Thermodynamics of Binary Two-Dimensional Phases on Nearly Perfect Substrates*

François Hommeril and Boyan Mutaftschiev

CNRS-Laboratoire Maurice Letort F-54600 Villers-les-Nancy, France

We present some results on stability and phase transitions of binary two-dimensional phases on the surfaces of nearly perfect substrates.

A simple theoretical model allows to get insight into the mutual enhancement of the condensation of the adsorption partners, resulting in the formation of two-dimensional mixture, and into the subsequent demixing of the layers, when the concentration of one of the components in the bulk phase continues to increase. Both continuous and discontinuous demixing can be expected, and other phase transformations, like two-dimensional solidification and melting, and/or different structural transitions, are possible when the molecules of the adsorbates have different shape and the substrate is not fully isomorphic with them. Some of the peculiarities regarding the physical realizations of the proposed model are shown on the example of the coadsorption of methane and krypton on exfoliated graphite.

1. INTRODUCTION

The preparation of nearly perfect, energetically homogeneous, surfaces of lamellar substrates with large specific area, e.g. exfoliated graphite, enabled the study, during the last 25 years, of step-wise isotherms of several rare gases[1-3], as well as of many light hydrocarbons[4-7] and their derivatives[8-9]. These isotherms, forseen in earlier theoretical works and partially studied eperimentally by Halsey and co-workers[10-12], gave access to complete thermodynamic description of the two-dimensional (2D) phases formed on the foreign substrate and their transformations, including two-dimensional condensation, melting, wetting transition, commensurate-incommensurate and other structural transitions, critical phenomena, etc. In this way have been demonstrated, not only the great experimental facilities offered by the physics in two dimensions, but also its richness in many fundamental problems, such

* Based on an invited lecture presented at the *8th »Ruđer Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces* Red Island, Rovinj, Croatia, Yugoslavia, June 22 — July 1, 1989.

as the physical realization of different theoretical models[13] and the study of their universality classes[14].

It is worth mentioning that most of the experimental results on the structures and structural transitions in condensed 2D phases, have been obtained only, or at first, from the shape of the isotherms[15-17]. LEED, X-ray and neutron scattering studies[18-21], as well as specific heat measurements[22,23] followed sometimes after many years.

The rare experimental studies on binary 2D mixtures[24-26] followed rather the opposite way. Technical difficulties in the measurements of adsorbed quantities and partial pressures of the two adsorption partners conditionned the choice of systems in which one[24-27], when not both[25,26], of the components had a vanishing vapor pressure at the temperatures of the experiment. The resulting low exchange rate with the medium is then similar to that in three dimensional systems and offers some experimental advantages. However, the procedure can be misleading for many reasons. One of them is the important lag of the equilibrium. The second is the impossibility of knowing the exact composition of the adsorbed layer at rising temperature and/or the 2D pressure exerted on it. In other words, we actually know much about the structures of different condensed binary 2D phases and few about the place of those phases in the corresponding phase diagrams, and about the order of the phase transitions.

The studies presented in this paper are supposed to give a beginning of answer to the need of thermodynamic description of binary adsorption layers on a perfect solid substrate. In Section II we stress the importance of the parameters defining the relative stability of condensed layers of two substances which do not form binary mixtures. These considerations will serve as guide-lines for the treatment in Section III of the adsorption isotherms of binary layers. For this purpose we use both the mean field aproximation and a Monte Carlo simulation. In Section IV we present some preliminary experimental results on the co-adsorption of krypton and methane on exfoliated graphite.

II. WETTING AND DISPLACEMENT OF IMMISCIBLE TWO-DIMENSIONAL PHASES[28]

Many classifications of »well wetting« and »poorly wetting« two-dimensional layers on one and the same substrate, depending on the values of the respective adsorption energies, have been given in the last couple of years[29,30]. The displacement of one condensed 2D phase by another has been experimentally studied and interpreted by energetic arguments as well[24,27].

In fact, it is not a new assertion that the displacement of any phase, wetting a foreign substrate, by another one is possible only if there is gain of surface work, and that, as far as two-dimensional phases are concerned, this gain can be calculated by integration of the Gibbs isotherm. The consequence of the above statement is that wetting and displacement of two-dimensional phases depend on one more parameter than the adsorption energies alone, namely on the pressure (or concentration) of the bulk phase with

which the adsorbed layer is in equilibrium. Using a simplified model which considers the degree of coverage Θ equal to zero before the »step« of the isotherm, corresponding to a first order phase transition 2D gas → 2D solid (Figure 1), and equal to one beyond it, the integration of the Gibbs isotherm yields:

$$\Delta\gamma = -\int \Gamma d\mu_{a} = -a^{-1}\int_{-\infty}^{\Delta\mu}\Theta d(\Delta\mu) = \begin{cases} 0 \text{ for } \Delta\mu \leq \Delta\mu^{*} & \text{(because } \Theta = 0) \\ a^{-1}(\Delta\mu^{*} - \Delta\mu) \text{ for } \Delta\mu > \Delta\mu^{*} & \text{(because } \Theta = 1) \end{cases} \quad (1)$$
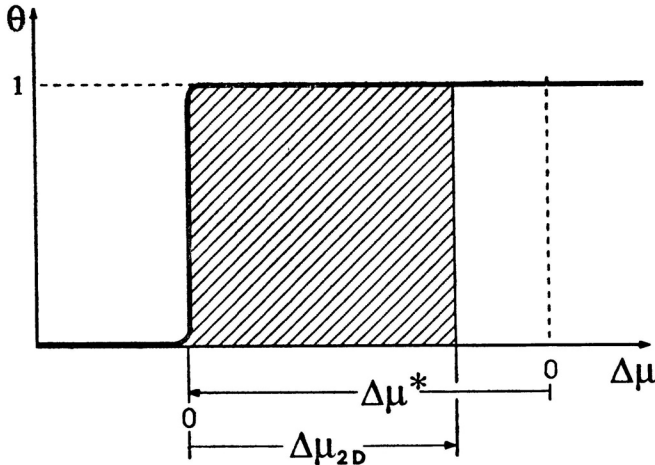

Figure 1: Idealized stepwise isotherm; the step corresponds to a first order phase transition 2D gas (degree of coverage zero) → 2D solid (degree of coverage one). $\Delta\mu^{*}$ is the undersaturation, with respect to the saturated vapor of the adsorbate, at which both 2D phases are in equilibrium with the vapor. If the latter state is taken as reference, the scaled supersaturation $\Delta\mu_{2D}$ is positive in the entire existence range of the condensed 2D phase. The shadowed area is a direct measure of the variation of the surface free energy of the substrate, due to adsorption.

Here $\Delta\gamma$ is the variation of the surface free energy, per unit area of the substrate, due to the adsorption; Γ is the number of adsorbed molecules on the same area, related to the degree of coverage by $\Theta = \Gamma a$, where a is the area occupied by one adsorbed molecule; μ_{a} and $\Delta\mu$ are respectively the chemical potential of the adsorbed molecules, equal at the equilibrium to that of the molecules in the bulk phase, and the difference between those potentials and the chemical potential in a reference state that is the infinite crystal (or the saturated vapor) of the same substance at the same temperature. $\Delta\mu$ can be refered as »generalized supersaturation« although in the domain of stability of the condensed 2D phases it is always negative. If the bulk phase is an ideal gas, $\Delta\mu = k_{B}T\ln(p/p_{o})$, where p is the actual pressure, p_{o} the pressure of the saturated vapor, T is the absolute temperature and k_{B} the Boltzmann constant.
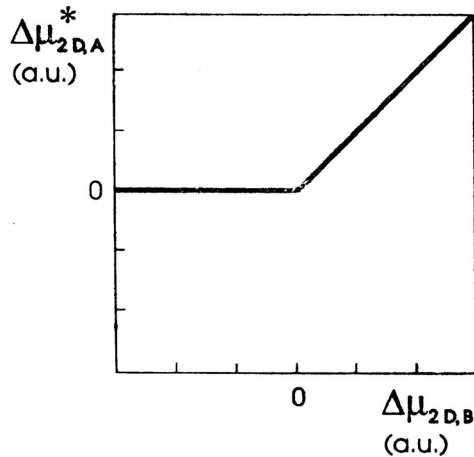
Figure 2: Scaled supersaturation of the step of a substance A as a function of the scaled supersaturation of a substance B at which this substance has been preadsorbed on the substrate. The adsorption isotherms of both adsorbates in the pure state are supposed to have the shape of the isotherm of Figure 1, and an immiscibility among A and B is assumed.

The »supersaturation of the step«, $\Delta\mu^*$ in eq.(1) plays a major role in the thermodynamics of the 2D phases. It has been shown[31] that it is equal, in first approximation, to the difference in the binding energes ψ° and ψ of a molecule adsorbed alone on the surface of its own substance, and on the surface of the actual substrate, respectively:

$$\Delta\mu^* \approx \psi^\circ - \psi \qquad (2)$$

$\Delta\mu^*$ defines nothing but the equilibrium (saturation) pressure of the 2D condensed phase at the given temperature. If this state is taken as reference rather than the saturation pressure of the 3D condensed phase, the new scaled supersaturation $\Delta\mu_{2D}$ has the merit to be independent of the interaction between the adsorbate and the adsorbent and is a direct measure of the gain of surface work per area a (cf Figure 1).

Let us suppose that a substance B is adsorbed on the substrate exactly at the supersaturation $\Delta\mu_B^*$, or at the scaled supersaturation zero. No work will be needed to remove B and to replace it by another substance A, even if the latter has a smaller binding energy and, according to simple ideas, »wets« the substrate not so good as the first one. Displacement takes place when the gain of surface work $\Delta\gamma_A$ due to the adsorption of the substance A exceeds the work $\Delta\gamma_B$ already won by the adsorption of B. In the case above, $\Delta\gamma_B = 0$, although the substance B is already condensed, and its displacement by A is possible for any $\Delta\mu_{2D,A} > 0$. In general, the displacement of B by A takes place when $\Delta\mu_{2D,A} > \Delta\mu_{2D,B}$. This means that, with respect to the supersaturation corresponding to the step of the isotherm of the substance A on the bare substrate, the same is translated by $\Delta\mu_{2D,B}$ to more positive values in

the case of a substrate previously coated with the substance B (it should be mentioned that for simplicity we have assumed that the areas occupied by a molecule of A and B are the same).

Figure 2 visualizes the above conclusions. The plot represents the scaled supersaturation corresponding to the step of the isotherm of A, $\Delta\mu_{2D,A}^*$, as a function of the scaled supersaturation, $\Delta\mu_{2D,B}$ at which B has been preadsorbed on the substrate. One sees that in this idealized model, where no interaction between an A and a B molecule is allowed, $\Delta\mu_{2D,A}^*$ is not affected by the presence of B until this substance starts to condense. Beyond this point $\Delta\mu_{2D,A}^*$ increases linearly by increasing $\Delta\mu_{2D,B}$ with a slope of unity.

The assertion that the parameters responsible for the »wetting« (and, hence, the displacement) of 2D phases is the difference between cohesion and adhesion energies per molecule, roughly equal to the binding energies ψ° and ψ, is true only at the saturation pressures of the 3D phases of the respective substances (provided that the 2D phases are still stable!). At the saturation, $\Delta\mu_{2D,A} = -\Delta\mu_A^*$ and $\Delta\mu_{1D,B} = -\Delta\mu_B^*$ and, according to eq.(2) the substrate will be irremediably coated by a layer of the substance having the larger difference $\psi - \psi^\circ$.

III. THERMODYNAMICS OF MIXED TWO-DIMENSIONAL PHASES ; MEAN-FIELD APPROACH AND MONTE-CARLO SIMULATION[31]

The isotherms of two coadsorbing substances on a foreign substrate can be easily calculated using the mean-field approach[33,34]. The model we used is that of the localized adsorption of two substances, A and B, having spherical molecules of the same size, on a substrate with a honeycomb structure. The shortest distance between two adsorption sites in assumed equal to the molecular diameters of the adsorbates, so that the complete adsorbed monolayer has a commensurate hexagonal structure.

Many interesting features of 2D phase transitions can be observed in the outlines of a first-nearest neigbor approximation, depending on the relative energy values, φ_{AA}, φ_{BB}, φ_{AB}, of the A-A, B-B and A-B intermolecular bonds inside the layer. Let us first recall that, according to the mean field approximation, the two-dimensional critical temperature of a condensed monomolecular layer is defined by the relation $n\varphi/k_BT = 4$, where n is the maximum number of first neighbors (two-dimensional coordination number), equal to six in our model. The two-dimensional condensation is a first order phase transition if $n\varphi/k_BT > 4$, where the energy parameter φ is equal to φ_{AA} for pure A layer, to φ_{BB} for a pure B layer and should have some weighted average value for a mixed A-B layer. When mixing or demixing takes place inside the condensed A-B layer, the energy parameter responsible for the order of the transformation is $\Delta\varphi = \varphi_{AA} + \varphi_{BB} - 2\varphi_{AB}$[33].

Two examples of isotherms of the component A as a function of its scaled supersaturation $\Delta\mu_{2D,A}$, at constant supersaturations of the component B are presented on Figures 3 and 4 (continuous curves). In Figure 3 the A-A and B-B bonds are strong, while the energy parameter $\Delta\varphi$ is small (the respective bond energies are expressed in units of k_BT). The bulk gas phase being undersaturated with respect to the 2D condensed layer of B ($\Delta\mu_{2D,B} = -0.5k_BT$), both adsorbed species form initially a 2D gas. By increa-
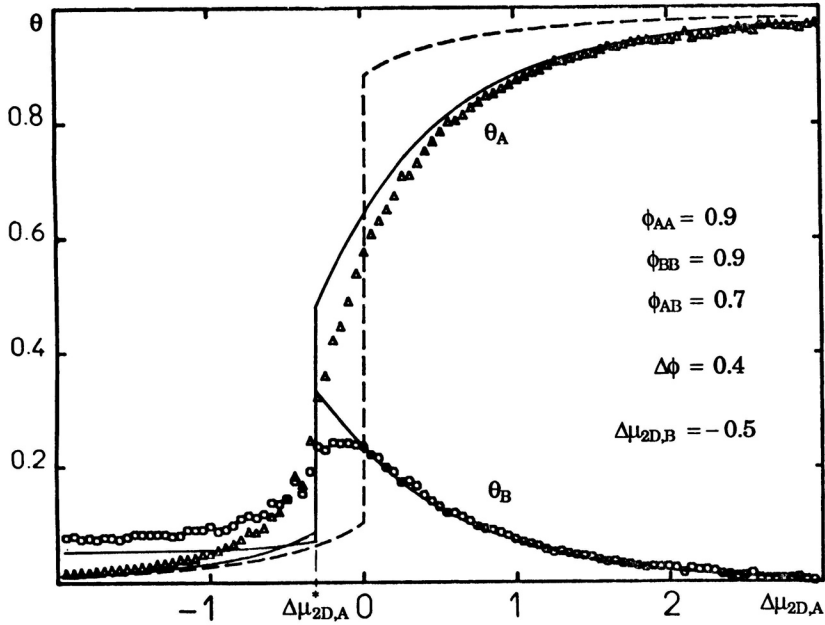
Figure 3: Theoretical isotherms of co-adsorption of two miscible isomorphic substances A and B on an isomorphic substrate, versus scaled supersaturation of A, at constant (negative) scaled supersaturation of B. Solid lines, mean field calculation; squares and triangles, Monte Carlo simulation. All φ's and $\Delta\mu$'s are in units of k_BT.
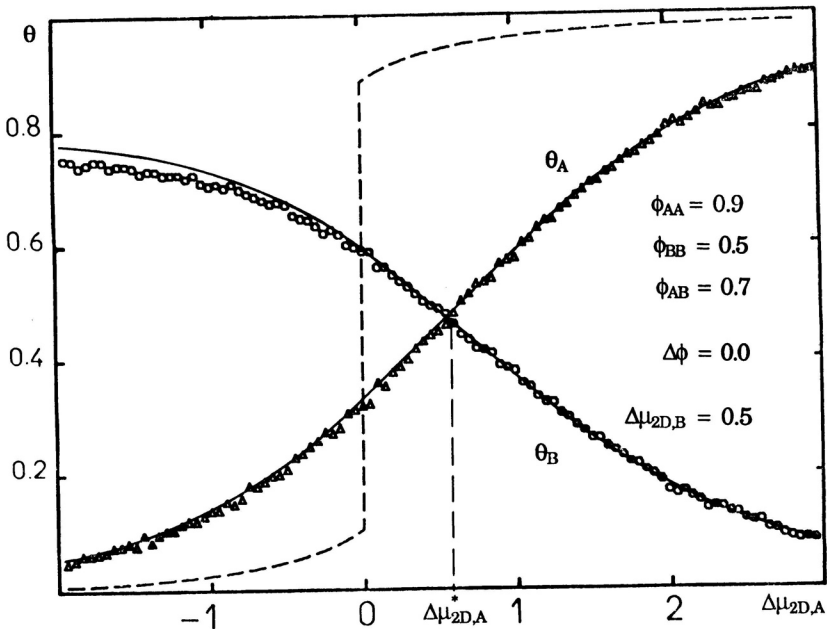

Figure 4: Same isotherms as in Figure 3, calculaed with different set of binding energies and at positive, constant, scaled supersaturation of B.

sing supersaturation $\Delta\mu_{2D,A}$ of A, the two components increase their degrees of coverage, φ_A and φ_B above the values for simple adsorption (cf the dashed curve which is the adsorption isotherm of the pure substance A), and condense at $\Delta\mu_{2D,A} = -0.3\,k_BT$ into a mixed layer following a first order transition. Beyond this value, the layer is continuously enriched on A while the concentration of B in the layer decreases.

In Figure 4 the binding energies are so chosen that $\Delta\varphi = 0$. Moreover, the scaled supersaturation of the component B is now $\Delta\mu_{2D,B} = 0.5\,k_BT$, i.e., before the beginning of adsorption of A, the surface is already covered by a condensed B layer. The isotherm of A is entirely governed in this case by $\Delta\varphi$ and has an overcritical character.

The »experimental points« (squares and triangles) of the same figures result from a Monte Carlo simulation using the same model and the same energy parameters. They correspond to the numerical solution of the Ising model[35] which, as known, tempers the some exaggerated tendency of the mean field approximation to find first order transition in too many cases, as in Figure 3. However, the change of slope of the isotherms between the transition 2D gas $\rightarrow$ 2D solid and the continuous displacement in condensed 2D phase is clearly visible. In the case of higher order transitions, as in the Figure 4, the fit between mean-field calculation and Monte Carlo simulation is almost perfect.
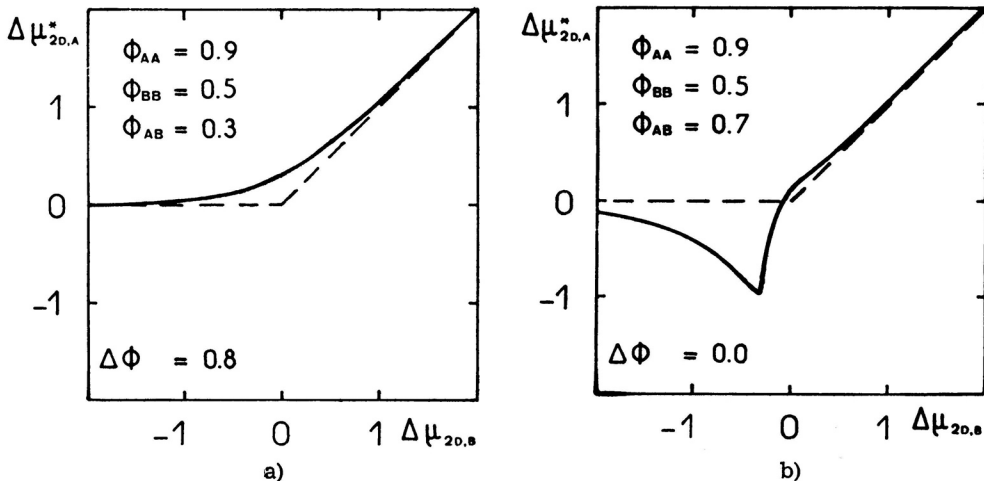

Figure 5: Same plots as that of Figure 2, issued from mean field calculation for coadsorbates A and B of different miscibility. The case of Figure 1 is represented on both plots by the dashed lines; a) weak interaction between A and B atoms; b) strong A-B interaction; one can notice in the latter case the enhacement of the 2D condesation of A due to the presence of B on the surface as 2D gas.

The dependence of the supersaturation of the step of A on the supersaturation at which B has been adsorbed is plotted on Figures 5a and b for two different sets of binding energies. In both cases the ideal behavior of Figure 2 is given for comparison by the dashed line. One sees that, while for a low energy φ_{AB} of the mixed bond (Figure 5a), the curve lies very near the ideal one, a strong A-B interaction results in enhancement of the condensation of A

(Figure 5b) at negative scaled supersaturations of $\Delta \mu_{2D,B}$, i.e. when B is present on the surface as a 2D gas. The run of the isotherm of Figure 3 has already demonstrated this effect. In both cases, when the supersaturation $\Delta \mu_{2D,B}$ is large, $\Delta \mu^*_{2D,A}$ tends asymptotically to the ideal behavior.
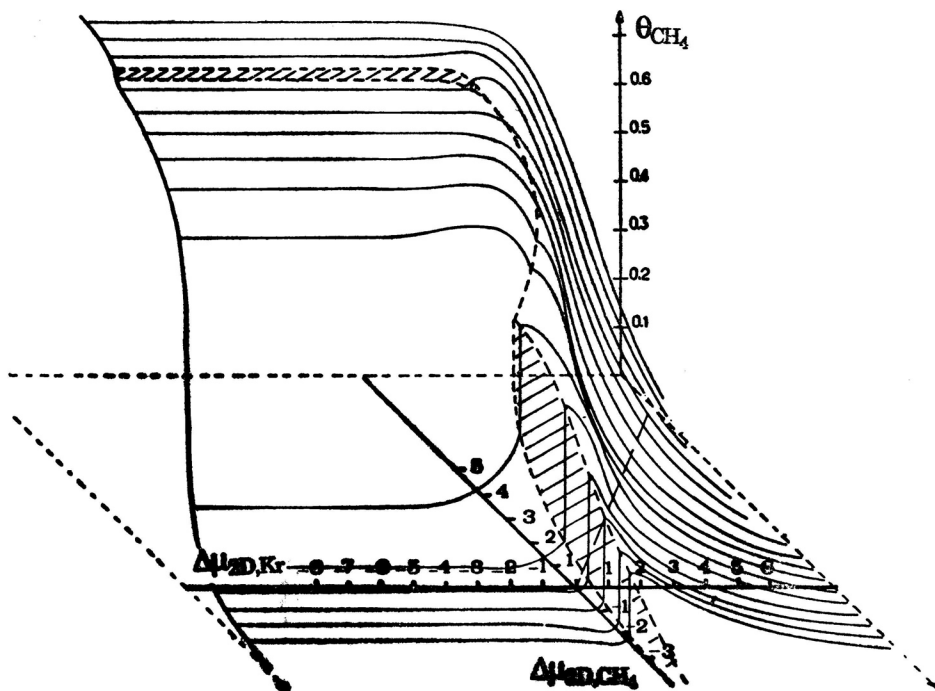

Figure 6: Experimental isotherm of methane on exfoliated graphite at 77.3 K in presence of krypton. The supersaturations of both methane and krypton are scaled with respect to the steps in the isotherms of the pure gases.

IV. EXPERIMENTAL STUDY OF THE CO-ADSORPTION OF Kr AND CH₄ ON GRAPHITE

In order to study co-adsorption in a binary system by classical volumetric methods, we developed a fully automatized apparatus which measures the total adsorbed quantity by the »method of rests«, i. e. a measurement of the total pressure in a calibrated volume before and after adsorption, plus the quantity of the adsorbed krypton only, by radioactivity measurement of the concentration of Kr^{85} in the gas mixture in the same volume, the adsorbed quantity of methane being then obtained by difference.

In this case, the degree of coverage of either component is a function of both supersaturation $\Delta \mu_{2D,CH_4}$ and $\Delta \mu_{2D,Kr}$, as shown in figure 6 and 7 where are plotted the isotherms of methane and krypton respectively at a temperature of 77.3 K. The shadowed parts of the surfaces illustrate the abrupt steps resulting from first order transitions.

Two-dimensional plots as those shown in Figures 3 and 4 are just cross sections of the three-dimensional surfaces of Figure 6 and 7, parallel to one of the planes $\Theta - \Delta \mu_{2D}$. In Figura 8 are plotted the isotherms of methane (curve a) and krypton (curve b) as a function of the supersaturation of methane, $\Delta \mu_{2D,CH_4}$, at constant scaled supersaturation of krypton $\Delta \mu_{2D,Kr} = -0.5 \, k_B T$. The dashed curve represents
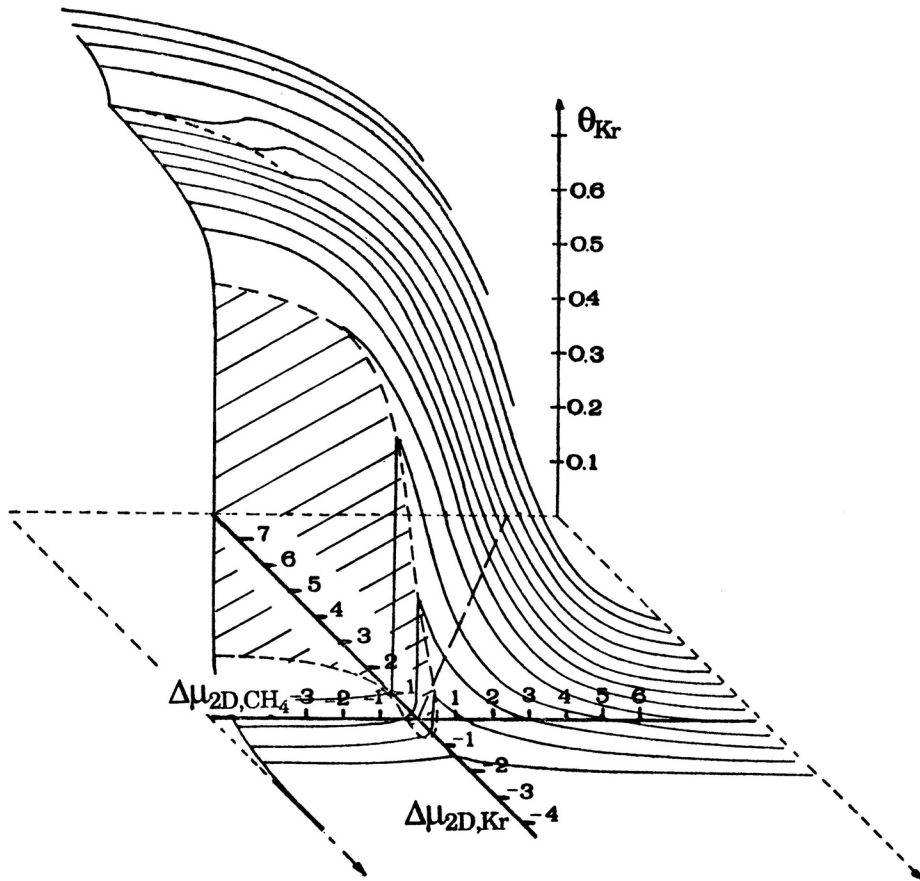
Figure 7: Experimental isotherm of krypton on exfoleiated graphite at 77.3 K in presence of methane, determined simultaneously with that of methane in Figure 6.

the isotherm of pure methane at the same temperature. The finite slope of the step of this isotherm indicates that methane transforms into a 2D overcritical liquid, the cricital temperature being about 69 K[36]. At almost complete coverage, the layer undergoes a new transformation to two-dimensional solid, visible from the small substep in the upper part of the isotherm.

The run of the isotherms of Figure 8 is very similar to that of the curves in Figure 3. As expected, the co-condensation of both methane and krypton occurs at negative scaled supersaturation of methane. Futhermore, the step isotherm becomes steeper, indicating probably a first order condensation of the mixed 2D gas into a mixed 2D solid of methane dissolved in a krypton matrix. The further increase of the concentration of methane proceeds smoothly as in an ideal solution. Whether or not the substep of the isotherm of pure methane subsists in presence of krypton, is yet not clear. If its existence were confirmed, the mixed layer methane-krypton would pass through four successive 2D phases by increasing supersaturation of methane and constant supersaturation of krypton, namely, 2D gas → 2D solid → 2D overcritical liquid → 2D solid.

In Figure 9 are plotted the same type of experimental isotherms at a constant scaled supersaturation of krypton $\Delta\mu_{2D,Kr} = 1.0k_BT$. Just as the theoretical curves

of Figure 4. the isotherms in this case show a continuous enrichment of the ini-
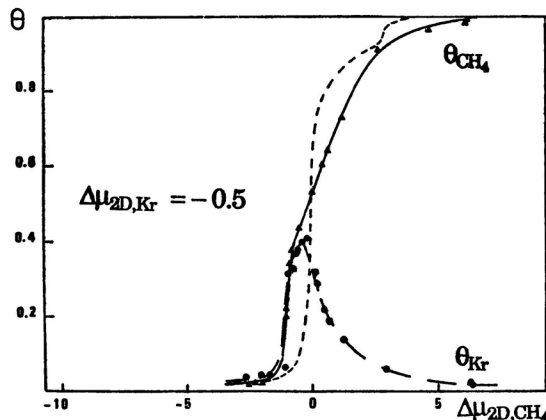tially pure condensed krypton layer by methane and their inflection points,

Figure 8: Cross sections of the experimental isotherms of methane and krypton of
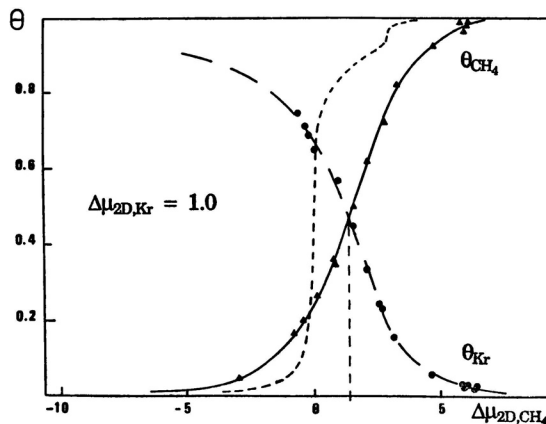Figures 6 and 7, paralellel to the plane θ - $\Delta\mu_{2D,CH4}$ at $\Delta\mu_{2D,Kr} = - 0.5$.

Figure 9: Same as Figure 8, $\Delta\mu_{2D,Kr} = - 0.5$.

roughly corresponding to the step half height, are translated with respect to the step
of the isotherm of pure methane, by some 1.29 k_BT (one may notice that in the
theoretical isotherms of Figure 4, the scaled supersaturation of the inflection points
of the isotherms is by 15—20% higher than the value (0.5 k_BT) corresponding to full
immiscibility).

In Figure 10 is plotted the experimental plot $\Delta\mu^*_{2D,CH4}$ vs $\Delta\mu_{2D,Kr}$, similar to
that of Figure 2 for immiscible coadsorbates and to those of Fig. 5a and b for mis-
cible isomorphic adsorption partners A and B. One can see the enhancement of the
coadsorption at $\Delta\mu_{2D,Kr} < 0$ compared to those given by the (idealized) dashed line.

V. CONCLUSION

The theoretical, as well as experimental, possibilities offered to the
physical endeavor in the realm of two-dimensional phases on nearly perfect
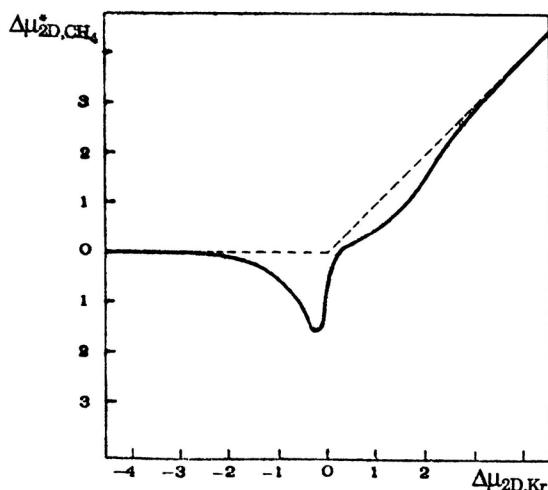substrates are considerable. To the variety of physical models issued from

Figure 10: Same plot as that of figures 2 and 5, determined experimentally in the case of coadsorption of methane and krypton. The idealized case of Figure 2 is represented by the dashed line.

the more or less good fit between the 2D structures of the substrate and the adsorbate, and the direct access to the »bulk« of the 2D phases in the detailed equilibrium with the medium, we have to add an even more important feature. Derisory changes in the pressure (or concentration) of the 3D medium are at the origin of considerable variations of the 2D spreading pressure throughout the layer. Since this force is applied to a layer of molecular thickness only, transposed to a unit area it can corresponds to pressure variations of many tons per square centimeter. One understands then why 3D pressure variations of the order of milibars, as in the case of the adsorption of methane or/and krypton on graphite, can induce important structural changes in the condensed 2D layer. For the same type of studies on 3D phases, a complex and expensive equipment is needed.

In a current X-ray diffraction study we try to give a structural support to the existence of mixed 2D phases methane-krypton on graphite and to the type of transitions among them. Further studies on systems with less ideal behavior of binary mixtures will be also of great interest.

REFERENCES

1. A. Thomy and X. Duval, *J. Chim. Phys. (Paris)* **66** (1969) 1966.
2. A. Thomy and X. Duval, *J. Chim. Phys. (Paris)* **67** (1970) 286.
3. A. Thomy and X. Duval, *J. Chim. Phys. (Paris)* **67** (1970) 1101.
4. M. Matecki and A. Thomy, *J. Chim. Phys. (Paris)* **71** (1974) 1484.
5. J. Menaucourt, A. Thomy and X. Duval, *J. Phys. (Paris)* **C4** (1977) 195.
6. J. Regnier, J. Menaucourt, A. Thomy and X. Duval, *J. Chim. Phys. (Paris)* **78** (1981) 552.
7. Y. Khatir, M. Coulon and L. Bonnetain, *J. Chim. Phys. (Paris)* **75** (1978) 796.
8. B. W. Davis and C. Pierce, *J. Phys. Chem.* **70** (1966) 1051.
9. P. Dolle, M. Matecki and A. Thomy, *Surf. Sci.* **91** (1980) 271.
10. W. M. Champion and G. D. Halsey, *J. Phys. Chem.* **57** (1953) 646.

11. J. H. Singleton and G. D. Halsey, *J. Phys. Chem.* **58** (1954) 1011.
12. C. F. Prenzlow and G. D. Halsey, *J. Phys. Chem.* **61** (1957) 1158
13. E. Domany, in *Interfacial Aspects of Phase Transformations*, B. Mutaftschiev, ed., Reidel Publ., Dordrecht, 1982, p. 119.
14. M. J. Tejwani, O. Ferreyra and O. E. Vilches, *Phys. Rev. Let.* **44** (1980) 159.
15. A. Thomy, J. Regnier, J. Menaucourt and X. Duval, *J. Cryst Growth* **13/14** (1972) 159.
16. J. Regnier, A. Thomy and X. Duval, *J. Chim. Phys.* *(Paris)* **74** (1977) 926.
17. M. Matecki, A. Thomy and X. Duval, *Surf. Sci.* **75** (1978) 142.
18. M. D. Chinn and S. C. Fain, *J. Vac. Sci Technol.* **14** (1977) 314.
19. T. Ceva and C. Marti, *J. Phys. Lett.* (1978) L221.
20. J. P. Coulomb, J. P. Biberian, J. Suzanne, A. Thomy, G. H. Trott, H. R. Danner and F. Y. Hansen, *Phys. Rev. Lett.* **43** (1979) 1878.
21. A. Glanchand, J. P. Coulomb, M. Bienfait and J. G. Dash, *J. Phys. Lett.* *(Paris)* **40** (1979) L-543.
22. G. B. Huff and J. G. Dash, *J. Low Temp. Phys.* **24** (1976) 155.
23. T. T. Chung and J. G. Dash, *Surf. Sci.* **66** (1977) 559.
24. C. Marti, T. Ceva, B. Croset, C. de Beauvais and A. Thomy, *J. Phys.* *(Paris)* **47** (1986) 1517.
25. H. You, S. C. Fain J. Satija and L. Passel, *Phys. Rev. Lett.* **56** (1986) 244.
26. P. W. Stephens. A. I. Goldmann, P. A. Heiney and P. A. Bancel, *Phys. Rev. B* **33** (1986) 655.
27. M. Bouchdoug, J. Menaucourt and A. Thomy, *J. Phys.* *(Paris)* **47** (1986) 1797.
28. B. Mutaftschiev, *Phys. Rev. B* **40** (1989) 779.
29. R. Pandit. M. Schick and M. Wortis, *Phys. Rev. B* **26** (1982) 5112.
30. M. Bienfait, J. L. Seguin, J. Suzanne, E. Lerner, J. Krim and J. G. Dash, *Phys. Rev. B* **29** (1984) 983.
31. J. M. Cases and B. Mutaftschiev, *Surf. Sci.* **9** (1968) 57.
32. F. Hommeril and B. Mutaftschiev, *Phys. Rev. B* **40** (1989) 296.
33. W. L. Bragg and E. G. Williams, *Proc. Roy. Soc. (London)* **145** (1934) 699; ibid. **151** (1935) 540.
34. B. Mutaftschiev and A. Bonissent, *Surf. Sci.* **34** (1973) 649.
35. E. Ising. *Z. Physik* **31** (1925) 253.
36. H. K. Kim and M. H. W. Chan, *Phys. Rev. Lett.* **53** (1984) 170.

SAŽETAK

Termodinamika binarnih dvo-dimenzionalnih faza na skoro perfektnim površinama

B. Hommeril i B. Mutaftschiev

Pokazani su neki rezultati izračunavanja stabilnosti i faznih prijelaza za dvo--dimenzionalne faze na površinama perfektnih supstrata.

Jednostavni teorijski model dozvoljava uvid u međusobno pojačavanje kondenzacije adsorpcijskih partnera i stvaranja dvo-dimenzionalne smjese. Isto se tako modelom može tumačiti razmiješavanje slojeva, kada koncentracija u otopini jedne od komponenata raste. Model se može tumačiti i kontinuirano i diskontinuirano razmiješavanje, te druge fazne transformacije, kao što su to dvo-dimenzionalna solidifikacija ili taljenje, te strukturalni prijelazi kada molekule adsorba imaju različite oblike, a supstrat nije s njima izomorfan. Primjerom ko-adsorpcije metana i kriptona na lisnatom grafitu ukazuje se na fizičku realnost pradloženog modela.