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On the limit of compression of a physisorbed monolayer

L. W. Bruch (*), J. M. Gay and J. Krim

Département de Physique (**), Faculté des Sciences de Luminy, Case 901, 13288 Marseille Cedex 9, France

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Résumé. — On discute des effets des variations du potentiel d'interaction ε_0 entre le substrat et la première couche et de la commensurabilité uniaxiale de la monocouche sur sa limite de compression. S'il y a une transition monocouche-bilayer avec seulement de faibles modifications de la distance entre proches voisins, la valeur du potentiel chimique dépend de l'interaction substrat-deuxième couche mais peu de ε_0 . On discute des effets des valeurs nettement différentes de ε_0 pour divers substrats dans le cas de l'hélium. On présente des calculs sur la limite de compression du système commensurable uniaxial Xe/Cu(110); le potentiel chimique à la transition est très proche de celui de la condensation du Xe tridimensionnel. On discute de la valeur de ε_0 pour Xe/Cu(110) et la détermination expérimentale de la chaleur latente d'adsorption de sa monocouche.

Abstract. — Effects on the limit of monolayer compression of large changes in the first layer adatom-substrate holding potential ε_0 and of uniaxial registry of the monolayer are discussed. It is shown that if the monolayer-to-bilayer transition occurs with only small changes in the nearest neighbour spacing, the chemical potential there depends on the second-layer binding, but little on ε_0 . Consequences of the particularly large variations in ε_0 for helium between substrates are discussed. Model calculations of the limit of compression for uniaxially registered Xe/Cu(110) are reported; the chemical potential at the transition is quite close to that for condensation of bulk Xe. The value of ε_0 for Xe/Cu(110) and the experimental determination of the monolayer latent heat of adsorption are discussed and a revised value is proposed for the latent heat.

1. Introduction.

Monolayer solids of physisorbed gases may be continuously compressed by increasing the chemical potential of the coexisting three-dimensional (3D) gas [1-6]. The limit of compression [7-10] is set by transitions to other phases and is an element of the initial stages of multilayer formation [11-13]. The theory of the monolayer-to-bilayer transition, as a limit on monolayer compression, has been developed for inert gas adsorbates (Ne to Xe) which have no registry with the substrate and for which the holding potential is relatively strong compared to the lateral interactions [7-10]. At low temperatures, such a monolayer-to-bilayer transition is essentially a condensation of the second atomic layer of adsorbate: at coexistence there is then only a very dilute second layer of gas above the monolayer

solid and the bilayer consists of two solid atomic layers with very few vacancies. Here we discuss departures from the systematic trends established for the classical systems which may arise in adsorption of quantum gases [14-19] and in examples where a classical monolayer solid is in uniaxial registry with the substrate [20-22].

The monolayer (2D) solid of xenon adsorbed on the (111) face of silver, Xe/Ag(111), displays the simplest pattern of compression [1, 7], with no registry phases and little effect of quantum zero-point energy. At monolayer condensation the nearest-neighbour spacing in the 2D solid is 2 % larger than the nearest-neighbour spacing L_s in the 3D solid at the sublimation curve. Under compression, the nearest-neighbour spacing decreases and at the transition to the bilayer solid, the lateral nearest-neighbour spacings in both the monolayer and bilayer are experimentally indistinguishable (equality to within 0.5 %) from L_s . This pattern is observed also for Kr/Ag(111) [1], Ar/Ag(111) [1], and argon adsorbed on the basal plane surface of graphite, Ar/Gr [2]. For Kr/Gr [3], at monolayer condensation there is a registry lattice, but at the bilayer formation the nearest-neighbour spacing is

(*) Permanent address: Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.

(**) Equipe de Recherche associée au Centre National de la Recherche Scientifique n° 899.

again close to L_s . For Ne/Gr there are appreciable effects of the zero-point energy and the initial dilation of the solid monolayer is larger [6, 10]; the limiting monolayer solid is compressed to about a 1 % smaller nearest-neighbour spacing than L_s [5, 6]. The monolayer solid of deuterated methane on graphite, CD_4/Gr [23], also follows the pattern of the classical inert gases. At 32 K, although there is a registry lattice, the nearest-neighbour spacing at the monolayer limit of compression is [24] within 0.5 % of L_s [25].

The driving force of the compression in all these cases is the relatively strong holding potential for the first adsorbed layer, which makes it energetically more favorable to compress the first layer than to initiate a dense second layer. Additionally, the holding potential sets the origin of the energy scale of the multilayer phase diagram [11, 26] relative to the chemical potential for condensation of a dense 3D phase. However, we show in section 2 that the chemical potential μ_{II} at the condensation of the bilayer of a given adsorbate varies little for large changes in the first layer holding potential; for adsorbed helium the limiting monolayer density does vary significantly with these changes.

Structural considerations provide a guide to limited layer growth phenomena : registry, symmetry and compression each play a role [13]. The molecular packings in the first adsorbed layers may be quite different from those in the 3D solids and compressible monolayers may be driven to smaller spacings than L_s [5, 6, 27]. Registry lattices near the limit of monolayer compression [4, 20-22] can precede either extended or limited layer growth. For Xe/Gr there are temperatures where a registry lattice at the monolayer limit is followed [4] by a bilayer solid with spacing close to L_s and then with an extended layer-by-layer growth of the Xe [12]. For uniaxial registry lattices of Xe on Ag(110) and Cu(110), reported for the monolayer regime [20, 21], there is only limited experimental information [22] on the growth beyond the monolayer solid; our model calculation for Xe/Cu(110) in section 3 shows it to be a marginal case for second-layer growth.

The organization of this paper is : in section 2 we discuss the classical pattern of the monolayer-to-bilayer transition, relating the insensitivity of the chemical potential μ_{II} at the transition under changes of first-layer holding potential ε_0 to the small (or zero) lattice constant discontinuities at the transition. Some estimates for the behaviour of compressed monolayers of helium, based on binding energies for single adatoms derived from atom-surface scattering experiments [14-19], are also given there. In section 3 we present our model calculation for the limit of compression of Xe/Cu(110), based on a first-layer interaction model constructed previously [28]. We propose an increase of the value for the monolayer latent heat of condensation of Xe/Cu(110) to make the calculations consistent with the observed compressions [21]. In section 4 we present some concluding remarks.

2. A classical pattern of adsorption.

For Xe, as for Kr, the first layer holding potentials on Gr and on Ag(111) are quite close in magnitude [29]. However, for He [15-17] and for H_2 [17, 18], the holding potentials on noble metals are quite different than on basal plane graphite [14, 19]. The lowest bound state energy (ε_0) of $^4He/Gr$ is 12.1 meV [14], while for the noble metals the values are : 4.5 meV for $^4He/Ag(110)$ [16], 6 meV for $^4He/Au(110)$ [15] and 4.6 meV for $^4He/Cu(113)$ [17]. However, the coefficient (C_3) of the van der Waals attraction to the substrate [30], which sets the scale of the interaction (ε_{II}) of second-layer adatoms with the substrate, is some 50 % larger for these metals than for He/Gr. Thus there is a large contrast in $\varepsilon_0 - \varepsilon_{II}$ for Gr and for noble metals. In this section we discuss the effects of such large changes in the holding potential on the monolayer-to-bilayer transition, using a zero temperature formalism previously applied to near-classical adsorbates [7]. We also comment on the system $^3He/H_2$ for which the ε_0 is approximately 1 meV [31, 32].

In addition to the adatom/substrate energies ε_0 and ε_{II} introduced in the preceding paragraph, we denote the adatom-adatom contributions to the internal energy of the monolayer and bilayer by ε_{I1} and ε_{I2} . The potential energies for ε_{I1} , ε_{I2} and ε_{II} in the case of classical adlayers are displayed in equations (3.8) and (3.11). The internal energy per adatom of the monolayer is

$$u_1 = \varepsilon_0 + \varepsilon_{I1} \quad (2.1)$$

and for the bilayer it is

$$u_2 = \frac{1}{2}(\varepsilon_0 + \varepsilon_{II} + \varepsilon_{I2}). \quad (2.2)$$

Denoting the areas per adatom in the monolayer and bilayer stacks by a_1 and a_2 , the zero temperature spreading pressures and chemical potentials (enthalpies) are

$$\begin{aligned} \phi_i &= -du_i/da_i \quad i = 1, 2. \\ \mu_i &= \mu_i + a_i \phi_i. \end{aligned} \quad (2.3)$$

At the monolayer-to-bilayer transition the conditions of mechanical and mass transfer equilibrium are

$$\begin{aligned} \phi_1 &= \phi_2 \\ \mu_1 &= \mu_2 = \mu_{II} \end{aligned} \quad (2.4)$$

so that the chemical potential is

$$\begin{aligned} \mu_{II} &= u_1 - a_1 \frac{(u_1 - u_2)}{(a_1 - a_2)} \\ &= \left[1 - \frac{1}{2} \frac{a_1}{a_1 - a_2} \right] (\varepsilon_0 + \varepsilon_{I1}) + \\ &\quad + \frac{1}{2} \frac{a_1}{a_1 - a_2} (\varepsilon_{II} + \varepsilon_{I2} - \varepsilon_{I1}). \end{aligned} \quad (2.5)$$

The chemical potential at monolayer condensation for a self-bound layer is

$$\mu_1 = \varepsilon_0 + \varepsilon_{l1}(\text{min}). \quad (2.6)$$

For near-classical adsorbates, without registry effects, there has been no observed discontinuity in the lateral nearest-neighbour spacing at the monolayer-to-bilayer transition [1-6]. This result can be expressed as

$$a_1/a_2 \simeq 2 \quad (2.7)$$

and μ_{II} is then

$$\mu_{II}(\text{classical}) \simeq \varepsilon_{II} + (\varepsilon_{l2} - \varepsilon_{l1}). \quad (2.8)$$

For Xe, Kr, and Ar on Ag(111) the experimental limit on the difference between the lateral near-neighbour spacings of the coexisting bilayer and monolayer is 0.01 Å [1]; then equation (2.7) is fulfilled to 0.5 % and the correction to equation (2.8) is of order 0.005 ε_0 (10 K for Xe). For Xe/Gr, at 60 K there is [4] a 2.5 % difference in the spacings at coexistence and a 5 % correction to equation (7); the corresponding corrections to equation (2.8) would include approximately 100 K from the first term on the right-hand side of equation (2.5) and a nearly offsetting correction (in this case) from the second term on the right-hand side of equation (2.5).

Equation (2.8) shows that when equation (2.7) is fulfilled the chemical potential at bilayer condensation is insensitive to the magnitude of ε_0 , but varies directly with C_3 (see Eq. (3.8)). While the energies ε_{li} vary rapidly with lateral spacing, the net change in ε_{l1} of a near-classical monolayer for the rather small lattice compressions between μ_1 and μ_{II} tends to be small. Further, for the classical adlayers where the energies are sums of adatom interaction potentials, the effects of substrate-mediated interactions among the first layer of adatoms largely cancel in the difference $\varepsilon_{l1} - \varepsilon_{l2}$, as can be seen by inspecting the way the first-layer lateral potential energy Φ_{11} enters in equations (3.11) for a classical adlayer. Thus the chemical potential at second-layer condensation μ_{II} , relative to the chemical potential μ_0 for bulk condensation, is only weakly dependent on substrate processes involving first-layer adatoms [30]. This analysis can be extended to the bilayer-to-trilayer solid transition, which was shown in a model calculation for a classical adlayer [7] to have a smaller lattice constant discontinuity than the corresponding monolayer-to-bilayer transition. These conditions approximate the conditions assumed in the construction of the Singleton-Halsey theory of multilayer adsorption [33].

We show data for the monolayer and bilayer condensations of Xe/Ag(111), Xe/Gr, and Xe/Pd(100) [1, 4, 34, 35] and the extrapolation of bulk sublimation [36] in figure 1. For Xe/Ag(111) and Xe/Gr the monolayer condensations nearly coincide; the slightly higher pressures for the Xe/Gr bilayer may reflect both the difference in C_3 and the small lattice constant discontinuity [4] at the solid bilayer formation for Xe/Gr.

Fig. 1. — Pressures of monolayer and bilayer condensation of adsorbed xenon as a function of temperature. The logarithm of the pressure of coexisting three-dimensional gas, in torr, is plotted as a function of inverse temperature (in K^{-1}) for Xe/Ag(111) (dot-dash lines, Ref. [1]), Xe/Gr (dashed lines, Refs. [4] and [34]), and Xe/Pd(100) (dot-dot-dash lines, Ref. [35]). The extrapolation of the bulk sublimation data of reference [36] to lower temperatures is also shown (solid line). The ordering of the bilayer condensation is different from the monolayer ordering; see section 2.

tinuity [4] at the solid bilayer formation for Xe/Gr. The insensitivity of the second-layer formation to the first-layer adsorption-induced interactions is strikingly shown in the Xe/Pd(100) data: for the conditions represented in figure 1 there was [35] no 2D island formation and no sharp monolayer condensation for the Xe/Pd(100), but the bilayer condensation is in the same regime as the other two cases.

Data for the bilayer formation of Ar and Kr on Ag(111) [1] and on Gr [2, 3] also only depend weakly on ε_0 . For example, the low coverage isosteric heat for Ar/Gr is 20 % larger than for Ar/Ag(111) [29] and the pressure of the coexisting 3D Ar gas at the monolayer condensation at 45 K is 50 times larger for Ag(111) [1] than for Gr [2]. Nevertheless, the estimated 3D gas pressure for the bilayer condensation on Gr [37, 2] is 2 times larger than on Ag(111) [1]. A calculation of the bilayer condensation pressure using a realistic interaction model for Ar/Gr gave very good agreement [9] with pressures extrapolated from Gilquin's data [37]. Gilquin also reported a multilayer isotherm at 64 K [37] which followed the Singleton-Halsey equation [33]. However, calculating the energy coefficient of the Singleton-Halsey equation in terms of the polarization potentials of Ar to bulk Ar and to Gr gives the same 50 % underestimate by theory already reported for Kr and Xe multilayers on Gr [38]. The modelling neglects thermally activated processes in the multilayer adsorption, which may account for this discrepancy.

The bilayer condensation for $^4\text{He}/\text{Gr}$ deviates from the pattern of the classical gases. The $^4\text{He}/\text{Gr}$ monolayer is highly compressible, as a result of quantum effects, and ε_0 is larger relative to the attractive forces

in the lateral interactions than for the heavier inert gases. The monolayer compression has been inferred from thermodynamic data [39, 40] and has been observed in neutron diffraction experiments [41]. The second layer at bilayer formation is believed to be a 2D quantum liquid [39, 41] which evolves to a solid after a further chemical potential increase. There are alternative interpretations [41] of the neutron diffraction data for the bilayer solid as reflecting two mutually incommensurate solid layers of different densities or as reflecting a mutually commensurate bilayer solid with an oblique unit cell. If the bilayer condenses directly into either of these structures, equation (2.7) is violated by 10 % and there is a direct contribution of ε_0 in μ_{II} , as indicated by equation (2.5). We develop the analysis of bilayer condensation here for the case of condensation of second-layer quantum liquid; again the chemical potential at bilayer condensation μ_{II} is only indirectly dependent on ε_0 .

The internal energy and chemical potential of the He monolayer are given by equations (2.1) and (2.3), where ε_{t1} is now a quantum 2D equation of state of compressed He which, for approximations, may be taken from model calculations [42-44] or from the extensive thermodynamic data for monolayer [40] He/Gr.

For the bilayer we use a different formulation than equation (2.2), to make contact with model calculations [43] and to reflect more directly the terms giving rise to the spreading pressure. Let the total number of atoms in the bilayer N_2 be divided into N_{21} first-layer and N_{22} second-layer atoms, with areas per atom α_1 and α_2 , respectively [45]. The number and area constraints are :

$$\begin{aligned} N_2 &= N_{21} + N_{22} \\ N_{21} \alpha_1 &= N_{22} \alpha_2 = N_2 \alpha_2. \end{aligned} \quad (2.9)$$

We take as an approximation for the bilayer energy

$$\mu_2 = (N_{21}/N_2) [\varepsilon_0 + \varepsilon_{t1}(\alpha_1)] + (N_{22}/N_2) [v_2(\alpha_1) + v_{22}(\alpha_2)]. \quad (2.10)$$

Here ε_0 is the binding energy of first-layer adatoms to the substrate and $v_2(\alpha_1)$ is the binding energy of a single second-layer atom to the combined substrate-first-layer system [43]. The lateral energy terms are $\varepsilon_{t1}(\alpha_1)$ for the first-layer solid [40, 42] and $v_{22}(\alpha_2)$ for the (second-layer) 2D quantum liquid [44].

The condition for mass transfer equilibrium between the first and second layers of the bilayer is

$$\begin{aligned} \mu_2 &= v_2(\alpha_1) + v_{22}(\alpha_2) - \alpha_2 dv_{22}/d\alpha_2 \\ &= \varepsilon_0 + \varepsilon_{t1}(\alpha_1) - \alpha_1 d\varepsilon_{t1}/d\alpha_1 - \\ &\quad - (N_{22} \alpha_1/N_{21}) dv_2/d\alpha_1. \end{aligned} \quad (2.11)$$

The conditions of mechanical and mass transfer equilibrium between the monolayer and bilayer are :

$$\begin{aligned} \phi_1 &= - [d\varepsilon_{t1}/d\alpha_1 + dv_{22}/d\alpha_2 + (N_{22}/N_{21}) dv_2/d\alpha_1] \\ \mu_1 &= \mu_2 = \mu_{II}. \end{aligned} \quad (2.12)$$

There is evidence [39] that the initial bilayer of $^4\text{He}/\text{Gr}$ has a low-density quantum liquid in the second layer ($N_{22}/N_{21} \lesssim 0.3$). Then equations (2.11) and (2.12) have an approximate solution with

$$\begin{aligned} dv_{22}/d\alpha_2 &\simeq 0 \\ a_1 &\simeq \alpha_1 + \{ (N_{22}/N_{21}) (dv_2/d\alpha_1) / d^2\varepsilon_{t1}/d\alpha_1^2 \} \\ \mu_{II} &\simeq v_2(\alpha_1) + v_{22}(\alpha_2). \end{aligned} \quad (2.13)$$

Thus μ_{II} is again only weakly dependent on ε_0 , through the dependence of the second-layer holding energy v_2 on the first-layer density. However, the extent of the compression of the monolayer density depends on the difference $\mu_{II} - \mu_I$.

Using the 2D ^4He equation of state [40, 42] and the ε_0 for He/Au(110) [15] in place of the value for $^4\text{He}/\text{Gr}$ leads to an estimate that the monolayer completion density will be 20 % smaller on Au(110) than on Gr. The 3D gas pressure for monolayer $^4\text{He}/\text{Au}(110)$ is larger than 10^{-5} torr above 3.5 K, so that ^4He monolayer adsorption on Au is experimentally accessible [46] near 4 K. There are already large thermal excitation effects in the He layers at such temperatures.

We have discussed the monolayer-to-bilayer transition primarily in terms of solid monolayers, but for very weak holding potentials the monolayer solid of He may not occur, as already noted by Richards [47] for the case of ^3He adsorbed on H_2 . In 3D the chemical potential changes [48] at zero temperature from liquefaction to solidification are 7.6 K for ^4He and 12.2 K for ^3He . For ^3He at 2 K the required chemical potential increase is 24.4 K. Model calculations [44] for the solidification of ^4He at 0 K in mathematical 2D can be used to make an estimate of 7 K for the zero temperature chemical potential increase from 2D liquefaction to solidification; the increase for 2D ^3He would be larger and might surpass the 10 K difference between the ε_0 of $^3\text{He}/\text{H}_2$ [31, 32] and the chemical potential $\mu_0 \simeq -2.5$ K of 3D liquid ^3He at 0 K. There have been some calculations [32] of the holding potential and bound states of ^3He on H_2 . A further investigation might include consideration of possible reorganization [49] of the bilayer H_2 film, of the effect of anisotropy [50] of the H_2 vibrations on the corrugation of the He holding potential, and of the effect of the coupling of the motions of the He and H_2 on the equation of state of the adsorbed He. The bilayer transition for close-packed triangular monolayer and bilayer lattices has been treated with quasiharmonic lattice dynamics [8] for D_2 parameters [51]; some information on these questions can be obtained with the phonon spectra calculated in that work.

3. A limit of stability for Xe/Cu(110).

At monolayer condensation, Xe forms a $\text{C}(2 \times 2)$ lattice on Cu(110) [20, 21]. Under compression, the

Xe monolayer becomes a uniaxially registered centred rectangular lattice : the Xe spacing along the $[1\bar{1}0]$ axis of the Cu surface decreases while the spacing between Xe rows in the $[001]$ direction remains constant. In the LEED experiments of Glachant *et al.* [21] near 70 K, a chemical potential increase of 800 K produced a 12 % decrease in the Xe spacing along the $[1\bar{1}0]$ axis from the 5.1 Å value at monolayer condensation. There was no evidence for bilayer or bulk formation [21]; however, Mason and Williams [22], with dosing experiments and analysis by He atom scattering, observed an expanded Xe structure at nominal coverages larger than the monolayer coverage.

Previously [28] the LEED data for Xe/Cu(110) [20, 21] were used to make estimates of the adatom-adatom and adatom-substrate interactions. Estimates were obtained for the leading Fourier amplitudes $2 V_1$ and $2 V_2$ of the holding potential along the $[001]$ and $[1\bar{1}0]$ axes. The adatom-adatom interactions were represented by Lennard-Jones 12-6 pair potentials of depth ε and separation r_0 at the potential minimum. Values of $\varepsilon = 230$ K and r_0 in the range 4.5 to 4.55 Å led to results for the monolayer compressibility which were in fair agreement with the LEED data [21]. Those calculations [28] did not depend on the value for the monolayer heat of adsorption (q_1).

In this section we formulate a zero temperature theory of the limit of stability of the Xe/Cu(110) monolayer against bilayer formation. We assume the monolayer remains in uniaxial registry, with zero misfit M_1 relative to the $[001]$ row spacing of the Cu, up to the bilayer (or bulk) condensation. In the previous calculations [28], for values of V_1 required in order that the monolayer condense with $M_1 = 0$, the monolayer remained in a state of zero M_1 for large chemical potential increases. We assume also that the bilayer is in uniaxial ($M_1 = 0$) registry with the substrate; this may be too strong a constraint and might lead to a fictitious stability of the compressed monolayer relative to bilayer formation. However, with the present experimental information on the first-layer holding potential, the compressed monolayer is calculated to be unstable with respect to the bilayer at lattice misfit and chemical potential increase corresponding to an experimentally stable monolayer [21]; relaxing the constraint on the bilayer structure in the calculation could only increase the monolayer instability. The calculations provide another example satisfying equation (2.8) : the chemical potential at the bilayer condensation is insensitive to ε_0 .

We extend the original zero temperature theory of bilayer formation for triangular lattices [7] by treating centred rectangular lattices and by including effects of the periodic potential along the $[1\bar{1}0]$ axis with perturbation theory [28]. The energies ε_{ti} of equations (2.1) and (2.2) are replaced by potential energies of the modulated centred rectangular lattices. If l denotes the nearest-neighbour spacing in the Cu (2.55 Å) and M_2 denotes the misfit of the Xe spacing along the $[1\bar{1}0]$

direction relative to the $C(2 \times 2)$ lattice, the areas a_i are

$$\begin{aligned} a_1 &= l^2 2\sqrt{2}(1 + M_2) \\ a_2 &= l^2 \sqrt{2}(1 + M_2). \end{aligned} \quad (3.1)$$

In a Cartesian coordinate system with $\hat{x}$ along the $[1\bar{1}0]$ direction and $\hat{y}$ along the $[001]$ direction, the basis vectors for the centred rectangular lattices are

$$\begin{aligned} \mathbf{b}_1 &= (1 + M_2) l \hat{x} + l \sqrt{2} \hat{y} \\ \mathbf{b}_2 &= -(1 + M_2) l \hat{x} + l \sqrt{2} \hat{y}. \end{aligned} \quad (3.2)$$

Apart a choice of the origin of coordinates, the centred rectangular lattice consists of points

$$\mathbf{R}_j = N_1 \mathbf{b}_1 + N_2 \mathbf{b}_2, \quad N_1, N_2 = \text{integers}. \quad (3.3)$$

We assume the modulated positions of the first- and second-layer atoms can be represented by

$$\begin{aligned} \mathbf{r}_{j1} &= \mathbf{R}_j + u(\mathbf{R}_j) \hat{x} \\ \mathbf{r}_{j2} &= \mathbf{R}_j + y \hat{y} + v(\mathbf{R}_j) \hat{x} + z_{12} \hat{z}. \end{aligned} \quad (3.4)$$

The first of equations (3.4) expresses the constraint that the first-layer atoms are in uniaxial registry with the Cu(110). The second of equations (3.4) includes a shift of the second-layer origin relative to the first-layer and a modulation of the second-layer positions along the x -axis only.

The substrate potential for the first-layer adatoms is represented by

$$\begin{aligned} V(\mathbf{r}_{j1}) &= \varepsilon_0 - 2 V_2 \cos\left(\frac{2\pi}{l} \hat{x} \cdot \mathbf{r}_j\right) \\ &= \varepsilon_0 - 2 V_2 \cos\left(\mathbf{q} \cdot \mathbf{R}_j + \frac{2\pi}{l} u(\mathbf{R}_j)\right) \end{aligned} \quad (3.5)$$

where the misfit wave vector is

$$\mathbf{q} = \frac{2\pi M_2}{l(1 + M_2)} \hat{x}. \quad (3.6)$$

The separation of ε_0 into a laterally averaged energy and the corrugation amplitude $2 V_1$ is not required here [28]. We denote the average first-layer corrugation potential energy for N_1 first-layer atoms by

$$\bar{v}_{cp} = - (2 V_2 / N_1) \sum_{j=1}^{N_1} \cos\left[\mathbf{q} \cdot \mathbf{R}_j + \frac{2\pi}{l} u(\mathbf{R}_j)\right]. \quad (3.7)$$

The second-layer adatoms interact with the substrate by the polarization potential

$$\varepsilon_{II} = - C_3 / (z_{12} + z_0)^3, \quad (3.8)$$

where z_{12} is the interplanar spacing of the bilayer, C_3 is the strength coefficient ($3.93 \times 10^4 \text{ KÅ}^3$ for Xe/Cu [30]) and z_0 is the distance from the first-layer to an effective electrodynamical image plane. In the absence of information specific to the Xe/Cu(110)

system, we take a value $z_0 = 2 \text{ \AA}$ used for Xe/Ag(111) models [7-9]; 10 % uncertainty in z_0 leads to 10 % uncertainty in ε_{II} for the Xe/Cu(110).

For the lateral interactions among the adatoms we use the Lennard-Jones 12-6 potential

$$\phi(r) = \varepsilon \{ (r_0/r)^{12} - 2(r_0/r)^6 \}, \quad (3.9)$$

with $\varepsilon = 230 \text{ K}$ and two choices of r_0 , 4.5 and 4.55 $\text{\AA}$. Sums of $\phi(r)$ for atoms both in the first-layer, both in the second-layer and one in each layer are defined by

$$\begin{aligned} \Phi_{11} &= \frac{1}{2} \sum_{j \neq 0} \phi_{11}(|\mathbf{r}_{j1} - \mathbf{r}_{01}|) \\ \Phi_{22} &= \frac{1}{2} \sum_{j \neq 0} \phi_{22}(|\mathbf{r}_{j2} - \mathbf{r}_{02}|) \\ \Phi_{12} &= \sum_j \phi_{12}(|\mathbf{r}_{j1} - \mathbf{r}_{02}|). \end{aligned} \quad (3.10)$$

This notation permits a separation of the effects of substrate-mediated interactions for first- and second-layer atoms; here, however, we use the same potential function ϕ , equation (3.9), throughout equations (3.10).

The internal energies for the monolayer and bilayer are written in terms of these functions as

$$\begin{aligned} u_1 &= \varepsilon_0 + \bar{v}_{cp} + \Phi_{11} \\ u_2 &= (\varepsilon_0 + \bar{v}_{cp} + \varepsilon_{II} + \Phi_{11} + \Phi_{22} + \Phi_{12})/2. \end{aligned} \quad (3.11)$$

The energy u_1 is evaluated as a function of $M_2(a_1)$, which requires determining the optimum modulation $u(\mathbf{R}_j)$ to minimize the energy at each value of M_2 . For the energy u_2 the two structural parameters y and z_{12} should be optimized, as well as the modulation functions $u(\mathbf{R}_j)$ and $v(\mathbf{R}_j)$. In our calculations, we use a perturbation approach and optimize the parameters y and z_{12} as a function of $M_2(a_2)$ for the uniform bilayer lattice, $u(\mathbf{R}_j) = v(\mathbf{R}_j) = 0$, as a first approximation. The minimization with respect to y is a separate step, not required in previous calculations, which arises here because the second-layer atoms for the centred rectangular bilayer lattice are not in exactly three-fold sites. We then complete the minimization of $u_1(M_2)$ and $u_2(M_2)$ using a perturbation-variation treatment for the dependences on the functions $u(\mathbf{R}_j)$ and $v(\mathbf{R}_j)$.

We take as trial functions for the modulations of the first- and second-layer adatoms

$$\begin{aligned} u_\alpha(\mathbf{R}_j) &= A_\alpha \sin(\mathbf{q} \cdot \mathbf{R}_j) \\ v(\mathbf{R}_j) &= B \sin(\mathbf{q} \cdot \mathbf{R}_j + \delta) \end{aligned} \quad (3.12)$$

and expand the energies u_1 and u_2 in powers of A_α and B ; the amplitude A_α differs for the monolayer and bilayer. The energy $\bar{v}_{cp}$ is carried to the first power of A_α . The energies Φ_{ij} are carried to second order in A_α and B ; in those expansions the coefficients of the linear terms vanish and the coefficients of the quadratic

terms are similar to the harmonic elastic coefficients used in the previous work [28] for Xe/Cu(110). Although we include a phase variable δ in equation (3.12), the minimum energy $u_2(M_2)$ occurs for δ equal to zero modulo π . Minimization with respect to A_α and B requires only the minimization of a quadratic form.

Within this perturbation theory, we also allowed for a y -component to the modulation of the second-layer positions r_{j2} in equation (3.4). However, with a modulation function of the form of $v(\mathbf{R}_j)$ in equation (3.12), we found the amplitude of the y -modulation to vanish in the minimum energy configuration.

We show the results of such calculations for Xe/Cu(110) in figure 2; parameters derived from the calculations are summarized in table I. The chemical potential as a function of spreading pressure is obtained with equation (2.3) using the functions $u_i(M_2)$ which have been minimized with respect to y , z_{12} , A_α , and B . The misfits at points along the $\mu - \phi$ curves are indicated in the figure. The effect in the results of allowing for the modulations $u(\mathbf{R}_j)$ and $v(\mathbf{R}_j)$, is rather small, as indicated by the dashed symbols in figure 2 showing the results of calculations for the nonmodulated uniform monolayer and bilayer centred

Fig. 2. — Zero temperature chemical potential μ (in K), as a function of spreading pressure ϕ (in $\text{K}/\text{\AA}^2$) for uniaxially registered monolayers and bilayers of Xe on Cu(110). The circles (squares) denote the results of perturbation calculations for centred rectangular bilayers (monolayers) at the indicated negative misfits ($-M_2$); see section 3 for a description of the perturbation-variation formalism. The dashed symbols denote results of calculations for uniform non-modulated lattices. The triangles are results for the monolayer taken from calculations including higher multiples of the misfit wave vector, reference [28]. The smooth lines are interpolations drawn through the points to help locate the monolayer-bilayer equilibrium. The parameters of the model are ε_0 , the average first-layer holding potential in the $[1\bar{1}0]$ troughs; $2V_2$, the corrugation amplitude along the trough; $\varepsilon = 230 \text{ K}$ and r_0 the energy and length scales of the Lennard-Jones pair potential, equation (3.9). The results of changing the ε_0 value by $\Delta\varepsilon$ are obtained by shifting the monolayer μ by $\Delta\varepsilon$ and the bilayer μ by $\Delta\varepsilon/2$. a) $r_0 = 4.5 \text{ \AA}$, $\varepsilon_0 = -1600 \text{ K}$; b) $r_0 = 4.55 \text{ \AA}$, $\varepsilon_0 = -2000 \text{ K}$.

Table I. — *Monolayer-bilayer coexistence for models of uniaxially registered Xe/Cu(110).*

r_0 (Å) ^(a)	4.5		4.55	
ε_0 (K) ^(b)	– 1 600	– 2 000	– 1 600	– 2 000
v_2 (°) ^(c)	0.19	0.19	0.09	0.09
μ_I (K) ^(d)	– 2 342	– 2 742	– 2 323	– 2 723
μ_{II} (K) ^(e)	– 1 997	– 1 996	– 1 979	– 1 978
$\mu_{II} - \mu_I$ (K)	345	746	344	745
ϕ (K/Å ²) ^(f)	20.3	44.8	19.8	43.9
M_{2_1} ^(g)	– 0.101	– 0.122	– 0.082	– 0.104
M_{2_2} ^(h)	– 0.106	– 0.117	– 0.085	– 0.097

^(a) Separation at the LJ(12-6) potential minimum, equation (3.9). The energy scale is $\varepsilon = 230$ K and the Cu spacing is $l = 2.55$ Å.

^(b) Single-adatom holding potential in first-layer trough, see equation (3.5).

^(c) Reduced corrugation amplitude is $[1\bar{1}0]$ direction, $v_2 = 2 V_2/\varepsilon$, equation (3.5), from reference [28].

^(d) Chemical potential at monolayer condensation in $C(2 \times 2)$ lattice.

^(e) Chemical potential at bilayer condensation; for this model bulk condensation occurs at $\mu_0 = -1980$ K.

^(f) Spreading pressure at the bilayer condensation.

^(g) Misfit M_{2_1} of the monolayer lattice at bilayer condensation.

^(h) Misfit M_{2_2} of the bilayer lattice at condensation.

rectangular lattices. The adequacy of the perturbation treatment for these values of M_2 and V_2 is tested by comparing the monolayer results with data from a more complete treatment of the monolayer distortions where phenomena such as misfit dislocations were treated [28]. Results of that earlier work are included in figure 2 and agree well with the $\mu(\phi)$ function derived from the perturbation theory.

As is apparent from figure 2, the chemical potential, spreading pressure, and misfits at the monolayer-to-bilayer transition change little whether or not the modulations of the adlayers are included in the calculations. The changes in the equilibrium misfits from the calculation with modulations to the calculation for the unmodulated lattices are about -0.002 in M_{2_1} and -0.001 in M_{2_2} . These amount to changes in the Xe spacing along the $[1\bar{1}0]$ trough of less than 0.02 Å, which are smaller than the uncertainties in the lengths derived from the LEED experiments [20, 21].

Changing the value ε_0 of the first-layer holding potential by 400 K changes μ_{II} by less than 5 K, which agrees with the discussion of section 2. However, the spreading pressure ϕ and the misfits M_{2_1} and M_{2_2} of the coexisting monolayer and bilayer do depend noticeably on ε_0 , as shown in table I. The results in table I are obtained from the equation of state with the modulation treated as a perturbation. The discontinuity in the Xe nearest-neighbour spacing along the $[1\bar{1}0]$ direction at the bilayer condensation is about 0.5% for the various cases treated in these calculations.

There are two more ways in which the calculated monolayer-to-bilayer transition can be compared to the data for Xe/Cu(110) [20-22]: the extent of mono-

layer compression without bilayer formation and the occurrence of a bilayer before bulk condensation.

The calculated μ_{II} values are exceedingly close to the chemical potential μ_0 for bulk condensation [52] with the LJ (12-6) potential model we have used, $\mu_0 = -1980$ K. The two r_0 cases give μ_{II} values within 20 K of μ_0 , and on opposite sides of it, so that the appearance of a bilayer before bulk condensation is highly sensitive to the compressibility of the layer. It also depends on the value taken for z_0 in equation (3.8). The data shown in figure 1 correspond to $\mu_0 - \mu_{II}$ differences at 60 K of 75 K for Xe/Gr and 110 K for Xe/Ag(111). The fact that μ_{II} is so close to μ_0 for the Xe/Cu(110) model is in accord with the idea that the constraint imposed by uniaxial registry may limit the growth to a single compressed monolayer before bulk formation. However, the Xe/Cu(110) interaction model is still rather primitive, with no explicit inclusion of adsorption-induced or substrate-mediated interactions [30]. These calculations show the combined effect of two structural considerations [11, 13], compression and registry, in limiting bilayer formation before bulk condensation. The growth mode for the physical system Xe/Cu(110) remains an open question.

The difference $\mu_{II} - \mu_I$ is linked to the amount of monolayer compression which occurs before bilayer formation. Initially we used the experimental q_1 value [21] for the latent heat of condensation in the $C(2 \times 2)$ lattice to determine a first-layer holding potential $\varepsilon_0 = -1600$ K. However, as shown by the entries in table I, there would then be only a chemical potential increase of 350 K permitted before bilayer (or

bulk) condensation. Near 70 K Glachant *et al.* [21] were able to increase the chemical potential by about 800 K without condensation beyond the monolayer; thermal effects alone do not seem large enough to account for the difference. Also, they observed monolayer misfits M_2 more negative than -0.11 , which would not be available to the monolayer in our model calculations with $\varepsilon_0 = -1\,600$ K. For these reasons we repeated the calculations with $\varepsilon_0 = -2\,000$ K, which corresponds to $q_1 \simeq -2\,700$ K and is a holding potential more in the range found for Xe adsorbed on Ag(111) and on basal plane graphite [29]. Then, as shown in table I, the chemical potential increase from the $C(2 \times 2)$ condensation to bilayer formation is about 750 K and the monolayer limit of compression is more in keeping with the LEED data [21]. As in the previous work [28], using the value $r_0 = 4.5$ Å reproduces the monolayer data a little better than calculating with the value 4.55 Å.

The Glachant *et al.* data [21, 53] become consistent with the adjusted ε_0 value if the two lowest temperature data points are dropped from the determination of q_1 . The monolayer latent heat (q_1) is derived from the pressure-temperature data for the $C(2 \times 2)$ condensation and deleting the lowest temperature points [53] from the slope determination leads to an increase of more than 10 % in the q_1 value. The actual magnitudes of the transition temperatures and pressures in the experiments [21] were close to the Xe/Ag(111) values [1], but including the lowest temperature points led to an anomalously small q_1 compared to the Xe/Cu(100) value [54] and to an anomalous entropy of adsorption [53] for Xe/Cu(110).

There were recognized to be slow adsorption kinetics [21, 53] at the lowest experimental temperatures, so dropping those points from the q_1 determination has some basis. We must note that our calculations are for zero temperature and the experiments near 70 K involve adlayers with thermal excitation. The change we propose for q_1 makes the systematic trends in the comparisons with Xe/Cu(100) [54] and Xe/Ag(111) [1] smoother.

4. Concluding remarks.

We have discussed the similarity of the value of the chemical potential at bilayer condensation μ_{II} for a given near-classical adsorbate on several substrates and have related it to the absence of (or small) lattice constant discontinuities in the adsorbate at the monolayer-to-bilayer transition. The analysis shows how the weakening of direct dependences of μ_{II} on the binding energy ε_0 of first-layer adatoms to the substrate and on adsorption-induced interactions among first-layer adatoms arises. We extended the discussion to the case of adsorbed helium for which the values of ε_0 derived from atom-surface scattering experiments are very different for noble metals and for graphite. The absence of a direct dependence of μ_{II} on ε_0 occurs again, but the monolayer ^4He density at the limit of compression may be 20 % less on Au than on Gr.

We presented a model calculation for the limit of monolayer compression of uniaxially registered Xe/Cu(110), where there may be an absence of bilayer formation before bulk condensation because of a combination of the structural effects of registry and compression. In order to account for the observed compression, we adjusted the value for ε_0 in a way which makes the Xe/Cu(110) holding potential fall more smoothly onto trends for Xe/Cu(100) and Xe/Ag(111).

Much work remains to be done in following the evolution of uniaxially registered monolayers to higher coverages and to relate the properties to other layer-growth observations.

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