

Mixing and displacement in binary two-dimensional condensed phases on a foreign substrate: Mean-field approach and Monte Carlo simulation

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Isotherms of binary adsorption layers on an isomorphous substrate, as a function of the partial pressures of both adsorption partners, are calculated using the mean-field approximation. Conditions for the enhancement or inhibition of adsorption at low coverages, for the variation of the equilibrium pressure between the two-dimensional (2D) gas and the 2D condensed phase, for successive transitions from the 2D gas to the condensed mixed 2D layer to separated 2D phases, and for critical phenomena inside the 2D condensed phases have been deduced. A Monte Carlo simulation confirms the general trends of the mean-field results.

I. INTRODUCTION

Although numerous experimental studies¹⁻⁵ have been recently devoted to the coadsorption of gases on homogeneous solid substrates, relatively little attention has been paid to the thermodynamics of the coadsorption. The influence of the partial pressures of the adsorbing partners on the two-dimensional phase diagram, in particular, has not been fully explored.⁶⁻⁸

In the present paper we propose, first, a mean-field approach to the computation of two-component adsorption isotherms. We discuss the main features of the coadsorption, namely, the transition from a two-dimensional (2D) gas to a two-dimensional solid, mixing and demixing, and critical phenomena in condensed binary layers. The link with the displacement of unmixable layers, treated elsewhere,⁹ will also be made. In the second part, we present the results of Monte Carlo simulation performed under the assumptions of the same physical model.

In view of the multitude and complexity of the phenomena expected in the cases of multiple layer coadsorption, e.g., establishment of concentration gradients or demixing on different layer levels, we shall restrict our interest in this paper to monomolecular layers of both coadsorbing substances. Also, in order to exclude the possibility of condensation on the top of a condensed layer of the other adsorption partner, before the surface of the substrate is fully occupied, one assumes that for both partners the interaction with the substrate is much stronger than the interaction between them. The latter is true in most cases studied experimentally, e.g., rare gases and light hydrocarbons on graphite.^{10,11}

II. MEAN-FIELD APPROACH

A. The adsorption isotherms

We shall apply the usual mean-field approximation for localized adsorption on an isomorphic substrate¹² (this simple model assumes one to one correspondence between maximum number of adsorbed molecules and number of available adsorption sites; moreover, a compact

monomolecular adsorbed layer is identical with an existing lattice plane in the three-dimensional lattice of the adsorbing substance), thus replacing the partition function of N monatomic molecules adsorbed on N_s adsorption sites,

$$Q_{N/N_s} = \frac{1}{N!} \Lambda^{-3N} \sum_i \left[g_i \left[\prod_{j=1}^N \bar{v}_j \right] \exp(-U_i/k_B T) \right] \quad (1)$$

by

$$Q_{N/N_s} = \frac{1}{N!} \Lambda^{-3N} \left[\sum_i g_i \right] \hat{v}^N \exp(-\bar{U}/k_B T). \quad (2a)$$

Here Λ is the de Broglie thermal wave length, $\Lambda = h/(2\pi m k_B T)^{1/2}$; U_i is the potential energy of the layer in the i th state, all molecules at rest, and g_i is the degeneracy of that state (number of configurations having the same U_i); \bar{v}_j is the configurational integral of vibration of an adsorbed molecule, sometimes called "mean vibrational volume." The mean-field approximation factorizes the second and third multipliers in the sum of Eq. (1), by giving mean values to both the vibrational term (a fairly acceptable assumption in view of the small differences among the volumes \bar{v}_j of molecules adsorbed in different sites of the surface, and also compared to that of a molecule in the three-dimensional lattice), and to the exponential energy term (the latter assumption is far more problematic, since it postulates a dependence of U_i on the number N of adsorbed molecules only and not on their configuration).

For a binary mixture of N_A and N_B molecules of the substances A and B , adsorbed on N_s sites, Eq. (2a) transforms to

$$Q_{(N_A+N_B)/N_s} = \Lambda^{-3(N_A+N_B)} \frac{\hat{v}_A^{N_A} \hat{v}_B^{N_B}}{N_A! N_B!} \times \sum_i g_i \exp(-\bar{U}/k_B T). \quad (2b)$$

We shall proceed as in the case of regular three-dimensional (3D) solid solutions,¹³ assuming that the two

coadsorbing substances A and B are isomorphic, that the intermolecular forces among adsorbed molecules are limited to first nearest neighbors only, and will set the binding energies between two molecules of the substance A , between two molecules of the substance B , and between one molecule of A and one of B , equal, respectively, to ϕ_{AA} , ϕ_{BB} , and ϕ_{AB} . As to the interaction of the adsorbed molecules with the isomorphic substrate, no restriction will be made for its range and nature, but that the binding energies, ψ_A and ψ_B must be larger than the corresponding energies, ψ_A^0 and ψ_B^0 , of an A molecule on a substrate of A and of a B molecule on a substrate of B . If the maximum number of first nearest neighbors of an adsorbed molecule in the plane of the surface (two-dimensional coordination number) is n , the average potential energy \bar{U} of the layer of $N_A + N_B$ molecules adsorbed on N_s sites is

$$\bar{U} = - \left[N_A \psi_A + N_B \psi_B + \frac{n}{2} N_A \Theta_A \phi_{AA} + \frac{n}{2} N_B \Theta_B \phi_{BB} + n N_A \Theta_B \phi_{AB} \right], \quad (3)$$

where the degrees of coverage, $\Theta_A = N_A/N_s$ and $\Theta_B = N_B/N_s$ are also the probabilities for a given molecule to have as first nearest neighbor a molecule of A and B , respectively. Using the same notations, the enthalpies of sublimation at the absolute zero point (neglecting the zero point vibrational energy) per molecule of the pure large 3D phases of A and B yield

$$\phi_A^0 = \psi_A^0 + \frac{n}{2} \phi_{AA} \quad (4a)$$

and

$$\phi_B^0 = \psi_B^0 + \frac{n}{2} \phi_{BB}. \quad (4b)$$

After substitution of \bar{U} from Eq. (3) into Eq. (2b), and taking into account that $\sum_i g_i$ is the number of ways to distribute $N_s - N_A - N_B$ empty sites over a total number N_s of sites, one has, for the chemical potentials, per molecule of the A and the B species,

$$\begin{aligned} \mu_A^{(a)} &= - \frac{\partial}{\partial N_A} k_B T \ln Q_{(N_A + N_B)/N_s} \\ &= \mu_{0A} - (\psi_A + n \Theta_A \phi_{AA} + n \Theta_B \phi_{AB}) \\ &\quad + k_B T \ln \frac{\Theta_A}{1 - \Theta_A - \Theta_B} - k_B T \ln \hat{\nu}_A \end{aligned} \quad (5a)$$

and

$$\begin{aligned} \mu_B^{(a)} &= - \frac{\partial}{\partial N_B} k_B T \ln Q_{(N_A + N_B)/N_s} \\ &= \mu_{0B} - (\psi_B + n \Theta_B \phi_{BB} + n \Theta_A \phi_{AB}) \\ &\quad + k_B T \ln \frac{\Theta_B}{1 - \Theta_A - \Theta_B} - k_B T \ln \hat{\nu}_B, \end{aligned} \quad (5b)$$

where $\mu_0 = k_B T \ln \Lambda^3$.

The chemical potentials $\mu_A^{(g)}$ and $\mu_B^{(g)}$ in the gas phase,

in equilibrium with the adsorbed layer, are in general different from those, $\mu_A^{(g)0}$ and $\mu_B^{(g)0}$, in the saturated vapor of the infinite 3D phases of A and B . The differences, $\Delta\mu_A = \mu_A^{(g)} - \mu_A^{(g)0}$ and $\Delta\mu_B = \mu_B^{(g)} - \mu_B^{(g)0}$ are the generalized "supersaturations" of the respective species (although condensed 2D phases are stable at undersaturation only, $\Delta\mu < 0$, to avoid ambiguity, we shall use the term "supersaturation," keeping in mind that it can take negative and positive values as well). Since the chemical potential of a species in the saturated vapor $\mu^{(g)0}$ is equal to its chemical potential $\mu^{(c)}$ in the infinite condensed 3D phase, one can write for the chemical potential of the supersaturated vapor of either component

$$\mu^{(g)} = \mu^{(c)} + \Delta\mu = \mu_0 - \phi^0 - k_B T \ln \bar{\nu}^0 + \Delta\mu, \quad (6)$$

where $\bar{\nu}^0$ is the mean vibrational volume of a molecule in the infinite crystal. When equilibrium is established between the vapor and the adsorbed layer, $\mu_A^{(g)}$ and $\mu_B^{(g)}$, calculated from Eq. (6), must be equal, respectively, to $\mu_A^{(a)}$ and $\mu_B^{(a)}$ from Eqs. (5a) and (5b). After substitution of ϕ_A^0 and ϕ_B^0 from Eqs. (4a) and (4b), one obtains the isotherms of coadsorption of A and B as a function of the partial supersaturations $\Delta\mu_A$ and $\Delta\mu_B$ from the solution of the system

$$\begin{aligned} k_B T \ln \frac{\Theta_A}{1 - \Theta_A - \Theta_B} &= - \frac{n}{2} \phi_{AA} (1 - 2\Theta_A) + n \phi_{AB} \Theta_B \\ &\quad - (\psi_A^0 - \psi_A) - k_B T \ln \frac{\bar{\nu}_A^0}{\hat{\nu}_A} + \Delta\mu_A, \end{aligned} \quad (7)$$

$$\begin{aligned} k_B T \ln \frac{\Theta_B}{1 - \Theta_A - \Theta_B} &= - \frac{n}{2} \phi_{BB} (1 - 2\Theta_B) + n \phi_{AB} \Theta_A \\ &\quad - (\psi_B^0 - \psi_B) - k_B T \ln \frac{\bar{\nu}_B^0}{\hat{\nu}_B} + \Delta\mu_B. \end{aligned}$$

It is worthwhile to point out that within the same model and the approximations made above, the adsorption isotherm of a pure layer, e.g., of the substance A , yields

$$\begin{aligned} k_B T \ln \frac{\Theta_A}{1 - \Theta_A} &= - \frac{n}{2} \phi_{AA} (1 - 2\Theta_A) - (\psi_A^0 - \psi_A) \\ &\quad - k_B T \ln \frac{\bar{\nu}_A^0}{\hat{\nu}_A} + \Delta\mu_A. \end{aligned} \quad (8)$$

Equations (7) and (8) can be greatly simplified if one chooses as reference state for the supersaturations $\Delta\mu_A$ and $\Delta\mu_B$ the equilibrium between the 2D gas, the 2D condensed phase, and the 3D vapor instead of the equilibrium between the 3D phase and its saturated vapor. For a pure layer, this state is characterized by $\Theta = 0.5$, and thus, e.g., for the coadsorbate A [cf. Eq. (8)], by the supersaturation

$$\Delta\mu_A^* = \psi_A^0 - \psi_A + k_B T \ln \frac{\bar{\nu}_A^0}{\hat{\nu}_A}. \quad (9)$$

The scaled supersaturation of the two-dimensional phase is, therefore,

$$\Delta\mu_{2D,A} = \Delta\mu_A - \Delta\mu_A^* ; \quad (10)$$

it is negative when the stable phase is a 2D gas, positive when the condensed phase is the only stable one, and zero when those phases are coexisting. With the help of Eqs. (10) and (9), the system of Eqs. (7) simplifies to

$$k_B T \ln \frac{\Theta_A}{1 - \Theta_A - \Theta_B} = -\frac{n}{2} \phi_{AA}(1 - 2\Theta_A) + n\phi_{AB}\Theta_B + \Delta\mu_{2D,A} , \quad (11)$$

$$k_B T \ln \frac{\Theta_B}{1 - \Theta_A - \Theta_B} = -\frac{n}{2} \phi_{BB}(1 - 2\Theta_B) + n\phi_{AB}\Theta_A + \Delta\mu_{2D,B} ,$$

and so does Eq. (8):

$$k_B T \ln \frac{\Theta_A}{1 - \Theta_A} = -\frac{n}{2} \phi_{AA}(1 - 2\Theta_A) + \Delta\mu_{2D,A} . \quad (12)$$

B. A qualitative overlook

One can interpret qualitatively some properties of the adsorption isotherms, in the extreme cases of very small and very high total surface coverages.

If both Θ_A and Θ_B are small compared to unity, the development of Eq. (7) yields

$$\Theta_A = \left\{ \frac{p_A^0}{p_A} \exp \left[\left[\frac{n}{2} \phi_{AA} + \psi_A^0 - \psi_A \right] / k_B T \right] \times \exp[(1 - n\phi_{AB}/k_B T)\Theta_B] + (1 - n\phi_{AA}/k_B T) \right\}^{-1}$$

and

$$\Theta_B = \left\{ \frac{p_B^0}{p_B} \exp \left[\left[\frac{n}{2} \phi_{BB} + \psi_B^0 - \psi_B \right] / k_B T \right] \times \exp[(1 - n\phi_{AB}/k_B T)\Theta_A] + (1 - n\phi_{BB}/k_B T) \right\}^{-1} ,$$

where the identity $\Delta\mu = k_B T \ln(p/p^0)$, valid for an ideal gas, has been used and the usual approximation, $\hat{v} \approx \hat{v}^0$, is made.

Compared to the same development in the case of adsorption of a pure A layer, derived from Eq. (8),

$$\Theta_A^0 = \left\{ \frac{p_A^0}{p_A} \exp \left[\left[\frac{n}{2} \phi_{AA} + \psi_A^0 - \psi_A \right] / k_B T \right] + (1 - n\phi_{AA}/k_B T) \right\}^{-1} ,$$

one states that Θ_A is larger than Θ_A^0 and increases by increasing Θ_B if $n\phi_{AB}/k_B T > 1$. Hence, at low coverages of both components A and B , the coadsorption results in an increase of their degrees of coverage with respect to the pure adsorption layers at the same supersaturation when the energy of the mixed bond ϕ_{AB} is sufficiently

large. In this case the molecules of one of the coadsorbates act as active centers for the adsorption of the other. Furthermore, since by increasing supersaturation of one of the components, e.g., A , the supersaturation of the other (B) being kept constant, a 2D gas to 2D condensed phase transition eventually occurs which increases considerably the degree of coverage Θ_A , it is clear that the degree of coverage Θ_B must pass through a maximum.

When the binding energy ϕ_{AB} is small ($n\phi_{AB}/k_B T < 1$), the presence of the coadsorbate decreases the degree of coverage of the other adsorption partner due to the partial occupation of the area available for adsorption.

When the total coverage Θ is nearly equal to one, so that one can set $\Theta_A \approx 1 - \Theta_B$, the system (7) results in the unique equation

$$k_B T \ln \frac{\Theta_A}{1 - \Theta_A} = -\frac{n}{2} \Delta\phi(1 - 2\Theta_A) + \Delta\mu_{2D,A} - \Delta\mu_{2D,B} , \quad (13)$$

where

$$\Delta\phi = \phi_{AA} + \phi_{BB} - 2\phi_{AB} . \quad (14)$$

Equation (13) reveals two general trends in the behavior of condensed binary layers.

(a) When adsorption of either one of the components takes place by displacement of molecules of the other component (no holes), the parameter $\Delta\phi$ of Eq. (14), responsible for the order of the 2D phase transition (i.e., for the existence of a miscibility gap in the composition of the 2D "alloy"), and for the value of the critical temperature of demixing T_c , is the same as that for a three-dimensional binary alloy in the original treatment of Bragg and Williams.¹³

(b) The transformation, at constant temperature, of a B -rich 2D alloy into an A -rich alloy, takes place at a supersaturation $\Delta\mu_{2D,A}$ higher by $\Delta\mu_{2D,B}$ than the supersaturation $\Delta\mu_{2D,A} = 0$ at which a pure 2D gas of A transforms into a pure 2D condensed layer on the empty surface of the same adsorbent:

$$\Delta\mu_{2D,A}^* = \Delta\mu_{2D,B} . \quad (15)$$

This result will be discussed in more detail with respect to displacement in Sec. II D.

To summarize, the coadsorption of a second component B contributes to the enhancement of the adsorption of A at low coverages of both components. However, when a condensed B layer is already occupying the surface of the substrate, the condensation of an A -rich layer is inhibited and the step in the isotherm $\Theta_A(\Delta\mu_A)$ is translated to more positive values of $\Delta\mu_A$ by roughly $\Delta\mu_{2D,B}$.

C. The isotherms of a two-dimensional binary mixture

The exact numerical solutions of the system of Eqs. (11) are represented by the isotherms of Figs. 1–4, where the degrees of coverage Θ_A and Θ_B of both components

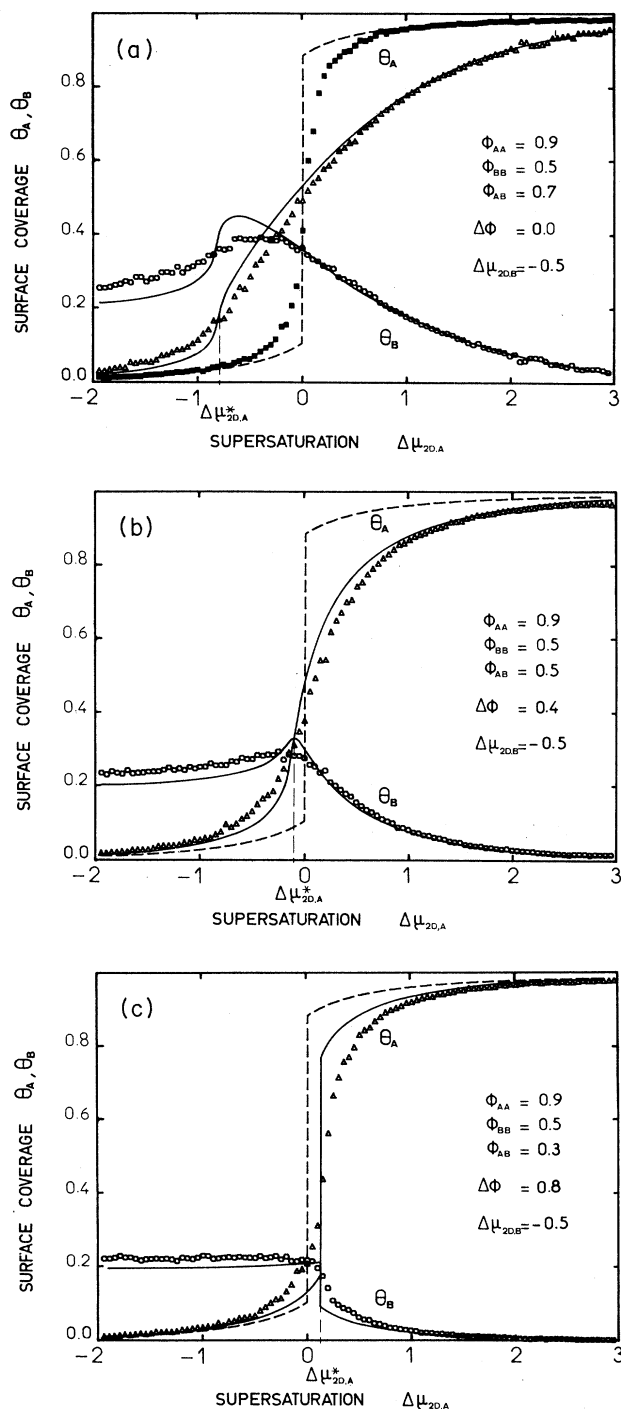


FIG. 1. Solid lines: coadsorption isotherms of A and B vs scaled supersaturation of A at a constant supersaturation of B , $\Delta\mu_{2D,B} = -0.5$ according to the mean field approximately [Eq. (15)]. The energy of the mixed bond ϕ_{AB} decreases from (a) 0.7 to (c) 0.3 whereby the value of $\Delta\phi$ increases from 0 (ideal solution) to 0.8 (first-order transition). The dashed line is the adsorption isotherm of the pure substance A . Triangles and circles represent, respectively, the values of Θ_A and Θ_B resulting from the simulation within the same set of parameters. All energies and supersaturations are in units of $k_B T$. In (a) are given also the experimental points (solid squares) of the simulation of a pure A layer.

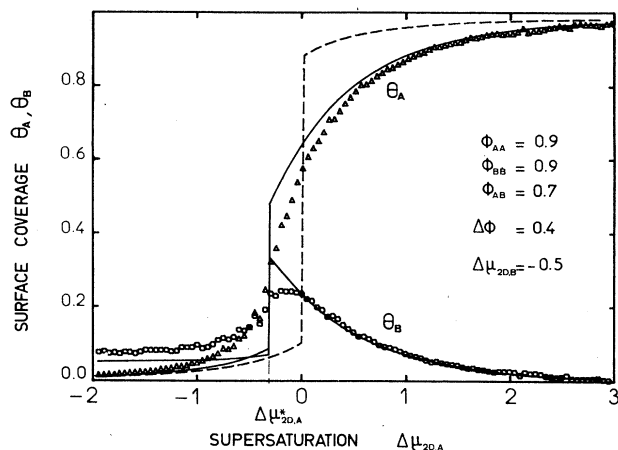


FIG. 2. Same as Fig. 1, as regards the values of ϕ_{AA} and $\Delta\phi$, but for the case of reinforced $B-B$ and $A-B$ bonds. Although $\Delta\phi = 0.4 < \frac{2}{3}$, the isotherms show a vertical part corresponding to a 2D gas-2D mixed solid ($\Theta_A = 0.493$, $\Theta_B = 0.340$) first-order transition, at $\Delta\mu_{2D,A} = -0.315$, followed by a second-order demixing of the condensed layer.

are plotted as a function of the scaled supersaturation $\Delta\mu_{2D,A}$ of A at constant supersaturation $\Delta\mu_{2D,B}$ of the other component. The interaction energies among the adsorbed molecules are chosen in a way that both first- and higher-order 2D phase transformations can be observed. The two-dimensional coordination number being $n = 6$ in all calculations (as well as in the simulations considered in Sec. III), the order of the transformation 2D gas to 2D solid in a pure one-component layer depends, according to the mean-field approximation, on the ratio $n\phi/4k_B T = 3\phi/2k_B T$. When this ratio is larger than one, $\phi/k_B T > \frac{2}{3}$, the transformation is a first-order one; when $\phi/k_B T < \frac{2}{3}$, the transformation is continuous, the equality $\phi/k_B T_c = \frac{2}{3}$ defining the critical temperature T_c . In the case of two-dimensional binary alloy AB , the same limits concern the value of $\Delta\phi$ from Eq. (14) indicating the existence of a miscibility gap ($3\Delta\phi/2k_B T > 1$) and defining the critical temperature of demixing.

In Figs. 1, 3, and 4, the forces among first nearest neighbors of the coadsorbate A are so chosen that its pure adsorption isotherm displays a first-order phase transition ($\phi_{AA}/k_B T = 0.9$; cf. the dotted curve in all figures), while the pure component B undergoes a continuous one ($\phi_{BB}/k_B T = 0.5$). Each of the three series of plots is characterized by a different, constant, value of the scaled supersaturation $\Delta\mu_{2D,B}$. In Fig. 1, $\Delta\mu_{2D,B} < 0$. In these conditions, if the coadsorbate B were alone to adsorb, it would have built a diluted layer (2D gas). In Fig. 3, $\Delta\mu_{2D,B} = 0$, i.e., the pure adsorbed layer of B would have been at the equilibrium between the 2D gas and the 2D solid. Finally, in Fig. 4, $\Delta\mu_{2D,B} > 0$. The pure adsorbed layer B is already a dense 2D phase which, when $\Delta\mu_{2D,A}$ is increased, is partially removed by or mixed with A .

Inside each of those three series of isotherms, the difference between the figures resides in the value of the

mixed bond energy $\phi_{AB}/k_B T$, and hence, of $\Delta\phi/k_B T$ which varies from zero to 0.8. In this $\Delta\phi$ range, the two-dimensional condensed phases change from ideal solutions to alloys with wide miscibility gap.

The remarkable feature of the isotherms of Fig. 1(a) is the strong enhancement of both coverages Θ_A and Θ_B for values of the scaled supersaturation $\Delta\mu_{2D,A}/k_B T$ as low as -0.9 . At slightly higher $\Delta\mu_{2D,A}$ values, the cov-

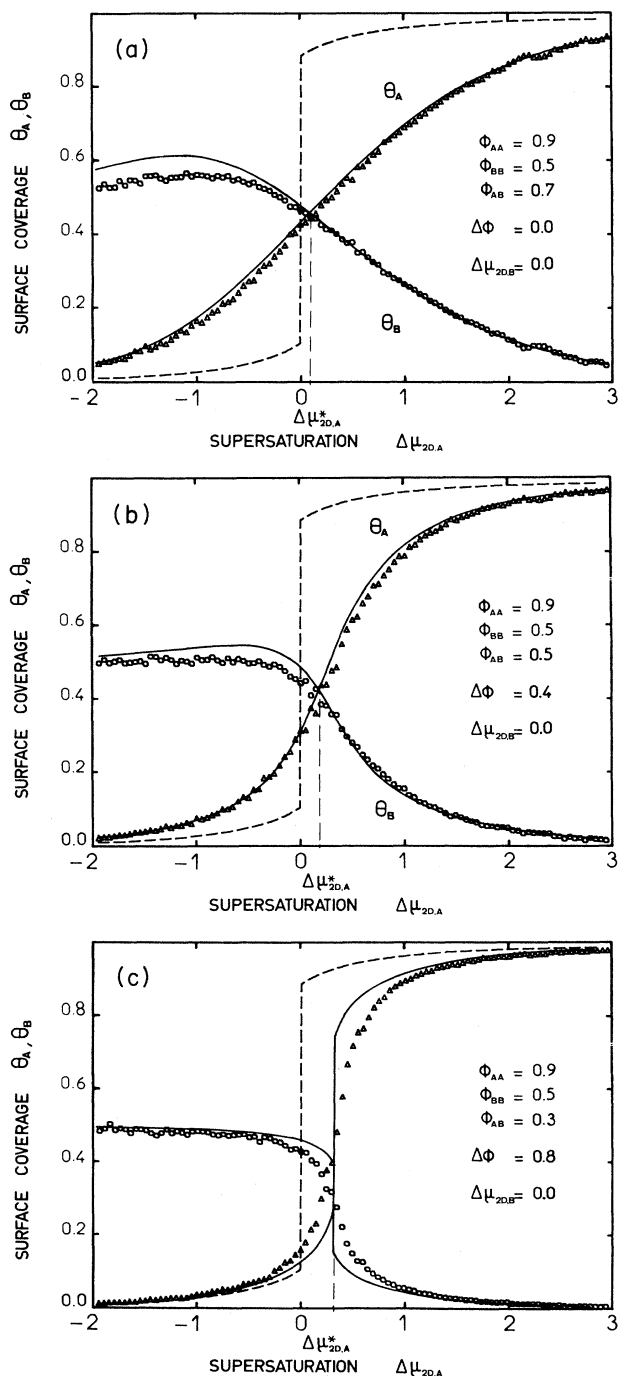


FIG. 3. Same as Figs. 1(a)–1(c) but at a supersaturation of B , $\Delta\mu_{2D,B}=0$.

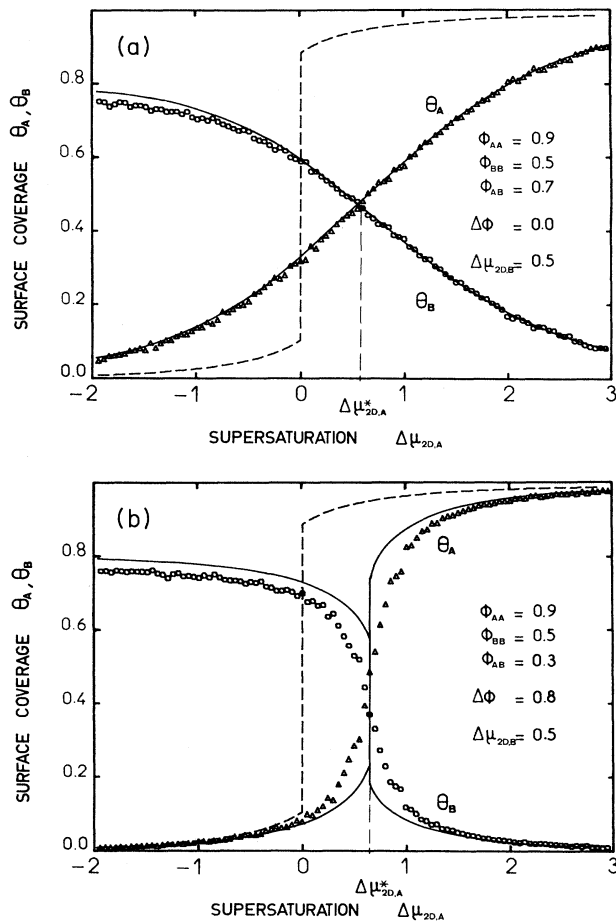


FIG. 4. Same as Figs. 1(a) and 1(c) but at a supersaturation of B , $\Delta\mu_{2D,B}=0.5$.

erage of B decreases. By its presence, however, it still inhibits the condensation of A which becomes a typical second-order transformation. The effect is reduced by decreasing the energy of the mixed AB bond [Fig. 1(b)], as expected from the qualitative considerations of the preceding section, and is almost nonexistent in the isotherms of Fig. 1(c) ($\phi_{AB}/k_B T=0.3$) where the increase of Θ_B in the supersaturation range $-2 < \Delta\mu_{2D,A}/k_B T < 0$ is negligible, despite the fact that Θ_A increases in the same time by a factor of 20. In this case the transformation is first order, the degrees of coverage passing abruptly from 0.182 to 0.778 for Θ_A and from 0.217 to 0.096 for Θ_B .

Figure 2 gives an example of two coadsorbents with equally high interaction energies, $\phi_{AA}/k_B T = \phi_{BB}/k_B T = 0.9$, and relatively large energy of the mixed bond, $\phi_{AB}/k_B T = 0.7$. In this case $\Delta\phi/k_B T < \frac{2}{3}$, and the isotherms should display a continuous transition, which seems to be true at higher supersaturations. However, as one can see in the figure, the degrees of coverage of both components increase suddenly at $\Delta\mu_{2D,A}/k_B T = -0.26$. This apparently contradictory behavior can be explained by the succession of two phase transitions. The first is

the condensation of a mixed 2D vapor to mixed 2D crystal. The energy parameter determining the order of the transition has presumably a value not very different from ϕ_{AA} and ϕ_{BB} . In the present case they are both large and, thus, the transformation is of first order. The degree of coverage of vacant adsorption sites, $1 - \Theta_A - \Theta_B$, having dropped during the 2D condensation from 0.827 to 0.165, the approximation $\Theta_A \simeq 1 - \Theta_B$, made in the preceding section, is fulfilled and Eq. (13) becomes fairly valid. The further transformation during which the layer becomes richer in A is now governed by the energy parameter $\Delta\phi$, and hence has a second-order character.

Among all isotherms presented in Figs. 1–4, those of Fig. 2 are also the only ones showing a scaled supersaturation $\Delta\mu_{2D,A}$ at which a first-order transformation occurs (supersaturation of the step), lower than that, $\Delta\mu_{2D,A} = 0$, of the pure A layer.

The next series of isotherms, Fig. 3, are calculated for the case when the scaled supersaturation of the component B is nil, i.e., when the continuous type isotherm of its pure adsorbed layer has an inflection point at $\Theta_B = 0.5$. In Figs. 3(a) and 3(b), the effect of the coadsorption of A on the isotherm of B is a small increase of Θ_B above 0.5, followed by a maximum. The isotherm of A displays in the entire $\Delta\mu_{2D,A}$ range a normal overcritical behavior, as should be expected from the values of $\Delta\phi/k_B T < \frac{2}{3}$, and so does the isotherm of B for $\Delta\mu_{2D,A}/k_B T \geq 0$. In Fig. 3(c) ($\Delta\phi/k_B T > \frac{2}{3}$) the transformation is abrupt and the related supersaturation $\Delta\mu_{2D,A}^*$ is sensibly larger than zero.

The isotherms of Fig. 4 are calculated in the case when $\Delta\mu_{2D,B}/k_B T = 0.5$, i.e., when the pure B layer is already a dense 2D phase. Therefore the adsorption of A can take place through partial or full displacement of B from the substrate, depending on the concentration of empty adsorption sites and on the value of the energy of the mixed bond ϕ_{AB} . The degree of coverage of vacant sites varies in the case of Fig. 4(a) (ideal 2D solution) from 0.04 to 0.16 in the entire $\Delta\mu_{2D,A}/k_B T$ range, while it changes during the first-order transformation of Fig. 4(b) from 0.18 to 0.07. This result shows that the approximation $\Theta_A \simeq 1 - \Theta_B$ made in the preceding section is fairly valid when $\Delta\mu_{2D,B}/k_B T > 0$, even if one of the components is in an overcritical state. As regards the translation to more positive values of the supersaturation at which the transformation takes place, some statements issuing from the simplified treatment in the preceding section should be made more precise.

D. Displacement

Strictly speaking, displacement from the substrate of a component B by the component A takes place in all cases described in Figs. 1–4, when by increasing supersaturation $\Delta\mu_{2D,A}$, Θ_B decreases. It is mostly admitted,^{14,15} however, that displacement means lack of miscibility of the adsorbing partners. If this is the case, the pure 2D layers of B before displacement, and of A after displacement, must also be compact. If they are not, the other adsorption partner can profit from the presence of holes to adsorb and, thus, form a mixed layer.

Nonmiscibility and compactness justified the assumption made in a previous paper,⁹ that the degree of coverage to be considered, of each component, is either zero or unity. The above approximation led to the simple result, identical to that obtained in Sec. II B, namely, a compact monomolecular layer, e.g., of B , condensed at the scaled supersaturation $\Delta\mu_{2D,B}$, cannot be removed by a compact monomolecular layer of A until the supersaturation $\Delta\mu_{2D,A}$ becomes higher than $\Delta\mu_{2D,B}$. In other words, the “supersaturation of the step” of the isotherm of A , $\Delta\mu_{2D,A}^*$, when B is previously condensed on the substrate, is translated by $\Delta\mu_{2D,B}$ with respect to the value (zero) which characterizes the condensation of A on the naked substrate [cf. Eq. (15)].

The supersaturations of the step of the isotherms in Figs. 1–4, noted by an asterisk, show that the result enunciated above is far from being verified in most cases. As regards the isotherms of Fig. 2, the strong attraction between the molecules of the two adsorption partners in the 2D gas is at the origin of the translation of $\Delta\mu_{2D,A}$ to negative values. In all other cases, however, the translation of $\Delta\mu_{2D,A}^*$ is to even more positive values than those expected from Eq. (15) and the deviation is larger, the stronger the first-order character of the transformation, i.e., the greater the miscibility gap. The latter statement is illustrated by comparison of the isotherms of Figs. 4(a) and 4(b). The (constant) supersaturation of B in both figures is $\Delta\mu_{2D,B} = 0.5$ and, according to Eq. (15), the step of the isotherm of A should have been translated from zero (pure A layer) to $\Delta\mu_{2D,A}^* = 0.5$. This is fairly true for the isotherm of Fig. 4(a) which is that of an ideal solution, while in the case of Fig. 4(b), representative for an almost “full displacement,” $\Delta\mu_{2D,A}^* = 0.613$.

In Fig. 5 are plotted the supersaturations of the step of the isotherms of A as a function of the supersaturation of B , for the same set of binding energies ϕ_{AA} , ϕ_{BB} , and ϕ_{AB} , as that used in the computation of the isotherms of Figs. 1, 3, and 4. The crosses and accompanying numbers designate couples $(\Delta\mu_{2D,B}, \Delta\mu_{2D,A}^*)$ already represented in the respective figures. The dashed line gives the solution in the ideal case:

$$\Delta\mu_{2D,A}^* = 0 \quad \text{for } \Delta\mu_{2D,B} \leq 0$$

and

$$\Delta\mu_{2D,A}^* = \Delta\mu_{2D,B} \quad \text{for } \Delta\mu_{2D,B} > 0$$

[cf. Eq. (15)].

Figure 5(a) depicts the case of a first-order displacement of B by A . The deviation of $\Delta\mu_{2D,A}^*$ from the ideal value is always positive, probably due to the lack of compactness, and tends to it asymptotically at large $\Delta\mu_{2D,B}$.

Figures 5(b) and 5(c) are representative of a second-order phase transition. The increasing energy ϕ_{AB} of the mixed bond enhances the adsorption of A when $\Delta\mu_{2D,B}$ is large and negative. However, when the condensation of B is approached, its presence on the substrate inhibits the condensation of A in a similar way as in the case of first-order transitions. The deviation of $\Delta\mu_{2D,A}^*$ from the ideal value decreases with decreasing $\Delta\phi$ (or increasing temperature).

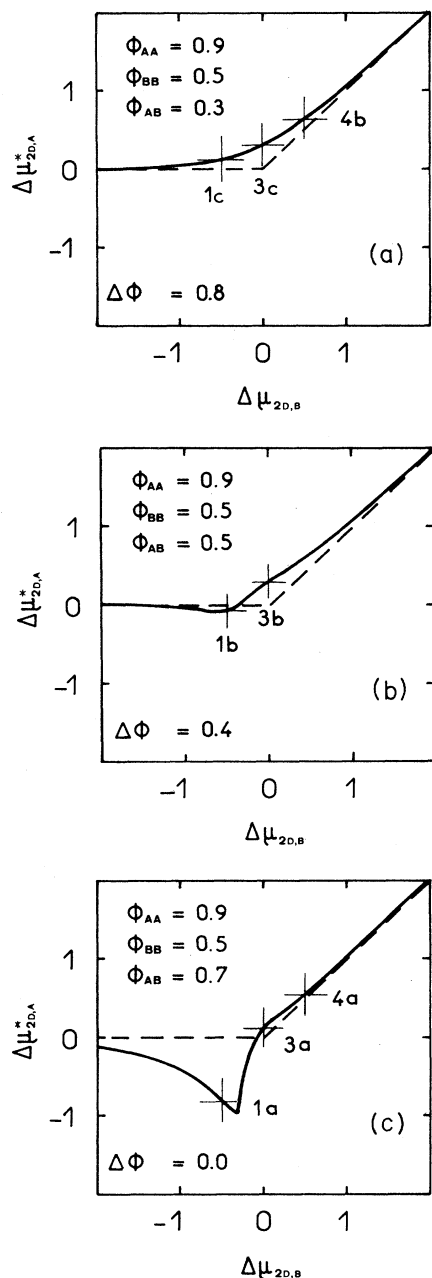


FIG. 5. Solid line: supersaturation of the step $\Delta\mu_{2D,A}^*$ (or inflection point in the case of second-order transition), of the coadsorption isotherms, vs supersaturation of B , $\Delta\mu_{2D,B}$. Dashed line: ideal case (see text). The crosses designate couples of variables ($\Delta\mu_{2D,B}$, $\Delta\mu_{2D,A}^*$) already represented in the preceding figures, the numbers of which are visible.

III. COMPUTER SIMULATION

The model used in the mean-field approach to coadsorption, and discussed in the preceding sections, that of localized adsorption and first-nearest-neighbor interac-

tion, served also for the simulation of equilibrium in the same systems. We used the simplified Monte Carlo procedure proposed long ago by Abraham and White,¹⁶ and since successfully applied to many problems of surface structure,¹⁷ nucleation,¹⁸ and growth¹⁹ of a crystal. By its very principle, this procedure results in the determination of equilibrium coverages or surface roughness, at different temperatures and supersaturations, close to those issued from the exact solutions (when available) of the Ising model.²⁰ Just as in the Ising model, the simulation generally moderates some of the exaggerated tendency of the mean-field approximation to find first-order phase transitions in too numerous cases.

The experimental points of Figs. 1–4 result from the simulation of the coadsorption of A and B in the same conditions, with respect to binding energies, temperature, and supersaturation, as the theoretical curves. To give an idea on the statistical reliability of these results, one must stress, first, that each point is the result of 5×10^4 successful Monte Carlo events (a total of 2×10^5 to 5×10^6 events per point). Furthermore, it has been established that the model of 200 adsorption sites is the smallest substrate for which finite-size effects can be neglected.

A few remarks can be made regarding the fit between mean-field approach and simulation: (a) the simulation confirms qualitatively the general trends of the isotherms obtained from the solutions of Eqs. (11); (b) an almost perfect fit is observed for ideal two-dimensional mixtures [when $\Delta\phi=0$, cf. Fig. 4(a)]; (c) both discontinuities and drastic changes in the degrees of coverage Θ_A and Θ_B , so common in the mean-field approach, are attenuated by simulation; so are the maxima of Θ_B preceding condensation [Figs. 1(a), 1(b), and 2], and the totality of the first-order transitions [Figs. 1(c), 2, 3(c), and 4(b)], as well as the condensation of a pure A layer represented, for comparison, in Fig. 1(a); (d) the latter statement does not mean that first-order two-dimensional condensation, or demixing of two-dimensional alloys, cannot be observed by simulation; the main point is that if one wishes to simulate adsorption at higher values of the energies ϕ_{AA} or ϕ_{BB} , i.e., at temperatures far below the two-dimensional critical temperature T_c , the efficiency of the Monte Carlo events drops dramatically and computer times become prohibitive; (e) as a consequence of the “smoothing” of the phase transitions, the simulation results in higher Θ_A values before, and lower Θ_A values after the transformation takes place, compared to the mean-field isotherms; conversely, when the component B is dominant before the transition [Figs. 3(a)–4(b)], the Θ_B values are overestimated by the mean-field approach before the transition, and underestimated after it, with respect to the simulation data; and (f) when the component B is in the state of undersaturation ($\Delta\mu_{2D,B} < 0$) and forms, before the transition takes place, a two-dimensional gas only, and when the interaction energy of the mixed bond ϕ_{AB} is high, the degrees of coverage Θ_A and Θ_B obtained by simulation are both initially higher than those expected by the mean-field approach, as seen in Fig. 1, and especially in Fig. 2, where the strong interaction between the two-dimensional gases A and B doubles their respective coverages.

IV. CONCLUSION

The realm of the two-dimensional binary phases, from extremely diluted gases to fully compact crystals, commensurate or not with the substrate, exhibits a great variety of phase transitions and continuous changes in the partial and total degrees of coverage of its surface. The physics of these systems is, therefore, richer than that of three-dimensional binary alloys or of their two-dimensional extension, the compact thin films.

From a thermodynamic point of view, the fact that the very existence of two-dimensional phases is due to the presence of a substrate is reflected by the introduction of more variables of state, such as surface area or spreading pressure. Thus the number of phases in equilibrium increases according to the Gibbs phase rule. Furthermore, relatively small variations of the absolute values of the pressure in the three-dimensional gas phase can result in large changes of the spreading pressure of the two-dimensional layer. In the case of adsorption of krypton on graphite at 77 K, for example, the equilibrium vapor pressure varies, between the formation of the first and of the second condensed layers, from 5×10^{-4} to 5.5×10^{-1} Torr, i.e., by some 733 dyn/cm². In the same time the spreading pressure of the first layer changes from zero to 47.3 dyn/cm. If one takes into account that the spreading pressure is exerted parallel to the substrate on a film of 4 Å thickness, the latter value is equivalent to a three-dimensional pressure of some 1.2×10^9 dyn/cm², or 1167 atm. It is, therefore, comprehensible that two-dimensional phase transitions, such as commensurate to incommensurate crystal, or melting, can be easily studied at constant temperature and by small external pressure variations, whereas the same studies on three-dimensional phases require high-pressure equipment.

Another important distinction of the physisorbed two-dimensional phases resides in their high rate of molecular exchange with the surrounding three-dimensional medium. Three-dimensional phases exchange molecules with the medium only through their surfaces. Since, by increasing dimensions, the number of molecules on the surface, compared to that in the volume, becomes rapidly negligible, and also volume diffusion in the solid state is extremely slow, the thermodynamic state of the medium (e.g., the partial vapor pressures of the components) is of no importance for the equilibrium and the possible phase transitions of an alloy; they are a function of the temperature only.

The situation is radically different when reversible (physisorbed) two-dimensional phases are concerned. A condensed layer exchanges molecules simultaneously through its "surface" (i.e., the ledges of the two-dimensional "islands") toward the two-dimensional gas, and directly from its "volume" (i.e., the interior of the same "islands") toward the three-dimensional medium. For this reason, the response of a two-dimensional phase to any variation in the state of its three-dimensional environment is quasi-immediate.

The above considerations indicate that, as far as two-dimensional phases are concerned, neither wetting and displacement, nor phase transformations in multicomponent systems, can be studied in detail without the exact knowledge of the equilibrium pressures of all adsorption partners.

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