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LATTICE DYNAMICAL ASPECTS OF PHASE TRANSITIONS IN ADSORBED MONOLAYERS

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Résumé. — Nous présentons quelques aspects des transitions de phase du second ordre liés à l'existence possible de modes mous de vibration. La théorie tient compte de la variation avec la température des constantes de force entre tous les atomes et spécialement entre l'adsorbé et le substrat. Cette variation peut faire apparaître à une température donnée un phonon mou.

Abstract. — We present some aspects of second order phase transitions in connection with the possible existence of soft surface modes. The theory takes due account of the variation with temperature of the force constants bounding all the atoms, especially the adatoms to the substrate. This variation may enable a phonon to become soft at a given temperature.

1. **Introduction.** — A great deal of theoretical and experimental activity has been expanded on the study of the effect of a surface with adsorbate on the lattice vibrations of a crystal.

The vibrational contribution is essential for the evaluation of the adsorption entropies [1, 3] which can be obtained by measuring the desorption rate of the adsorbed particles as a function of temperature [4] or by analyzing the adsorption isotherms determined by Auger spectroscopy [2]. The mean square displacements (M.S.D.) of adsorbed atoms can be measured in L.E.E.D. [3, 5-6] and Mössbauer [7] experiments. Those M.S.D. were found to diverge logarithmically [8] when the ratio between the force constant coupling the physisorbed atoms to the substrate and the force constant coupling the physisorbed atoms between themselves is diverging.

The variation of the low temperature specific heat due to the adsorption of a monolayer was also studied. Einstein approximations gave an exponential variation [9] with the temperature T . But a more exact analysis of Debye type predicts a T^3 behaviour [10-12]. It was shown that the phonon contribution to the free energy of interacting adatom pairs is attractive [13].

The localized modes of vibration due to adsorption were calculated for several geometries

[1, 11, 14-20]. The optical modes were measured by inelastic low energy electron diffraction [21-25] and infrared absorption [26-27]. It is possible also to measure the variation of the speed of Rayleigh waves when a monolayer is adsorbed (¹).

The phonon density of states of a substrate with an adsorbed monolayer can be obtained from inelastic neutron scattering [28-29].

In the present work we present some lattice dynamical aspects of second order phase transitions in adsorbed monolayers. Our approach to this problem (section 2) consists of first calculating the thermal expansion of the crystal, especially in the vicinity of the surface and of the adsorbed monolayer. The temperature dependent relaxations of the interplanar spacings arise from cubic anharmonic terms in the crystal potential energy. Then we calculate the change in force constants [31] and finally the variation with temperature of the surface phonons. It may happen that the adsorbate-substrate system under consideration is already unstable at the absolute zero of temperature, or that it becomes unstable at a given transition temperature. The instability appears in our theory through a soft surface phonon.

We apply in section 3 this theory to a (001) monolayer of He, Ne, Ar, Kr and Xe on a solid

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(¹) Depoorter M., Pouliquen J., private communications.

substrate of Ne, Ar, Kr and Xe. The model consists of first and second neighbor central interactions. The values of the Lennard-Jones parameters are deduced from the experimental measurements of the virial coefficients of the different rare gases and their mixture. The approximations used in this work and the results are discussed in section 4.

2. Theory. — We apply to an adsorbed monolayer, the formalism used before [30] for the study of a free surface thermal expansion. We begin by expanding the potential energy of a crystal in powers of the displacements of the atoms from their static equilibrium positions [30]

$$\begin{aligned} \Phi = \Phi_0 + \sum_{l\alpha} \Phi_\alpha(l) \xi_\alpha(l) + \\ + \frac{1}{2} \sum_{ll'\alpha\beta} \Phi_{\alpha\beta}(ll') \xi_\alpha(l) \xi_\beta(l') + \\ + \frac{1}{6} \sum_{ll'l''\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(ll'l'') \xi_\alpha(l) \xi_\beta(l') \xi_\gamma(l'') + \dots \quad (1) \end{aligned}$$

In this expression Φ_0 is the value of the static potential energy. $\xi_\alpha(l)$ is the α Cartesian component of the displacement of the l th atom. The first-order atomic force constants $\{\Phi_\alpha(l)\}$ are nonzero only for sites l near the surface. $\Phi_{\alpha\beta}(ll')$ and $\Phi_{\alpha\beta\gamma}(ll'l'')$ are the harmonic and anharmonic force constants, respectively.

We suppose that $\xi_\alpha(l)$ is the resultant of three terms, the first of which describes a homogeneous deformation of the crystal, the second of which represents the dynamical displacements of the atoms due to the free surfaces, and the third of which describes arbitrary displacements of the atoms from their new positions in the deformed crystal :

$$\xi_\alpha(l) = s_\alpha(l) + d_\alpha(l) + u_\alpha(l), \quad (2)$$

where

$$s_\alpha(l) = \sum_\lambda \varepsilon_{\alpha\lambda} x_\lambda(l). \quad (3)$$

For simplicity, in what follows we will use the notation :

$$\eta_\alpha(l) = s_\alpha(l) + d_\alpha(l). \quad (4)$$

The vector $x(l)$ is the vector to the equilibrium position of the l th atom in the undeformed crystal. The parameters $\{\varepsilon_{\alpha\lambda}\}$ describe a homogeneous deformation of the crystal. We now substitute eq. (2) into eq. (1) and collect terms in powers of the displacement components $\{u_\alpha(l)\}$, to obtain $\Phi = \Phi_s + \Phi_D$, where Φ_s is the static potential and Φ_D has terms of first and second order in the $\{u_\alpha(l)\}$. From Φ_D one obtains [30] to first order in the $\{\Phi_\alpha(l)\}$ and $\{\Phi_{\alpha\beta\gamma}(ll'l'')\}$ the vibrational contribution $F(T)$ to the Helmholtz free energy. Finally the total free energy of the crystal is :

$$\mathcal{F}(T) = \Phi_s + F(T) \quad (5)$$

with :

$$\begin{aligned} \Phi_s = \Phi_0 + \sum_{l\alpha} \Phi_\alpha(l) \eta_\alpha(l) + \\ + \frac{1}{2} \sum_{ll'\alpha\beta} \Phi_{\alpha\beta}(ll') \eta_\alpha(l) \eta_\beta(l') + \\ + \frac{1}{6} \sum_{ll'l''\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(ll'l'') \eta_\alpha(l) \eta_\beta(l') \eta_\gamma(l'') + \dots \quad (6) \end{aligned}$$

and :

$$\begin{aligned} F(T) = F^0(T) + \frac{1}{2} \sum_{ll'\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(ll'l'') \times \\ \times \langle u_\alpha(l) u_\beta(l') \rangle \eta_\gamma(l'') + \dots \quad (7) \end{aligned}$$

where $F^0(T)$ is the harmonic contribution to the vibrational free energy.

Let us note that the temperature dependent correlation functions $\langle u_\alpha(l) u_\beta(l') \rangle$ are calculated in the harmonic approximation

$$\begin{aligned} \langle u_\alpha(l) u_\beta(l') \rangle = \\ = \frac{\hbar}{2(M_l M_{l'})^{1/2}} \left[D^{-1/2} \coth \left(\frac{1}{2} \frac{\hbar D^{1/2}}{k_B T} \right) \right]_{l\alpha, l'\beta} \quad (8) \end{aligned}$$

where D is the harmonic dynamical matrix and M_l the mass of the l th atom.

At each temperature T , we can obtain the new equilibrium positions of all the atoms by minimizing the free energy $\mathcal{F}(T)$ as function of the $\{\varepsilon_{\alpha\lambda}\}$ and $\{d_\alpha(l)\}$.

The bulk equilibrium distances are obtained from :

$$\begin{aligned} \frac{\partial \mathcal{F}(T)}{\partial \varepsilon_{\nu\lambda}} = \sum_l \Phi_\nu(l) x_\lambda(l) + \\ + V \sum_{\beta\mu} C_{\nu\lambda\beta\mu} \varepsilon_{\beta\mu} + F_{\nu\lambda}(T) = 0 \quad (9) \end{aligned}$$

where V is the volume of the crystal, the elastic constants

$$C_{\nu\lambda\beta\mu} = \frac{1}{V} \sum_{ll'} \Phi_{\nu\beta}(ll') x_\lambda(l) x_\mu(l') \quad (10)$$

and :

$$F_{\nu\lambda}(T) = \frac{1}{2} \sum_{ll'l''\alpha\beta} \langle u_\alpha(l) u_\beta(l') \rangle \Phi_{\alpha\beta\nu}(ll'l'') x_\lambda(l''). \quad (11)$$

Similarly the minimization of $\mathcal{F}(T)$ in respect to $d_\alpha(l)$ gives :

$$\begin{aligned} \Phi_\alpha(l) + \sum_{l'\beta} \Phi_{\alpha\beta}(ll') \eta_\beta(l') + \\ + \frac{1}{2} \sum_{l'l''\beta\gamma} \Phi_{\alpha\beta\gamma}(ll'l'') \eta_\beta(l') \eta_\gamma(l'') + \\ + F_\alpha(l/T) = 0 \quad (12) \end{aligned}$$

where :

$$F_\alpha(l'' | T) = \frac{1}{2} \sum_{ll'\alpha\beta} \langle u_\alpha(l) u_\beta(l') \rangle \Phi_{\alpha\beta\gamma}(ll'l''). \quad (13)$$

The eqs. (9) and (12) provide us with the new equilibrium positions at a given temperature T of all the atoms as well in the bulk as in the vicinity of the adsorbed monolayer. The expansions done above can be performed around any well defined positions for the atoms. In what follows we will take these positions to be the static equilibrium ones, taking due account of the static relaxation of the atomic planes near the surface. Then in eq. (9) the term $\sum_l \Phi_v(l) x_\lambda(l)$ vanishes as well as $\Phi_\alpha(l)$ in eq. (12).

Knowing the new equilibrium positions, we can calculate the renormalized harmonic force constants and then the variation with temperature of the vibration frequencies. If a surface phonon becomes soft, a super-structure may appear. It is possible to obtain in this approach the transition temperature T_c characterizing such a phase transition. Our approach will give only the order of magnitude of T_c . Indeed the correlations functions are diverging when a soft phonon appears and so do the anharmonic terms in eqs. (9) and (12), which then are not really small in the perturbation approach we use.

3. Application to a monolayer of a « rare gas » on another « rare gas » substrate. — As a first application of the preceding theory to an adsorbed monolayer, we chose the simplest realistic system, namely a monolayer of a *rare gas* in epitaxy with a (001) surface of another *rare gas* solid. In such a system the interatomic interactions are well described by Lennard-Jones potentials :

$$\varphi(r) = 4 \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (14)$$

where r is the distance between two atoms and the numerical values for ε and σ are obtained through measurements of the virial coefficients of rare gases [32] (Table I). For two unlike rare gas atoms,

TABLE I

	ε/k (K)	σ (Å)	Melting (K) temperatures
He	10.22	2.556	3.5
Ne	35.6	2.749	24.5
A	125.2	3.405	84
Kr	182.9	3.591	116
Xe	228	4.027	155

the interaction potential is commonly adopted to be of the same form as above with coefficients ε_{AS} and σ_{AS} related to the coefficients (ε_S, σ_S) and (ε_A, σ_A) of the substrate and of the adsorbate through the following rules [32] :

$$\varepsilon_{AS} = 2 \varepsilon_A \varepsilon_S / (\varepsilon_A + \varepsilon_S), \quad \sigma_{AS} = \frac{1}{2} (\sigma_A + \sigma_S). \quad (15)$$

Taking due account of the symmetries of our problem, we have [30] :

$$\varepsilon_{\nu\lambda} = \varepsilon_{\nu\nu} \delta_{\nu\lambda}; \quad C_{\sigma\sigma\sigma\sigma} = C_{11}, \quad C_{\sigma\sigma\sigma'\sigma'} = C_{12} \text{ for } \sigma \neq \sigma';$$

$C_{11} = C_{12} + 2 C_{44}$ (Cauchy relation for central interactions) and $d_\alpha(l)$ are non zero only for the direction $\alpha = Z$ perpendicular to the surface. It was shown [30] that $d_z(l)$ is decreasing exponentially when one is going inside the bulk. Therefore we will suppose for simplicity that among the variables $d_z(l)$ only the distance $b/2$ between the adsorbed monolayer ($l = 0$) and the surface plane of the substrate ($l = 1$) is varying. The distance between two adjacent (001) atomic planes of the substrate is $a/2$ where a is the lattice parameter.

The bulk static stability in an f.c.c. lattice with central interactions between first and second neighbors gives :

$$\frac{\varphi'_s(r_0)}{r_0} + \frac{\varphi'_s(a)}{a} = 0 \quad (16)$$

where $r_0 = a \sqrt{2}/2$. Similarly for the planes $l = 0$ and $l = 1$, one has :

$$\frac{2b}{r_{01}} \varphi'_{AS}(r_{01}) + \varphi'_{AS}(r_{02}) = 0 \quad (17)$$

where

$$r_{01} = (b^2 + a^2)^{1/2}/2; \quad r_{02} = (b + a)/2. \quad (18)$$

The solution of eqs. (16), (17) with the help of a Lennard Jones potential (14) provides us with the static distances $a^0 = \sigma_s \left(\frac{258}{17} \right)^{1/6}$ and b^0 (Table II).

As we will see later, some systems have soft phonons already at 0 K. Table II gives the values of b^0 only for the stable systems.

The bulk thermal expansion can be calculated from eq. (9) :

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = - \frac{1}{V} \frac{F_B(T)}{C_{11} + 2 C_{12}} \quad (19)$$

where :

$$F_B(T) = F_{\nu\lambda}(T) \delta_{\nu\lambda} \quad (20)$$

and :

$$C_{11} + 2 C_{12} = \frac{4}{a} [\varphi''_s(r_0) + \varphi''_s(a)]. \quad (21)$$

The coefficients entering eqs. (19)-(21) are evaluated for the static equilibrium distances a^0 . At a given temperature T , the lattice parameter is then :

$$a(T) = a^0 [1 + \varepsilon_{xx}(T)]. \quad (22)$$

Similarly the surface thermal expansion can be calculated from eq. (12) neglecting terms of second order in the $\{\eta_\alpha(l)\}$ as in réf. [30] :

$$d_z(0) = [F_z(0 | T) + \sum_{l\beta} \Phi_{z\beta}(0, l') s_\beta(l')]/K \quad (23)$$

TABLE II

Stable systems at $T=0$ K	b^0/a^0 (static)	b/a at 0 K			Transition température (K)	
		Einstein approximation	Einstein approximation + correction	Ref. [12]	Einstein approximation	Einstein approximation + correction
Ne/Ne	1.009	1.021	1.019	—	—	—
Ne/A	0.804	0.854	0.849	0.887	24	29
Ne/Kr	0.755	0.807	0.803	0.823	34	40
Ne/Xe	0.650	0.701	0.698	0.745	52	59
A/A	1.009	1.013	1.012	—	—	—
A/Kr	0.956	0.968	0.967	0.973	—	—
A/Xe	0.847	0.863	0.861	0.897	67	83
Kr/A	1.063	1.058	1.058	—	—	—
Kr/Kr	1.009	1.011	1.010	—	—	—
Kr/Xe	0.897	0.904	0.903	0.951	104	129
Xe/Xe	1.009	1.010	1.010	—	—	—

where :

$$K = \frac{b^2}{r_{01}^2} \varphi''_{AS}(r_{01}) + \frac{a^2}{r_{01}^3} \varphi'_{AS}(r_{01}) + \varphi''_{AS}(r_{02}). \quad (24)$$

The coefficients K and $F_z(0 | T)$ are calculated for the static distances a^0 and b^0 .

The correlations functions (8) are calculated first within the Einstein approximation and then with the first order corrections to the Einstein approximation [30].

We studied the adsorption of He, Ne, A, Kr, Xe on solid substrates of Ne, Ar, Kr, Xe varying the temperature from 0 K to the melting temperature of the substrate given in Table I. Only the systems given on Table II were found stable at 0 K. We give there the values of b/a at 0 K in the Einstein approximation and with the first correction to this approximation. These results are in good agreement with those obtained before [12] through a more sophisticated numerical approach. Let us note however that our results underestimate the surface thermal expansion when compared to those of ref. [12].

The variation with temperature of the thermal expansion can be compared to bulk experimental results obtained for A^{34} , Kr^{35} , Xe^{36} as well as to former theoretical results [36] for free surfaces of A, Kr and Xe. On figures 1 and 2 we give for A the variation with temperature of :

$$\frac{\Delta a}{a} = \frac{a(T) - a(0)}{a(0)} = \frac{\varepsilon(T) - \varepsilon(0)}{1 + \varepsilon(0)} \simeq \varepsilon(T) - \varepsilon(0)$$

and of

$$\frac{\Delta b}{b} = \frac{b(T) - b(0)}{b(0)}.$$

One sees that the experimental and former theoretical results [36] are bigger than our two approximations (Einstein and Einstein + first corrections). This is due to the fact that we did our expansions around the static equilibrium positions

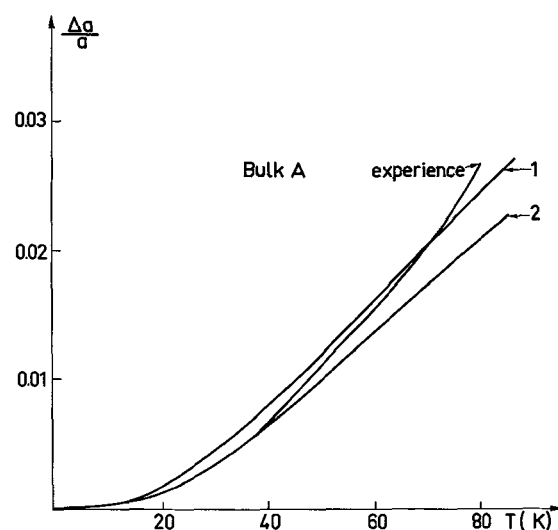


FIG. 1. — Relative variation $\Delta a/a$ with temperature of the bulk lattice parameter of solid A. The curves 1 and 2 give the calculated values respectively in the Einstein approximation and in this approximation with the first order correction.

and then the correlation functions and the quantities depending on them, especially $\Delta a/a$ and $\Delta b/b$ exhibit a linear dependance on temperature. A self-consistent calculation [36] would increase the thermal expansion at high temperatures.

The figures 3-5 give for the first time the temperature dependent thermal expansion for the adsorbate-substrate systems under study here.

Once the new equilibrium positions of the atoms are known at each temperature, we can calculate from the Lennard Jones potential the renormalized harmonic force constants. Then we calculate the temperature dependent surface phonon frequencies. Here we use the frozen substrate approximation, which is a good approximation, for the calculation of localized modes especially when these modes are far

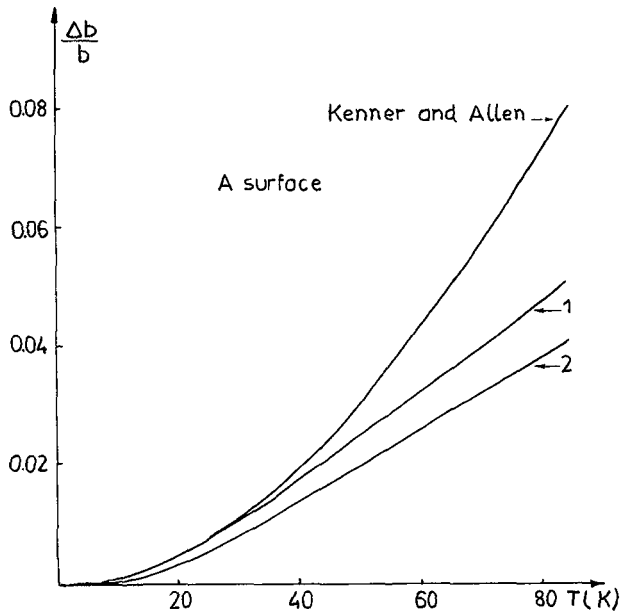


FIG. 2. — Relative variation $\Delta b/b$ with temperature of the distance between the first two (001) surface planes of A. Our results are given by curves 1 and 2 with the same approximations as in figure 1.

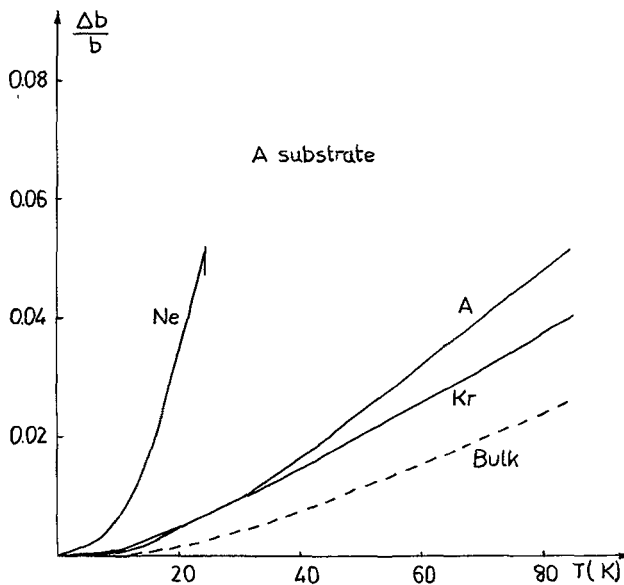


FIG. 3. — Relative variation $\Delta b/b$ with temperature of the distance between an adsorbed monolayer and an (001) surface of A. The results are given within the Einstein approximation. These curves are stopped by a vertical line at the transition temperature T_c when this exists.

from the bulk bands, which is the case when one is looking for soft phonons.

The systems adsorbate-substrate given on Table II have a soft phonon for $k_x = k_y = \pi/2 a$, at a given transition temperature T_c given in this table. This soft phonon is polarized in the surface plane. However the separation between parallel and perpendicular surface polarizations is a consequence of our frozen substrate approximation.

Let us discuss our approximations and results in the next section.

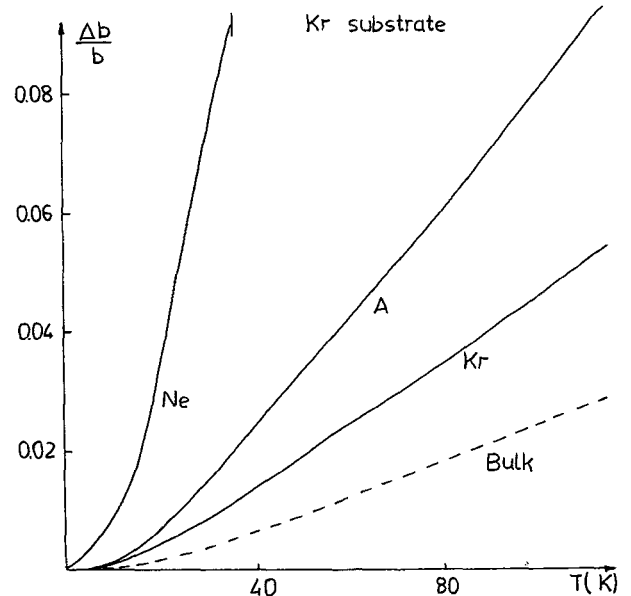


FIG. 4. — Same as figure 3 but for a Kr substrate.

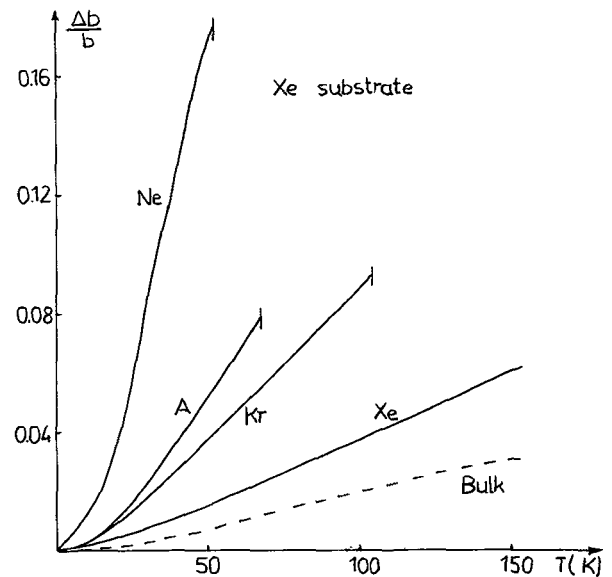


FIG. 5. — Same as figure 3 but for a Xe substrate.

4. Discussions. — We started from an adsorbed monolayer in epitaxy with the substrate. This starting point may be reasonable for the adsorption of a smaller (lighter) atom on a substrate of bigger (heavier) atoms. However this hypothesis is probably not very good in the contrary case for which other models should be tried. As a matter of fact, we find in our model that these systems are unstable already at 0 K, except for Kr on A for which the interatomic distances are very close one to each other.

The results obtained for the bulk and free surface thermal expansions (Figs. 1-2) are rather precise, taking account of the fact that we used only the third

order anharmonic terms, an expansion around the static equilibrium positions and an Einstein like approximation in the calculation of the correlation functions. In the same way the thermal expansions of the adsorbate-substrate systems (Figs. 3-5) should be rather good.

However the interatomic distances are not as precise. For example the bulk $a(T)$ (eq. (22)) are by a few percent greater than the experimental values. As in the calculation of the interatomic force constants enter the ratio σ/a , an increase of a gives a decrease of the phonon frequencies and of the transition temperature T_c . On the contrary, the frozen substrate approximation overestimates the phonon frequencies. In other words when a soft phonon appears with this approximation, it will also exist in an exact diagonalization of the dynamical matrix [37].

The existence of a soft phonon is in principle predicting a second order phase transition and the apparition of a new superstructure [38]. *In the great majority of known cases of second-order phase transition the more symmetrical phase corresponds to higher temperatures and the less symmetrical to*

lower temperatures. This rule, however, is not a thermodynamic law and hence admits of exceptions [38]. The systems studied here may be among these exceptions. However the results given here must be considered only as qualitative. In fact, some of the transition temperatures calculated here are relatively close to the melting temperature of the bulk adsorbate. It may happen then that before the T_c calculated here the monolayer becomes *liquid* or even desorbs. An experimental study of this system as well as a more sophisticated theoretical analysis including in particular the study of the mean square displacements of adsorbed atoms, may help to solve this problem.

The study of more complicated systems as (111) monolayers of a *rare gas* on another *rare gas* substrate or a rare gas monolayer on a graphite substrate, may also be done along the same lines as here. The transition between a localized and a delocalized monolayer [39-40] may be perhaps also studied in the approach described here.

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$$A_{ii} = \sum_j P_{ij} D_{jj} (P^{-1})_{ji} = \sum_j |P_{ij}|^2 D_{jj}.$$
- If $\forall_j D_{jj} > 0$
- then $\forall_i A_{ii} > 0$.
- Conversely, if one of the A_{ii} is negative, there exists one at least of the D_{jj} which is negative. This demonstration can be generalized to the case where we are interested not to one of the A_{ii} but to the diagonalization of a submatrix of A .
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DISCUSSION

M. SCHICK. — Is it correct to say that the effects of the soft mode would only be visible provided that the temperature at which the mode becomes soft is less than any disordering temperature? If so, can you determine under what conditions this circumstance is likely?

L. DOBRZYNSKI. — The first statement is correct (see our conclusion).

The second question is an open one.