid adsorbents such as graphite. The "two-dimensional" behaviour of adsorbed layers allow us to use for the description of it state two-dimensional approximation. And it is natural that two-dimensional wan-der-Waals model was one of the first models used for the description of adsorbed fluids. As well as in three dimensional world it allow to distinguish two-dimensional gas and two-dimensional liquid. With the help of this model the critical point of the layer of adsorbed molecules was estimated. It is easy to show that if such simple model is applicable, two-dimensional critical temperature should be equal half of correspond three-dimensional value. The ideal two-dimensional model though could not explain the existence of two-dimensional crystal and a lot theoretical considerations has been given to solve this problem. Shortly speaking it was proved that from theoretical point of view long range positional order cannot be observed, but other types of topological order can exist (see for example ref. 18).

It is clear that notion of uniform adsorption potential and an ideal two-dimensional state approximations can be satisfactory applied to adsorption monolayers only at high temperatures when the periodic changes of adsorption potential in the plane parallel to the surface can be neglected. At the same time at these temperatures adsorbed molecules can be considered as effectively spherical symmetric due to their intensive reorientating. Due to this reasons wan-der-Waals model can be used under this conditions as a good approximation.

If study of the nature of adsorption phases are made at low temperatures a number of new facts should be taken in consideration. First of all it is already mentioned influence of the periodicity of adsorption potential in the plane parallel to the surface of the adsorbent. If this changes of the potential will be taken in to account we should say that adsorbed molecules can be localized in positions corresponded to minima of adsorption potential. It means that the structure of adsorbed film should depend of the structure of adsorption field. Such specifically adsorption phases which cannot be formed in three-dimensional systems got the name commensurate or epitaxial phases. The existence of commensurate phases the new type commensurate-incommensurate phase transition made possible.

Formation of commensurate phase possible in that cases when two-dimensional structure formed by molecules of adsorbate themselves is close to the structure of adsorption field. The main role here play the sizes of molecules and their shapes. It is impossible to achieve the complete commensurability of adsorbed layer and adsorption potential. Due to asymmetry of intermolecular potential the real commensurate phase usually has lower density compare to possible density of ideal two-dimensional layer. The classification of possible commensurate adsorption layers on the graphite surface were considered in (ref. 19).

The most known example of commensurate phases formation is the Kr ' monolayers adsorbed on the surface of graphite (ref.18). The surface plane of this adsorbent is made up of hexagons of carbon atoms and minima of adsorption potential Kr - graphite located in the centres of these hexagons. Kr atom has such size that no more then 1/3 of adsorption sites can be occupied. The length of side

of unit cell of adsorption crystal in this case √3 times larger
compare to the side of unit cell of the graphite surface. The
angle between sides unit cells mentioned is equal 30 degrees. As a
result commensurate two-dimensional crystal of Kr is formed on the
surface of graphite. The name of this commensurate phase is
(√3·√3)-30°. The stabilising influence of adsorption field is so
strong, that commensurate phase can exist at temperatures much
higher when it can be expected. Due to this circumstances the
region of two-dimensional liquid disappear on the phase diagram
for the system under consideration. The critical point disappear
from phase diagram as well. We should to agree that in this case
simple wad-der-Waals model does not applicable.

More complicated behaviour can be observed if layers of adsorbed
molecules but not atoms are under consideration. In these cases
effects of different orientationaly ordered structures formed on
the surface play very important role. For example interaction
energies and effective size for N_2 molecule are similar to those
of Kr atom. From this point of view phase diagram of nitrogen
adsorbed on the graphite surface should be resemble to phase
diagram Kr/graphite. It is only partly true at high temperatures
where the N_2 rotation is free or nearly free (where no critical
point on N_2/graphite diagram as well). But at temperatures lower
27 K different commensurate in-plane orientationally ordered phase
are formed. Although the in-plane orientational disordering of
adsorbed nitrogen molecules is complete at 70 K, computer
simulation (ref. 10) show that the distribution of molecule
orientation relative to the surface plane are not random and
depend upon both coverage and temperature. It means that an
accurate description of the thermodynamics of such systems should
take in to account the orientational changes.

One of the most interesting features of the orientational
distributions obtained for the N_2/graphite system is the coupling
between orientation and maximum discovered for the first layer
coverage (ref. 10). Changes in the first layer coverage are in
turn strongly associated with changes in the density of molecules
in the second layer. It means that often used model of adsorption
of second and higher located layers on the unperturbed first layer
is far from reality. It worth to stress here that the mentioned
maximum of the density of the first adsorption layer N_2 as well as
detailed picture of process taking place during adsorption was
possible to prove only on the base of computer simulation study of
this system.

Anisotropy of intermolecular interaction plays very important role
as well when layers of adsorbed molecules are considered. In the
case of N_2/graphite system for example electrostatic interactions
between nitrogen molecules define the formation of orientational
structure of adsorbed layer.

The anisotropy of benzene-benzene interaction determine the main
special features of benzine/graphite adsorption system. It was
shown (ref. 15) that due to mainly electrostatic part of
interaction the energy of T-shape configuration of C_6H_6 molecules
(the most typical configuration for three-dimensional crystal)
approximately three times large then the interaction energy of the
molecules located in one plane. But such "coplanar" orientations
are the most typical for the benzine molecules adsorbed on the
graphite surface. The changes in molecule-molecule interaction for
this system occur with reorientation of adsorbed molecules
practically completely compensated by changes of molecule-
adsorbent interaction and give the well experimentally known
surprisingly constant value of the heat of adsorption. The
weakness of interaction between benzene molecules in adsorption

layer should considerably lower the value of critical temperature of this system. This give the explanation of the fact that observable critical temperature of benzene monolayer at least on 100° lower compare to the value which can be estimate on the base of three-dimensional critical temperature and mentioned wan-der-Waals rule states that two-dimensional critical temperature should be equal to 1/2 of it three-dimensional value.

The size of benzene molecule considerably large compare to the sizes of Kr atom and N_2 molecule but it is proven that in this case the commensurate layer on the surface of graphite at low temperatures forms also. The difference is in the periodic structure: instead of ($\sqrt{3} \cdot \sqrt{3}$) phase the formation of ($\sqrt{7} \cdot \sqrt{7}$) commensurate crystal observed. Other characteristic feature of benzene/graphite system is the places of the location of adsorbed molecules above the graphite surface. The minima of adsorption potential in this case are not in the middle of the hexagons but above the surface carbon atoms. Very important role here plays the electrostatic interaction of C_6H_6 with graphite.

Low temperature commensurate benzene crystal is orientally ordered with all molecules rotated on approximately 40 °in the plane parallel to the surface. The orientation structure of adsorption layer in this case determined first of all by the shape of the molecules. Increasing the temperature leads to the melting of adsorption layer. At coverage equal to the half of monolayer this melting occur at ≈145 K (ref. 17). The sharp drop of average energy per molecule observed at this temperature testify that it is the first order melting of the adsorbed solid. In the case of monolayer coverage though computer simulations show (ref.17) that the melting became continuous. Such behaviour is not unusual for monolayer films of non-spherical molecules and have been observed previously for nitrogen as well.

The reason for changing the order of the phase transition with the coverage of the adsorption system is in the different mechanisms of the melting. At densities lower than monolayer coverage two-dimensional crystal have the possibility for the thermal expansion and melting without reorientation or the second layer promotion of molecules. So in this case all changes of the phase state of adsorbed layer can be realised in the same plane. If the density of the layer increases (became close to the complete monolayer coverage) where is no possibility for the thermal expansion of two-dimensional phases in the same layer. In this case melting of the monolayer can be realised through the stage either reorientation (as in the case of benzene/graphite system) or the second layer promotion (as in the case of nitrogen/graphite system) of the molecules. It means that the third dimension of the system become to play very important role. Melting of the layer in this case happened locally and become continuous. The change of the nature of the phase transition allow us to suppose the possibility of critical point presence not only in the case of coexistence two-dimensional liquid and two-dimensional gas but in the case of two-dimensional crystal and two-dimensional fluid coexistence as well.

It is impossible to consider all aspects of phase transitions in adsorption layers in short presentation. We tried no show here how the nature of phases formed in adsorption layers differ from the three-dimensional phases and from simple wan-der-Waals model. We tried to illustrate the most noticeable effects of most general use for the physisorbed layers. Now it is clear that even in such simple case variety of adsorbed phases and corresponded phase diagrams are much reacher compare to three-dimensional state and phase transitions here can be much more peculiar. The main

peculiarities of "adsorption" phases mentioned in this paper connected with

- the possibility of commensurate phases formation,
- the mutual influences of orientational and translational ordering of adsorbed molecules in adsorption layers,
- the influence of higher located layers on the structure of the first adsorption layer,
- the dependence of nature of the phase transition in adsorption layer upon the coverage of the surface.

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