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Miscibility and phase diagram of mixed submonolayers: mean field and hard hexagon approximation

Miscibility and phase diagram of mixed submonolayers: mean field and hard hexagon approximation

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Abstract. The equations which determine the equilibrium between commensurate and incommensurate solid phases of a mixed (Xe–Ar) or (Xe–Kr) submonolayer adsorbed on graphite are written in a mean field theory which takes thermal expansion into account. The mean field potential is given by an integral equation which is solved to first order in temperature. The agreement with experimental data is poor. In the case of Xe–Kr mixtures, when the size difference is small, a phenomenological theory gives good results. At low temperature it is possible to go beyond the mean field approximation and to obtain the qualitative phase diagram. The particular case of a solid of small atoms (Ar) with a weak concentration of big atoms (Kr) can be treated by an approximate version of Baxter's hard hexagon model and the results are promising. An interpolation between mean field and hard hexagons, which we call the tough hexagon model, is also introduced.

1. Introduction

It is well known [1–4] that adsorbed monolayers on crystal surfaces can be either commensurate or incommensurate with the substrate according to the nature of the constituents (adsorbate and substrate) and to temperature and pressure. The most widely studied systems are probably rare gases on graphite [1, 2] because of their simplicity. The only gases which form a commensurate, two-dimensional solid phase are Kr [1, 2, 4, 5], He [6–8] and (under high pressure) Xe [9, 10]. However, as observed by Bohr [11], mixtures of Xe and Ar can form a commensurate, $\sqrt{3} \times \sqrt{3}$ phase in equilibrium with the two-dimensional gas ('submonolayer') although each constituent is incommensurate in the same circumstances if isolated. Analogously, Marti *et al* [12] and de Beauvais [13] realized that mixed submonolayers of Xe and Kr can have a commensurate solid (cs) phase even at high Xe concentrations. The essential experimental data are displayed in figure 1 and the main geometric information in figure 2.

In the present paper, various theoretical approaches to the problem are discussed. As usual in statistical physics, the first step is a mean field theory. In the present paper, *mean field equations* which take into account thermal expansion in a consistent way are written for the first time. An accurate solution of these equations turns out to be very difficult. Moreover, a mean field theory, which by definition neglects short-range order, can only give a qualitative agreement with experiment. The agreement is particularly

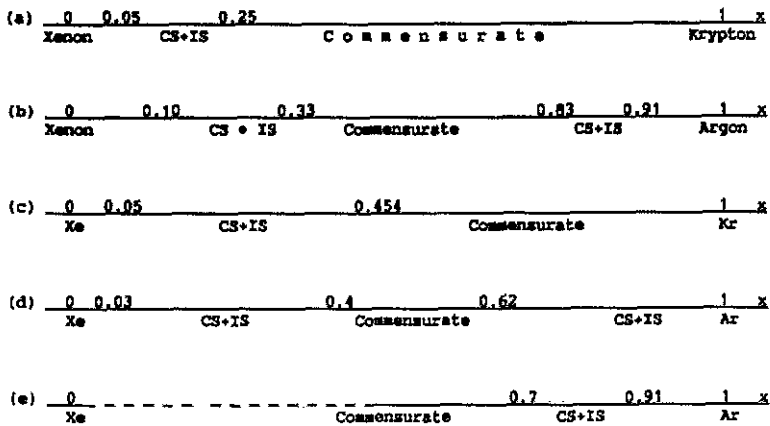† Permanent address: Departamento de Física, ICEx, UFMG, Brazil.

Figure 1. The phase diagram at about 45 K. (a) and (b) Experimental data according to de Beauvais [13]. (c) and (d) Mean field approximation (section 4 of the present article). In case (d) an argon rich incommensurate solid (IS) phase is stable for $x > 0.99983$. (e) The hard hexagon approximation (section 5). This approximation is only appropriate for Ar-rich Xe–Ar mixtures.
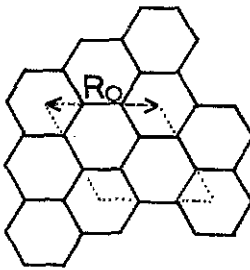

Figure 2. The geometry of adsorbed rare-gas monolayers on graphite. The corners of the hexagons are graphite atoms. Easy adsorption sites are the centres of the hexagons. The dotted quadrangle shows the commensurate unit cell and R_0 denotes the interatomic distance in the commensurate phase.

bad in rare gas mixtures when hard-core effects become important. Possible alternative theories are discussed in sections 5 and 6, and some predictions on the low temperature part of the phase diagram are made.

The following theory is in principle not restricted to the case of submonolayers. The effect of the chemical potential in completed monolayers might also be investigated, as it has been by Hommeril and Mutafschiev [14] in a mixture which seems more adequate than rare gases for a mean field treatment.

2. The model

The monolayer will be treated as strictly two-dimensional and classical. Classical mechanics allow the momentum variables to be integrated out. Then the atoms are characterized by their position vectors R_n, which have two components. The approximations involved in this description are described in [3]. The monolayer consists of N atoms of two species A ($= Xe$) and B ($= Kr$ or Ar). Let x be the concentration in B atoms and $R_0 = 4.26$ Å the atomic distance in the CS, $\sqrt{3} \times \sqrt{3}$ phase (figure 2). Let N_0

be the number of atoms in the commensurate phase. It is convenient to characterize the degree of expansion or contraction. In the incommensurate solid (IS) phase the interatomic distance is $R = R_0 \sqrt{N_0/N}$. In agreement with the basic assumptions of the mean field approximation, it is assumed to be constant. This cannot be expected to be very good, but the mean field approximation is the first, and unavoidable step of a hierarchy of approximations which will be sketched in the last section.

For the determination of the structure, the free energy Nf can be defined [3] by

$$\exp(-\beta Nf(x, R, T)) \frac{1}{N_A! N_B!} \prod_n \left(\int \frac{\mathrm{d}^2 R_n}{R_0^2} \right) \exp[-\beta \mathcal{H}(\{R\})] \tag{1}$$

where $T = 1/\beta$ is the temperature, $N_A = N(1 - x)$ and $N_B = Nx$. Energies are measured in Kelvin, so that the Boltzmann constant is 1. The factor $1/R_0^2$ under the integral is arbitrary, and would not be appropriate for the determination of the specific heat. Changing this factor would add to f, the free energy per atom, a constant proportional to temperature. The Hamiltonian is assumed to have the form

$$\mathcal{H} = \mathcal{H}_{AA} + \mathcal{H}_{AS} \tag{2}$$

where the first term is a pair interaction between adatoms,

$$\mathcal{H}_{AA} = \tfrac{1}{2} \sum_{n,n'} \sum_{\alpha,\gamma} U_{\alpha\gamma}(R_n - R_{n'}) \rho_\alpha(R_n) \rho_\gamma(R_{n'}). \tag{3}$$

$\alpha, \gamma = A, B$, $\rho_A(R_n) = 1$ if the atom at R_n is of kind A and $\rho_B(R_n) = 1 - \rho_A(R_n)$. The three pair potentials $U_{\alpha\beta}$ will be approximated by Lennard-Jones potentials:

$$U_{\alpha\gamma}(r) = 4\varepsilon_{\alpha\gamma}[(\sigma_{\alpha\gamma}/r)^{12} - (\sigma_{\alpha\gamma}/r)^6]. \tag{4}$$

The second term in (2) is the substrate potential

$$\mathcal{H}_{AS} = \sum_{\alpha=A,B} \sum_n W_\alpha(R_n) \rho_\alpha(R_n) \tag{5}$$

that is periodic and can be expanded in Fourier series, introducing Fourier coefficients A_α.

$$W_\alpha(r) = \sum_Q A_\alpha(Q) \cos(Q \cdot r). \tag{6}$$

To discuss phase coexistence, it is appropriate to work in the grand ensemble. Two chemical potentials μ_A, μ_B are introduced, and one has to minimize the grand potential

$$\Omega = Nf - \mu_A(1-x) - \mu_B Nx = N_0(f(x, R, T) - \mu_A(1-x) - \mu_B x)R_0^2/R^2. \tag{7}$$

3. Phase coexistence

The quantity which has been measured is the concentration of the light element (Kr or Ar) at coexistence between the two-dimensional gas, the two-dimensional commensurate solid (CS) and the incommensurate solid (IS). Let x (similarly y) be this

concentration in the IS (similarly CS) phase. We wish to calculate them. At coexistence, the associated grand potentials Ω_g, Ω_c, Ω_i should be equal.

$$\Omega_g(T, \mu_A, \mu_B) = \Omega_c(T, y, \mu_A, \mu_B) = \Omega_i(T, x, R, \mu_A, \mu_B). \tag{8}$$

On the other hand, Ω_g and Ω_c should be minimum with respect to x and y, respectively, and Ω_i should be minimum with respect to R:

$$(\partial\Omega_i/\partial x)_{T,R,\mu_A,\mu_B} = (\partial\Omega_c/\partial y)_{T,\mu_A,\mu_B} = (\partial\Omega_i/\partial R)_{T,x,\mu_A,\mu_B} = 0. \tag{9}$$

As remarked by Marti *et al* [12], and rederived at the end of this section, the density of the two-dimensional gas is so low at the temperatures of interest that its grand potential is practically zero. Thus, relation (8) may be replaced to a good approximation by

$$\Omega_c(T, y, \mu_A, \mu_B) = \Omega_i(T, x, R, \mu_A, \mu_B) = 0. \tag{10}$$

This allows for a simplification of the last formula (9). Actually this formula can be written as

$$(1/N)(\partial/\partial R)[N(\Omega_i/N)] = (\partial/\partial R)(\Omega_i/N) + (\Omega_i/N)(\partial/\partial R)\ln N = 0$$

and the second term vanishes according to (10). The resulting equation

$$(\partial/\partial R)(\Omega_i/N) = 0 \tag{11}$$

turns out to be simpler.

We now outline the proof that Ω_g can be neglected in (8). In the gas the free energy is obtained from (1) with $\mathcal{H}$ replaced by (5). The result is

$$\Omega_g = TN_A \ln(N_A/N_0 e) + TN_B \ln(N_B/N_0 e) - \mu_A N_A - \mu_B N_B$$
$$- TN_A \ln J_A - TN_B \ln J_B$$

where

$$J_\alpha(T) = \int_{\text{Maille}} \frac{d^2R}{c_0^2} \exp(-\beta W_\alpha(R)).$$

Minimization with respect to N_A and N_B yields $N_\alpha = N_0 J_\alpha \exp(\mu_\alpha/T)$ and therefore $\Omega_g = -TN = -T(N_A + N_B)$.

N_A and N_B can be seen to be so small in the two-dimensional vapour phase that this expression can be replaced by zero as stated above.

4. Mean field theory for the two-dimensional solid phases

4.1. Basic formulae

In the available mean field theories [12, 14], thermal expansion was not taken into account self-consistently. In the following, a self-consistent theory will be formulated. In principle, the mean field approximation can be defined as the best approximation of the partition function by a product of single-atom partition functions z_i [15]. This would, however, be too ambitious. Therefore the z_i's will be forced to be those of harmonic oscillators. Thus, we are looking for the best Einstein model. After a tedious calculation

(appendix A) the grand potential of the commensurate and incommensurate solid phase, respectively, is seen to be, to first order in T, equal to

$$\Omega_c/N_0 = T\{y\ln(yK_{cB}R_0^2/\pi T) + (1 - y)\ln[(1 - y)K_{cA}R_0^2/\pi T]\}$$
$$+ (1 - y)W_A(0) + yW_B(0) + \tfrac{1}{2}[(1 - y)^2\hat{U}_{AA}(R_0)$$
$$+ 2y(1 - y)\hat{U}_{BA}(R_0) + y^2\hat{U}_{BB}(R_0)] - (1 - y)\mu_A - y\mu_B \qquad (12)$$

and

$$\Omega_i/N = T\{x\ln(xK_{iB}R^2/\pi T) + (1 - x)\ln[(1 - x)K_{iA}R^2/\pi T]\}$$
$$+ \tfrac{1}{2}[(1 - x)^2\hat{U}_{AA}(R) + 2x(1 - x)\hat{U}_{BA}(R) + x^2\hat{U}_{BB}(R)]$$
$$- (1 - x)\mu_A - x\mu_B \qquad (13)$$

where

$$\hat{U}_{\alpha\gamma}(R) = \sum_j U_{\alpha\gamma}(R_i - R_j) \qquad (14)$$

for an interatomic distance R. Generally, interactions between nearest neighbours will be assumed, so that $\hat{U}_{\alpha\gamma}(R) = 6U_{\alpha\gamma}(R)$. K_α is the strength of the Einstein oscillator for atoms of kind α. In formula (12) the first expression between square brackets is the entropy and the next terms are the energy in the mean field approximation. The entropy consists of a configurational contribution $x\ln x + (1 - x)\ln(1 - x)$, and a vibrational contribution, containing $\ln K_\alpha$. This contribution is responsible for thermal expansion, since at higher temperatures the atoms want to have more room for their vibrations. K_α can be expanded in powers of T. The first order expansion was found at the cost of a terrific and hopefully correct calculation to be

$$K_{c\alpha} = \sum_\gamma y_\gamma Q_{\alpha\gamma}(R) + \frac{1}{24}\sum_\gamma y_\gamma\left(\frac{15T}{2K_{c\alpha}} + \frac{12T}{K_{c\gamma}}\right)\Lambda_{\alpha\gamma}(R) + \tfrac{1}{2}W''_\alpha \qquad (15)$$

with $y_A = 1 - y$ and $y_B = y$. $K_{i\alpha}$ is given by an analogous equation without the last term, and with y replaced by x. We have used

$$Q_{\alpha\gamma}(R) = \frac{1}{4}\sum_j\left(\frac{U'_{\alpha\gamma}(R)}{R} + U''_{\alpha\gamma}(R)\right) \qquad (16a)$$

and

$$\Lambda_{\alpha\gamma}(R) = 288(\varepsilon_{\alpha\gamma}/R^4)[3082(\sigma_{\alpha\gamma}/R)^{12} - 305(\sigma_{\alpha\gamma}/R)^6]. \qquad (16b)$$

In (16b) and (16a), interactions between non-nearest neighbours have been neglected. W''_α is defined by the harmonic approximation of W_α valid near its minimum at $r = 0$,

$$W_\alpha(r) = W(0) + \tfrac{1}{2}W''_\alpha r^2. \qquad (17)$$

Equation (16a) and the zero'th order approximation of (15) are derived in appendix B. The five equations (9) and (10) determine the five unknowns R, x, y, μ_A and μ_B when the potentials $W_A(0)$, $W_B(0)$, $\varepsilon_{\alpha\gamma}$ and $\sigma_{\alpha\gamma}$ are known. As usual, the chemical potentials

can be eliminated because they appear linearly. One obtains

$$-W_A(0) = T\left[\ln\frac{K_{cA}R_0^2}{\pi T} - y\sum_\gamma \frac{y_\gamma}{K_{c\gamma}}\frac{dK_{c\gamma}}{dy}\right] - T\left[\ln\frac{K_{iA}R_0^2}{\pi T} - x\sum_\gamma \frac{x_\gamma}{K_{i\gamma}}\frac{dK_{i\gamma}}{dx}\right]$$
$$+ \tfrac{1}{2}\hat{U}_{AA}^c - \tfrac{1}{2}\hat{U}_{AA}^i - \tfrac{1}{2}y^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c)$$
$$+ \tfrac{1}{2}x^2(\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i) - T\ln[(1-x)/(1-y)] \tag{18a}$$

which should be *positive*, as well as

$$-W_B(0) = T\left[\ln\frac{K_{cB}R_0^2}{\pi T} - (1-y)\sum_\gamma \frac{y_\gamma}{K_{c\gamma}}\frac{dK_{c\gamma}}{dy}\right]$$
$$- T\left[\ln\frac{K_{iB}R_0^2}{\pi T} - (1-x)\sum_\gamma \frac{x_\gamma}{K_{i\gamma}}\frac{dK_{i\gamma}}{dx}\right]$$
$$+ \tfrac{1}{2}\hat{U}_{BB}^c - \tfrac{1}{2}\hat{U}_{BB}^i - \tfrac{1}{2}(1-y)^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c)$$
$$+ \tfrac{1}{2}(1-x)^2(\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i) - T\ln(x/y). \tag{18b}$$

4.2. Numerical results and difficulties

Since (12) and (13) are correct to order T only, the Λ term in (15) should be neglected. On the other hand (15) cannot be replaced by its first term if R is too large because (16a) turns out to be negative. This happens, for instance, for Q_{BB} in Xe-rich Xe–Ar mixtures. A negative value of K is unphysical as seen from appendix B, formula (B.1). A possible solution of our troubles is to neglect vibrational entropy, i.e. to replace the K's in (12) and (13) by 1. For each value of R and y, it is easy to compute x from (13), and then the $W_\alpha(0)$'s are given by (18). The values of R and y can be adjusted until the desired values of the $W_\alpha(0)$'s are obtained. We have chosen the Lennard-Jones parameters and substrate potential values close to those used by Steele [16] and Novaco and McTague [17], with suitable modifications in order, in particular, to stabilize the commensurate phase of pure Kr. The values are given by the following table, to be complemented by the familiar rules [16, 17] $\varepsilon_{AB} \approx \sqrt{\varepsilon_{AA}\varepsilon_{BB}}$ and $\sigma_{AB} \approx (\sigma_{AA} + \sigma_{BB})/2$.

	ε_{AA}	ε_{BB}	σ_{AA}	σ_{BB}	$W_A(0)$	$W_B(0)$	R_0
Xe–Ar	221	122	4	3.44	40	33	4.26
Xe–Kr	221	171	4	3.62	40	34	4.26

These values are certainly not the most up to date but, as shown by Marti *et al* [12], refinements of the potentials would not improve the agreement with experiment much, which turns out to be poor as seen from figure 1.

The theoretical miscibility is seen to be much weaker than experimentally observed. This disagreement between theory and experiment is due to two factors. First of all, the mean field approximation neglects short-range order. This is certainly a very bad approximation for the argon-rich, incommensurate phase of the Xe–Ar mixtures. Indeed these phases should have an atomic distance close to that of pure, two-dimensional argon, namely 3.86 Å according to Lauter *et al* [18]. For such short distances the

energy of a Xe–Xe pair is very large. Thus, the real concentration of Xe–Xe pairs should be much lower than the mean field approximation, which therefore cannot predict the correct concentrations at coexistence (83% and 91% according to figure 1). An approximation more appropriate to this case will be presented in section 6.

The second reason for the bad agreement with experiment is, as already mentioned, that the vibrational entropy could be evaluated with reasonable accuracy at the temperature of interest only if the power series in T were pushed to a high order. As seen above, this difficulty is especially serious for Xe rich mixtures of Xe and Ar, where (16a) becomes negative for $\alpha = \gamma = B = Ar$.

4.3. A phenomenological approach

To circumvent the second difficulty we have used another method and we tried to fit the experimental data by equations (12) and (13) with a fixed value of K_α, to be included in the chemical potentials, but with adjustable potentials $\hat{U}_{\alpha\gamma}$. These potentials are assumed to have the form (4), which is certainly better than the harmonic approximation of appendix B. The Lennard-Jones parameters are thus adjustable. The temperature-dependent renormalization is intended to account for vibrational entropy which is too difficult to calculate accurately. Our procedure was the following.

(i) Start with the experimental values of x and y.

(ii) Neglect the temperature-dependent terms in (12), (13) and (18) *except the configurational entropy* (last term of (18)), but replace the Lennard-Jones parameters and the substrate potentials $W_\alpha(0)$ by effective (temperature dependent) parameters. Thus, the *ab initio* evaluation of the vibrational entropy is replaced by a phenomenological renormalization of the parameters, which physically corresponds to this vibrational entropy.

(iii) Look for reasonable values of these parameters which satisfy equations (12), (13) and (18).

Technically, we proceeded as follows. Insertion of (13) into (11) yields x as a function of R through an algebraic equation of second degree, so R is easily obtained when x and the Lennard-Jones parameters $\varepsilon_{\alpha\gamma}$ and $\sigma_{\alpha\gamma}$ are known; then $W_A(0)$ and $W_B(0)$ are given by (18). Various sets of Lennard-Jones parameters have been tested. The Lennard-Jones parameters of the pure system are fairly well known. In particular, σ_{AA} and σ_{BB} should fit the data of the pure system. The interatomic distance is $d = 3.86$ for Ar and 4.45 for Xe. This imposes $\sigma_{Xe-Xe} \approx 3.96$ Å (lower than Steele's [17] value 4.05 which is frequently used [18]) and $\sigma_{Ar-Ar} \approx 3.44$ Å. For the cross-parameters, the starting point is the familiar rule [17, 18] $\sigma_{AB} \approx (\sigma_{AA} + \sigma_{BB})/2$. However, in the Xe-rich phases, it has been necessary to take σ_{BA} appreciably bigger than $(\sigma_{AA} + \sigma_{BB})/2$. The difference is especially large for Ar–Kr mixtures, i.e. when the difference between the radii is particularly large. The physical meaning of this effect can be understood from the fact that the atom wants to increase its vibrational entropy. For the energy parameters we have taken values close to those of Steele. However, we have been obliged to attribute a very small value to the substrate potential in the case of Ar. Again, the large difference between radii makes the use of the mean field approximation difficult. For $T = 50$, the most reasonable values that we have found are the following.

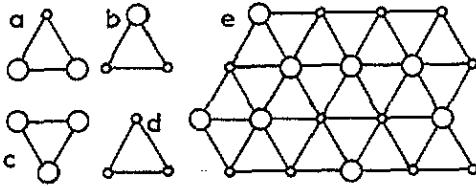|	ε_{AA}	ε_{AB}	ε_{BB}	σ_{AA}	σ_{AB}	σ_{BB}	W_A	W_B	x	y	R_{inc}
Ar	221	165	122	3.97	3.85	3.5	45	8	0.096	0.3	4.441
Kr	221	200	171	3.97	3.86	3.65	47	27	0.064	0.25	4.445

Figure 3. (*a*) and (*b*) Mixed triangles. (*c*) and (*d*) Other types of triangles. (*e*) A ground state when (22) is satisfied. Only mixed triangles are present.

For the Xe-poor phase of the Ar mixture, the mean field approximation cannot be used because short-range order is too strong as explained above.

The values listed in the table are effective ones, which may be different from real values [16, 17, 19, 20] for various reasons (thermal expansion, non-next-nearest neighbours, three-body interactions). However, this is not sufficient to explain the low value of the substrate potential for Ar.

5. The low temperature regime

At zero temperature the equilibrium state of a submonolayer can be obtained by minimizing the energy at fixed N and x, without chemical potential. Interactions between nearest neighbours only will be assumed, and local strains will be neglected. This is reasonable in the commensurate phase. Therefore, the nature of the ground state will now be investigated within the assumption that the ground state is commensurate. The correctness of this assumption will then be discussed, and the qualitative phase diagrams of figure 4 will be derived. In the C phase, the adsorbate–adsorbate interaction energy E_{aa} can be expressed as a function of the numbers $\nu_{\alpha\gamma}$ of $\alpha\gamma$ pairs and the corresponding energies $U_{\alpha\gamma}(R_0)$. In the commensurate phase, this energy is

$$NE_{aa} = \nu_{AA}U_{AA}(R_0) + \nu_{AB}U_{AB}(R_0) + \nu_{BB}U_{BB}(R_0) \tag{19}$$

where $N = N_0$ since one deals with the C phase. The index 0 will be omitted for simplicity. On a triangular lattice, the formulae

$$2\nu_{AA} + \nu_{AB} = 6N(1 - x) \qquad 2\nu_{BB} + \nu_{AB} = 6Nx \tag{20}$$

hold and allow us to rewrite (19) as

$$NE_{aa} = 3NU_{AA}(R_0) + 3Nx[U_{BB}(R_0) - U_{AA}(R_0)]$$
$$- \tfrac{1}{2}\nu_{AB}[U_{AA}(R_0) - 2U_{AB}(R_0) + U_{BB}(R_0)] \tag{21}$$

This is the Hamiltonian of an antiferromagnetic Ising model on a triangular lattice with interactions between nearest neighbours of strength $J = \frac{1}{4}[U_{AA}(R_0) - 2U_{AB}(R_0) + U_{BB}(R_0)]$ in a magnetic field $H = 3J - 3[U_{BB}(R_0) - U_{AA}(R_0)]$. The identification with the usual Ising form

$$\mathcal{H} = -J \sum_{\langle RR' \rangle} \sigma_R \sigma_{R'} - H \sum_R \sigma_R = -J(\nu_{AA} + \nu_{BB}) + J\nu_{AB} - HN(1 - 2x)$$

is easily made after using (20). The interaction can be seen to be positive, i.e. antiferromagnetic. The physical meaning is that, on the rigid, commensurate lattice, big ions tend to form a mixture with small ions in order to exploit the available space as well as possible. In contrast with usual magnetism, the energy (21) should be minimized at constant magnetization $x - \frac{1}{2}$ rather than fixed magnetic field H. However, if one solves the Ising problem in zero field, the magnetization is clearly zero. Thus, the case $x = \frac{1}{2}$ corresponds to a vanishing magnetic field $H = 0$. The interest in this remark is that the antiferromagnetic Ising model on a triangular lattice is exactly soluble for $H = 0$. It has no transition. This means that there is *no superstructure* for $x = \frac{1}{2}$ and, presumably, for x close to $\frac{1}{2}$.

On the other hand, for $x = \frac{1}{3}$, the ground state is non-degenerate and shows a superstructure with three sublattices, two of them being occupied by A atoms and the third one by B atoms. This is easily seen from (21) because the minimum of E_{aa} corresponds to the maximum of ν_{AB}, and ν_{AB} turns out to be equal to the number of 'mixed' triangles. A triangle is called mixed if it is an AAB or ABB triangle (figure 3). The number of triangles is equal to $2N$. It is easily seen that all triangles can be of the 'mixed' kind (AAB or ABB) if

$$\tfrac{1}{3} \leqslant x \leqslant \tfrac{2}{3}. \tag{22}$$

If condition (22) is satisfied, the minimum adatom–adatom interaction energy in the cs phase is, according to (21),

$$NE_{aa} = 3NU_{AA}(R_0) + 3Nx[U_{BB}(R_0) - U_{AA}(R_0)]$$

$$- N[U_{AA}(R_0) - 2U_{AB}(R_0) + U_{BB}(R_0)]. \tag{23}$$

For $x = \frac{1}{3}$ (or $\frac{2}{3}$) the condition that all triangles are mixed is sufficient to determine the configuration of the system, which is its ground state. It has the superstructure described above. Presumably the superstructure is also present for x close to $\frac{1}{3}$.

On the other hand, if $x > \frac{2}{3}$, the maximum number of mixed triangles is obtained when there is a maximum number of ABB triangles, and therefore no AAA and no AAB triangle. Two cases should be considered.

(i) If the pure B phase is incommensurate, the rigid lattice model cannot be applied. Energy is gained if all BBB triangles are grouped to form a pure B phase which becomes incommensurate. Thus there is phase separation. This occurs for Xe–Ar mixtures for $x > \frac{2}{3}$, but also for Xe–Ar and Xe–Kr mixtures for $x < \frac{1}{3}$ (figure 4(a)).

(ii) If the pure B phase is commensurate, the rigid lattice model is applicable. Thus, one has to maximize the number of ABB triangles. The solution is highly degenerate and the concentration can be varied continuously. This occurs in Kr-rich, Xe–Kr mixtures (figure 4(a)).
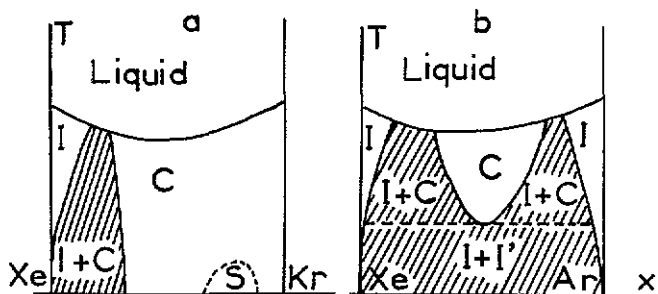
Figure 4. Qualitative phase diagrams. Hatched regions are coexistence domains. C = commensurate phase. I, I' = incommensurate phases. S = commensurate phase with superstructure.

The above discussion is incomplete because the stability of the commensurate phase with respect to phase separation has not been taken into account when (22) is satisfied. Stability implies that the energy of the commensurate phase is lower than the energy of a system of coexisting pure phases A and B, which is for Xe–Ar and Xe–Kr mixtures, respectively:

$$3N(1 - x)U_{AA}(R_A) + 3NxU_{BB}(R_B)$$

$$3N(1 - x)U_{AA}(R_A) + 3Nx[U_{BB}(R_0) + w_B]$$

where $3w_\alpha = - W_\alpha(0)$, and $R_\alpha = 2^{1/6}\sigma_{\alpha\alpha}$ is the atomic distance of the pure α phase, so that $U_{\alpha\alpha}(R_\alpha) = - \varepsilon_{\alpha\alpha}$. According to (23) the stability condition of the CS phase at $T = 0$ is therefore for Xe–Ar

$$(1 - x)[\hat{U}_{AA}^c - \hat{U}_{AA}(R_A) + W_A(0)] + x[\hat{U}_{BB}^c - \hat{U}_{BB}(R_B) + W_B(0)]$$

$$- \tfrac{1}{4}(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c) < 0 \qquad (24a)$$

and for Xe–Kr

$$(1 - x)[\hat{U}_{AA}^c - \hat{U}_{AA}(R_A) + W_A(0)] - \tfrac{1}{4}(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c) < 0. \qquad (24b)$$

The values of the Lennard-Jones parameters found in section 4.2 are not reliable because they are spoilt by approximations and thermal effects. Therefore more conventional values will be used to see whether (24) is satisfied. First of all we assume [16, 17] $\varepsilon_{\alpha\gamma}^2 = \varepsilon_{\alpha\alpha}\varepsilon_{\gamma\gamma}$ and $2\sigma_{\alpha\gamma} = \sigma_{\alpha\alpha} + \sigma_{\gamma\gamma}$.

5.1. Xe–Kr mixtures

We take [16, 17] $\varepsilon_{AA} = 221$ K, $\varepsilon_{BB} = 171$ K, $\sigma_{AA} = 3.97$ Å, $\sigma_{BB} = 3.65$ Å. Then $\hat{U}_{AA}^c = -1198$ K, $\hat{U}_{AB}^c = -1165$ K, $\hat{U}_{BB}^c = -981$ K, $\hat{U}_{AA}(R_A) = -6\varepsilon_{AA} = -1326$ K, and $\hat{U}_{BB}(R_B) = -6\varepsilon_{BB} = -1026$ K. Taking [16, 18] $W_A(0) \approx W_B(0) \approx 30$ K, relation (24b) is seen to be satisfied for all values of $x > \tfrac{1}{3}$. Figure 4(a) can be guessed from these $T = 0$ results.

5.2. *Xe–Ar mixtures*

Now $\hat{U}_{AA}^c = -1198$ K, $\hat{U}_{AB}^c = -977$ K, $\hat{U}_{BB}^c = -624$ K, $\hat{U}_{AA}(R_A) = -1326$ K and $\hat{U}_{BB}(R_B) = -732$ K. It turns out that (24a) is *not* satisfied, so that Xe and Ar do not mix at $T = 0$. From these zero-temperature results one can guess the phase diagram of figure 4(b). Mixing of Xe and Ar occurs when the configuration entropy overcompensates the energy loss, say above 10 K according to a rough evaluation. This conclusion may be altered if more recent data [19, 20] are used.

6. The tough hexagon model

The mean field approximation underestimates badly the solubility of big A atoms among small B ones, e.g. Xe in Ar. This is because AA pairs 'cost' a huge energy.

In this section we propose an approximation appropriate to big A atoms among small B ones.

The simplest idea would be to forbid AA pairs completely. The problem is then to calculate the entropy of an AB mixture at the sites of a triangular lattice, when A atoms cannot touch. This is Baxter's *hard hexagon problem* [21]. This model has an exact, but complicated solution. Instead, an approximate solution (appropriate for small values of $1 - x$) will be presented. Also, BB pairs will not be strictly forbidden, but only a proportion $(1 - p)$ of the $N(1 - x)^2$ BB pairs allowed by MFA will be accepted. The number of AA and AB pairs is then obtained from (20), and the energy is

$$N\mathscr{E} = \tfrac{1}{2}N(1-p)(1-x)^2 \hat{U}_{AA} + N(1-x)(x+p-px)\hat{U}_{AB} + \tfrac{1}{2}N(x^2 - p(1-x)^2)\hat{U}_{BB}.$$

$$(25)$$

This model will be called the 'tough hexagon model'. The parameter p is a variational parameter which has to minimize the free energy. Now the entropy $T \ln g(p, x)$ will be calculated approximately. g is the number of ways to distribute $N(1 - x)$ big A atoms among N sites on a triangular lattice. We assume first that the Nx A atoms are labelled $1, 2, 3, \ldots, N(1 - x)$, and then the result will be divided by the number $(N(1 - x))!$ of labellings. The first atom can be placed in N different ways. Then a proportion p of the six neighbours of the first A atom are discarded. The number of remaining sites is $N - 1 - 6p = N - q$, where $q = 6p + 1$. One of these sites is randomly chosen and the second A atom is placed there. The number of ways to place two marked atoms is therefore $N(N - q)$, and $N(N - q)$ for atoms which are not marked. Then a proportion p of the six neighbours of the second A atoms are discarded. The number of remaining atoms will be approximated by $N - 2q$. This is an underestimation because the two A atoms can have common neighbours. Then the third A atoms are placed randomly among the remaining sites, etc. Iterating the argument, the number of ways to place $N(1 - x)$ A atoms is seen to be

$$N(N-q)(N-2q) \ldots (N-N(1-x)q+1) = q^{N(1-x)}[(N/q)!]/[(N/q) - N(1-x)]!.$$

For non-marked atoms the result is therefore

$$g = q^{N(1-x)}(N/q)!/(N/q - N(1-x))!(N(1-x))!$$

and, using the Stirling formula, the entropy turns out to be

$$\ln g = -N[1/(1 + 6p) - (1-x)] \ln[1 - (1 + 6p)(1-x)] - N(1-x) \ln(1-x). \quad (26)$$

In the hard hexagon model ($p = 1$) formula (26) reads

$$\ln g = -N[\tfrac{1}{7} - (1-x)] \ln[1 - 7(1-x)] - N(1-x) \ln(1-x). \quad (27)$$

The entropy is seen to vanish for $x = 6/7$. The correct value is obviously $\tfrac{1}{3}$, when the

hard hexagons form a close packing. Thus, our approximation is poor for large values of $(1-x)$.

Neglecting vibrational entropy, the free energy per atom $F = (\mathscr{E} - T \ln g)/N$ is then obtained by addition of (25). Adding the chemical potentials, the grand potential in the incommensurate phase is

$$
\begin{aligned}
\Omega_i/N = {} & T[1/(1+6p) - (1-x)] \ln[1 - (1+6p)(1-x)] + T(1-x) \ln(1-x) \\
& + \tfrac{1}{2}(1-p)(1-x)^2 \hat{U}_{AA}(R) + 2(1-x)(x+p-px)\hat{U}_{AB}(R) \\
& + (x^2 - p(1-x)^2)\hat{U}_{BB}(R)] - (1-x)\mu_A - x\mu_B.
\end{aligned}
\tag{28}
$$

The approximation developed in this section is particularly appropriate for Ar-rich, Xe–Ar mixtures. In that case $\hat{U}^i_{AA}$ takes very large values, which are even positive for R close to the pure Ar value. Then the mean field approximation is catastrophic as stressed before, while the hard hexagon approximation ($p = 1$) is quite reasonable. For the sake of simplicity, the final result, replacing (18), will only be given for $p = 1$, while the general formula can be found in appendix C:

$$
-W_B(0) = \tfrac{1}{2}\hat{U}^c_{BB} - \tfrac{1}{2}\hat{U}^i_{BB} - \tfrac{1}{2}(1-y)^2(\hat{U}^c_{AA} - 2\hat{U}^c_{AB} + \hat{U}^c_{BB}) - T\ln[1 - 7(1-x)]^{1/7}/y
\tag{29a}
$$

$$
\begin{aligned}
-W_A(0) = {} & \tfrac{1}{2}\hat{U}^c_{AA} - \tfrac{1}{2}y^2(\hat{U}^c_{AA} - 2\hat{U}^c_{AB} + \hat{U}^c_{BB}) + \tfrac{1}{2}(-2\hat{U}^i_{AB} + \hat{U}^i_{BB}) \\
& - T\ln[(1-x)/(1-y)] - (6T/7)\ln[1 - 7(1-x)].
\end{aligned}
\tag{29b}
$$

The main feature of these equations is that $\hat{U}^i_{AA}$, the energy of a Xe–Xe pair in incommensurate Ar, has disappeared. This is what we wanted since the failure of the mean field approximation is due to the large value of this energy. The price paid is a reduced, but not drastically reduced, configurational entropy. For $x = 0.95$, the entropy deviates from the mean field value by only 5%.

These equations have been applied to Ar-rich, Xe–Ar mixtures using the technique described in section 5. Using Steele's values of the Lennard-Jones parameters and $T = 50$ K, a typical set of values is given in the following table.

R	x	y	W_A	W_B
3.99	0.905	0.7	38	31

The values of W_A and W_B are plausible. The value of x is very close to the real one. y is too small. However, in view of the fact that lattice relaxation has not been taken into account, the agreement is quite encouraging.

7. Conclusion and open questions

Three different mixed monolayer approaches have been investigated: a mean field

theory taking thermal expansion into account; a low-temperature argument; and a tough hexagon approximation which takes short-range order into account.

The tough hexagon approximation has been applied only to Ar-rich Xe–Ar mixtures, when Xe–Xe pairs are forbidden because of their huge energy. The results are promising and could presumably be improved if strains were taken into account. The main effect would be a modification of $\hat{U}^i_{AB}$, the energy of a Xe atom in an Ar matrix. This would not be difficult to calculate, but this complication is left for future work.

We predict very different phase diagrams at low temperatures for Xe–Kr and for Xe–Ar mixed submonolayers at equilibrium. In Xe–Ar mixtures, we find no commensurate phase at low temperature. This result is not really in disagreement with the observations of Bohr *et al* [11] because equilibrium is not easily reached at low temperatures. The phase studied by Bohr *et al* may well have been metastable. On the other hand, we have heard from experimentalists that Bohr's experiments are not easy to reproduce because of the uneasy miscibility of Ar and Xe (Lauter, private communication). Thus, our phase diagram (figure 4(b)) is not without relation to experiment. The miscibility of Kr–Xe mixtures at *zero* temperature is a remarkable property of an adsorbed film. Without substrate, only stoichiometric solid solutions are possible at $T = 0$ in any system. On the other hand, our theoretical phase diagram would be modified if longer range interactions were taken into account, but the modifications would be far beyond any experimental relevance.

Our other contribution is a mean field theory which takes the vibrational entropy and thermal expansion into account. This theory generalizes that of Gordon and Villain [22] valid for a pure system. In both theories, only the lowest order in T has been explicitly calculated, and this is a serious drawback for experimental applications. Note that our treatment is different from usual self-consistent theories of the commensurate–incommensurate transition [23], where only the substrate potential is renormalized.

We have not succeeded to a greater extent than Marti *et al* [12] in obtaining a quantitative agreement between the experimental phase diagram and the mean-field theory. Although we have improved the theory of Marti *et al* by taking vibrational entropy into account through the coefficients K_α of formulae (12) and (13), we have not been able to calculate these coefficients with a sufficient accuracy. In the case of Xe–Kr mixtures, the experimental data have been adjusted by phenomenological potentials, which is equivalent to adjusting the coefficients K_α. In the case of Xe–Ar mixtures this method implies an effective substrate potential for Ar which is much too low in the Xe-rich side, and completely fails in the Ar-rich side. Thus, the mean field approximation yields acceptable qualitative results only when the difference between atomic radii is not too large.

It is of interest to recall that three-dimensional rare-gas crystals of Xe and Kr, and of Ar and Kr, are miscible [24–29] in all proportions near the melting curve. This is in agreement with the mean field approximation, an extremely crude version of which is presented below. Neglecting the configurational entropy, the grand potential is given by a formula analogous to (28) with $p = 0$ and the $\hat{U}_{\alpha\gamma}$'s replaced by $2\hat{U}_{\alpha\gamma} = 12\,U_{\alpha\gamma}$:

$$\Omega^{3d}/N_0 = T[x \ln x + (1-x)\ln(1-x)] + [(1-x)^2 \hat{U}_{AA}(R)$$
$$+ 2y(1-x)\hat{U}_{BA}(R) + x^2 \hat{U}_{BB}(R)] - (1-x)\mu_A - x\mu_B.$$

At the critical point the first three derivatives of Ω with respect to x vanish. For the sake of simplicity, R will be assumed to be fixed. For instance, $\partial^2(\Omega/N)/\partial x^2 = 0$ will be written instead of $\partial^2\Omega/\partial x^2 + (\partial^2\Omega/\partial x \partial R)\mathrm{d}R/\mathrm{d}x = 0$. This is presumably sufficient to

obtain an order of magnitude. Then

$$\partial(\Omega^{3d}/N)/\partial x = T[\ln x - \ln(1-x)] + 2[(x-1)\hat{U}_{AA}(R)$$
$$+ (1-2x)\hat{U}_{BA}(R) + x\hat{U}_{BB}(R)] + \mu_A - \mu_B = 0.$$
$$\partial^2(\Omega^{3d}/N)/\partial x^2 = T[1/x + 1/(1-x)] + 2[\hat{U}_{AA}(R) - 2\hat{U}_{BA}(R) + \hat{U}_{BB}(R)] = 0$$
$$\partial^3(\Omega^{3d}/N)/\partial x^3 = T[-1/x^2 + 1/(1-x)^2] = 0.$$

The last equation yields $x = \frac{1}{2}$ and the critical temperature is then obtained from the previous one:

$$T_c^{3d} = \tfrac{1}{2}[\hat{U}_{AA}(R) - 2\hat{U}_{BA}(R) + \hat{U}_{BB}(R)].$$

This rough evaluation yields quite low values, less than 40 K. Experimentally, the only thing known is that T_c is lower than the melting temperature, in agreement with the above evaluation.

Coming back to the two-dimensional case, an open question is as to whether super-structures can be stable at low temperature. None has been found experimentally [11, 12]. Theoretically, the ground state has been seen to be highly degenerate when (21) is satisfied. A high ground-state degeneracy generally implies absence of order, so that presumably there is no superstructure, at least in the present approximation where elastic effects and interactions beyond nearest neighbours have been neglected.

It is clear that the mean field approximation is a first step in a hierarchy of approximations. The next step would treat correctly one atom and its seven neighbours in the rigid potential created by the average lattice. In view of the difficulties encountered in the mean field approximation, it should be difficult.

Acknowledgments

Appendix A. The mean field approximation

The present appendix applies to any sublattice structure. In appendix B, the equations will be solved in the absence of superstructure.

The mean field approximation is understood here as corresponding to the 'best' density matrix [15] of the form

$$\check{Z}^{-1}\exp(-\beta\check{\mathcal{H}}) \tag{A1}$$

with

$$\check{Z} = \text{Tr}\exp(-\beta\check{\mathcal{H}}) \tag{A2}$$

$$\check{\mathcal{H}} = \sum_{i\alpha}\rho_i^\alpha \check{V}_{i\alpha}(r_i) \tag{A3}$$

and

$$\text{Tr} = \prod_i \left(\sum_{\rho_i^A = 0}^1 \int d^2 r_i / R_0^2 \right). \tag{A4}$$

The notation $\rho_i^\alpha = \rho_\alpha(\langle R_i \rangle)$ has been used.

The 'best' density matrix is given, according to Bolgoljubov's variational rule [15], by the minimum of the grand potential

$$\tilde{\Omega} = - T \ln \tilde{Z} + \left\langle \mathcal{H} - \tilde{\mathcal{H}} - \sum_{i,\alpha} \mu_\alpha \rho_i^\alpha \right\rangle^{\sim} \tag{A5}$$

$$\langle A \rangle^{\sim} = \tilde{Z}^{-1} \text{Tr} \, A \exp(-\beta \tilde{\mathcal{H}}). \tag{A6}$$

The first term of (A5) is given by

$$\tilde{Z} = \prod_i (\tilde{z}_{iA} + \tilde{z}_{iB}) \tag{A7}$$

where

$$\tilde{z}_{i\alpha} = \int (d^2 r_i / R_0^2) \exp(-\beta \tilde{V}_{i\alpha}(r_i)). \tag{A8}$$

The third term of (A5) is

$$\langle \tilde{\mathcal{H}} \rangle^{\sim} = \sum_{i\alpha} \int \frac{(d^2 r_i / R_0^2) \tilde{V}_{i\alpha}(r_i) \exp(-\beta \tilde{V}_{i\alpha}(r_i))}{(\tilde{z}_{iA} + \tilde{z}_{iB})}. \tag{A9}$$

The second term of (A5) contains a part

$$\langle \mathcal{H}_{AA} \rangle^{\sim} = \tfrac{1}{2} \sum_{ij} (\tilde{z}_{iA} + \tilde{z}_{iB})^{-1} (\tilde{z}_{jA} + \tilde{z}_{jB})^{-1} \sum_{\alpha\gamma} \left(\int d^2 r_i / R_0^2 \right) \left(\int d^2 r_j / R_0^2 \right)$$

$$\times U_{\alpha\gamma}(R_i - R_j + r_i - r_j) \exp(-\beta \tilde{V}_{i\alpha}(r_i)) \exp(-\beta \tilde{V}_{j\gamma}(r_j)) \tag{A10}$$

and, in the commensurable phase, also the term

$$\langle \mathcal{H}_{AS} \rangle^{\sim} = \sum_{i\alpha} \int (d^2 r_i / R_0^2) W_\gamma(r_i) \exp(-\beta \tilde{V}_{i\alpha}(r_i)) / (\tilde{z}_{iA} + \tilde{z}_{iB}). \tag{A11}$$

The last term of (A5) contains the average value

$$x_i^\alpha = \langle \rho_i^\alpha \rangle^{\sim} = (\tilde{z}_{iA} + \tilde{z}_{iB})^{-1} z_{i\alpha}. \tag{A12}$$

In order to apply Bogoljubov's variational principle we need the variations of the various terms of (A5) associated with any given variation of $V_{i\alpha}(\tilde{r}_i)$. For instance

$$\delta_{\alpha, r_i} \langle \tilde{\mathcal{H}} \rangle^{\sim} = (\tilde{z}_{iA} + \tilde{z}_{iB})^{-1} \delta_0 [\tilde{V}_{i\alpha}(r_i) - \langle \tilde{V}_{iA} \rho_i^A + \tilde{V}_{iB} \rho_i^B \rangle^{\sim} - T] \tag{A13}$$

where δ_0 is the variation of $\exp[-\beta \tilde{V}_{i\alpha}(r_i)] / R_0^2$.

$$\delta_0 = \delta[\exp(-\beta \tilde{V}_{i\alpha}(r_i)) / R_0^2]. \tag{A14}$$

The variation of the first term of (A5) is

$$T \delta_{\alpha, r_i} \ln \tilde{Z} = T(\tilde{z}_{iA} + \tilde{z}_{iB})^{-1} \delta_0. \tag{A15}$$

The variation of (A12) is

$$\delta_{\alpha,r_i}\langle\mathcal{H}_{AA}\rangle^{\sim} = (\bar{z}_{iA} + \bar{z}_{iB})^{-1}\sum_j\int (\mathrm{d}^2r_j/R_0^2)(\bar{z}_{jA} + \bar{z}_{jB})^{-1}$$

$$\times \sum_\gamma U_{\alpha\gamma}(R_i - R_j + r_i - r_j)\exp(-\beta\bar{V}_{j\gamma}(r_j))\,\delta_0 - 2(\bar{z}_{iA} + \bar{z}_{iB})^{-1}$$

$$\times \left\langle\sum_{\alpha\gamma j} U_{\alpha\gamma}(R_i - R_j + r_i - r_j)\rho_j^\gamma\right\rangle^{\sim}\delta_0. \tag{A16}$$

where

$$\left\langle\sum_{\alpha\gamma j} U_{\alpha\gamma}(R_i - R_j + r_i - r_j)\rho_j^\gamma\right\rangle^{\sim} = \tfrac{1}{2}\sum_{\alpha\gamma}(\bar{z}_{iA} + \bar{z}_{iB})^{-1}(\bar{z}_{jA} + \bar{z}_{jB})^{-1}$$

$$\times \left(\int (\mathrm{d}^2r_i/R_0^2)\left(\int (\mathrm{d}^2r_j/R_0^2)U_{\alpha\gamma}(R_i - R_j + r_i - r_j)\exp(-\beta\bar{V}_{i\alpha}(r_i))\right.\right.$$

$$\times \exp(-\beta\bar{V}_{j\alpha}(r_j)).$$

The variation of the last term of (A5) is

$$\delta_{\alpha,r_i}\sum_\lambda \mu_\lambda\delta\langle\rho_i^\lambda\rangle^{\sim} = (\bar{z}_{iA} + \bar{z}_{iB})^{-1}\left(\mu_\alpha - \sum_m \mu_\lambda\langle\rho_m^\lambda\rangle\right)\delta_0. \tag{A17}$$

The variation of (A11) is

$$\delta_{\alpha,r_i}\langle\mathcal{H}_{AS}\rangle^{\sim} = \delta_0(\bar{z}_{iA} + \bar{z}_{iB})^{-1}W_\alpha(r_i) - \delta_0(\bar{z}_{iA} + \bar{z}_{iB})^{-1}$$

$$\times \sum_\alpha\int (\mathrm{d}^2r_i/c_0^2)W_\gamma(r_i)\exp(-\beta\bar{V}_{i\alpha}(r_i))/(\bar{z}_{iA} + \bar{z}_{iB}). \tag{A18}$$

The variation of (A5), which should be zero, is the sum of (A14) to (A18) with appropriate weights. Dividing by the common factor $(\bar{z}_A + \bar{z}_B)^{-1}\,\delta_0$ and equating to zero, one finds

$$\bar{V}_{i\alpha}(r) = \sum_j\int (\mathrm{d}^2r_j/R_0^2)(\bar{z}_{jA} + \bar{z}_{jB})^{-1}\sum_\gamma U_{\alpha\gamma}(R_i - R_j + r_i - r_j)$$

$$\times \exp(-\beta\bar{V}_{j\gamma}(r_j)) + W_\alpha(r) - \mu_\alpha + \mu_A(1 - x_i) + \mu_B x_i + L_i(T, x). \tag{A19}$$

The constants L_i are given, according to the previous argument, by an expression which has not to be calculated. Indeed, if (A19) is inserted in the right-hand side of (A5), it turns out that $\langle\mathcal{H}\rangle^{\sim}$ and $\langle\rho_i^\alpha\rangle^{\sim}$ are independent of the constant L_i, while $-T\ln\bar{Z}$ contains a term L_i which is exactly compensated by a term $-L_i$ coming from $-\langle\mathcal{H}\rangle^{\sim}$. Thus, (A5) is independent of L_i. These constants have therefore no physical meaning. The L_i may be chosen such that the last three terms of (A19) vanish. Then

$$\bar{V}_{i\alpha}(r) = \sum_j\int (\mathrm{d}^2r_j/R_0^2)(\bar{z}_{jA} + \bar{z}_{jB})^{-1}\sum_\gamma U_{\alpha\gamma}(R_i - R_j + r_i - r_j)$$

$$\times \exp(-\beta\bar{V}_{j\gamma}(r_j)) + W_\alpha(r) - \mu_\alpha. \tag{A20}$$

This system of integral equations should be solved with the constraints (A12) and (A8) for given $x_B = x$ and $x_A = 1 - x$. This is the central difficulty of the problem. Inserting (A20) into (A9) and using (A10) and (A11), one finds

$$\langle \mathcal{H} \rangle^{\sim} = 2\langle \mathcal{H}_{AA} \rangle^{\sim} + \langle \mathcal{H}_{AS} \rangle^{\sim} - \mu_\alpha \langle \rho_{i\alpha} \rangle^{\sim}. \tag{A21}$$

Comparison with (A5) shows that the grand potential is given in the mean field approximation by

$$\bar{\Omega} = -T \sum_i \ln(\bar{z}_{iA} + \bar{z}_{iB}) - \langle \mathcal{H}_{AA} \rangle^{\sim}. \tag{A22}$$

Inserting (A12) one finds

$$\bar{z}_{iA} + \bar{z}_{iB} = \bar{z}_{iA}[1 + x_i/(1 - x_i)] = \bar{z}_{iA}(1 - x_i)^{-1} = \bar{z}_{iB}/x_i. \tag{A23}$$

Using this equation, (A22) can be written in the following form where the configurational entropy explicitly appears.

$$\bar{\Omega} = T \sum_i \{x_i \ln(x_i/\bar{z}_{iB}) + (1 - x_i) \ln[(1 - x_i)/\bar{z}_{iA}]\} - \langle \mathcal{H}_{AA} \rangle^{\sim}. \tag{A24}$$

In the absence of superstructure, $\bar{V}_{i\alpha}$, $\bar{z}_{i\alpha}$ and x_i are replaced by $\bar{V}_\alpha$, $\bar{z}_\alpha$ and x in the basic formulae (A19), (A12) and (A24).

Appendix B. The harmonic approximation

It will now be assumed that no superstructure is present. Thus, the system (A19) consists 'only' of two integral equations. Even one would be too much. The best one can do is to assume a certain form for $\bar{V}_\alpha$, which depends on a finite number of numerical parameters. Insertion into (A19) then yields an equation which can be solved if additional approximations are made.

An additional difficulty is that, even if some functional form of $\bar{V}_\alpha$ is assumed, the integrals in (A19) can generally not be analytically performed. An appropriate form of the $\bar{V}_\alpha$, which allows an analytical calculation, is the harmonic approximation, which unfortunately is physically not good except at low temperature. A square-well potential would solve the mathematical problem as well but physically it would be even worse. Thus, the following form will be assumed.

$$\bar{V}_\alpha(r) = \bar{V}_\alpha(0) + K_\alpha r^2 \qquad \alpha = A, B. \tag{B1}$$

The four parameters K_α and $\bar{V}_\alpha(0) = \lambda_\alpha$ can be obtained by inserting (B1) into (A19) and replacing $U_{\alpha\gamma}$ by its Taylor expansion limited to second order. The same results are obtained more consistently by looking directly for the 'best' potential of the form (B1). This can be done by inserting (B1) into (A5). The integrals are over Gaussians and are easily performed, yielding

$$\bar{z}_\alpha = (\pi T/K_\alpha R_0^2) \exp(-\beta \bar{V}_\alpha(0)) \tag{B2}$$

$$\langle \mathcal{H} \rangle^{\sim} = N \sum_\alpha x_\alpha \bar{V}_\alpha(0) - NT \tag{B3}$$

$$\langle \mathcal{H}_{AA} \rangle^{\sim} = \frac{N}{2} \sum_{\alpha\gamma} \bar{U}_{\alpha\gamma} x_\alpha x_\gamma + N \sum_{\alpha\gamma} \frac{T}{K_\gamma} x_\gamma x_\alpha Q_{\alpha\gamma}. \tag{B4}$$

In (B4), the Taylor expansion of $U_{\alpha\gamma}$ has been limited to second order. One must do better if one wants to obtain the Λ-term in (15). The above relations can be inserted into (A5) and the derivatives are easily calculated with the help of (A12). In particular

$$\partial x_\zeta/\partial K_\alpha = (x_\alpha x_\zeta - \delta_{\alpha\zeta}x_\alpha)/K_\alpha \tag{B5}$$

$$\partial x_\zeta/\partial \lambda_\alpha = (K_\alpha/T)\partial x_\zeta/\partial K_\alpha. \tag{B6}$$

For the sake of simplicity, the calculation will be restricted to the incommensurate phase. It follows from (A5) and (B2–B6) that

$$\partial \tilde{\Omega}/\partial \lambda_\alpha = (K_\alpha/T)\partial \tilde{\Omega}/\partial K_\alpha + \frac{N}{K_\alpha}\sum_\gamma Q_{\alpha\gamma}x_\alpha x_\gamma - Nx_\alpha.$$

Since both derivatives of $\tilde{\Omega}$ should vanish according to Bogoljubov's formula, it follows that

$$K_\alpha = \sum_\gamma Q_{\alpha\gamma}x_\gamma. \tag{B7}$$

This is formula (15) in the incommensurate phase to order 0 in T.

Equation $\partial \tilde{\Omega}/\partial \lambda_\alpha = 0$ yields, after a short calculation,

$$\sum_\zeta \left(\sum_\xi \hat{U}_{\xi\zeta}x_\xi + T\sum_\xi Q_{\xi\zeta}x_\xi/K_\xi + T\sum_\xi Q_{\xi\zeta}x_\xi/K_\zeta - \lambda_\zeta - \mu_\zeta \right) \partial x_\zeta/\partial \lambda_\alpha = 0.$$

The expression in brackets should vanish. One finds

$$\lambda_\zeta = \sum_\xi \hat{U}_{\xi\zeta}x_\xi + T\sum_\xi Q_{\xi\zeta}x_\xi/K_\xi + T - \mu_\zeta. \tag{B8}$$

$\tilde{\Omega}$ can be given by several equivalent formulae one of which is

$$\tilde{\Omega} = TN\{(1 - x)\ln[(1 - x)K_A R_0^2/\pi T] + x\ln(xK_B R_0^2/\pi T)\}$$

$$+ N\sum_\alpha x_\alpha\lambda_\alpha - \frac{N}{2}\sum_{\alpha\gamma} \hat{U}_{\alpha\gamma}x_\alpha x_\gamma - NT\sum_{\alpha\gamma} Q_{\alpha\gamma}x_\alpha x_\gamma + NT. \tag{B9}$$

To obtain this equation, use should be made of the following equation deduced from (B7).

$$1 = \sum_\alpha x_\alpha = \sum_\alpha x_\alpha \sum_\gamma (Q_{\alpha\gamma}x_\gamma/K_\alpha) = \sum_{\alpha\gamma} Q_{\alpha\gamma}x_\alpha x_\gamma. \tag{B10}$$

Equation (13) can be obtained from (B8–B10).

Appendix C. The tough hexagon model

The derivative of (28) with respect to x should be equated to 0, yielding

$$\partial(\Omega_i/N)/\partial x = T\ln[1 - (1 + 6p)(1 - x)] - T\ln(1 - x)$$

$$+ \{(1 - p)(x - 1)\hat{U}_{AA}(R) + (1 - 2x - 2p + 2px)\hat{U}_{AB}(R)$$

$$+ [x - p(x - 1)]\hat{U}_{BB}(R)\} + \mu_A - \mu_B = 0. \tag{C1}$$

In the commensurate phase, formula (12) will be used again, but deprived of its vibrational entropy, i.e.

$$\Omega_c/N_0 = T[y \ln y + (1-y) \ln(1-y)] + (1-y)W_A(0) + yW_B(0)$$
$$+ \tfrac{1}{2}[(1-y)^2 \hat{U}_{AA}(R_0) + 2y(1-y)\hat{U}_{BA}(R_0) + y^2 \hat{U}_{BB}(R_0)]$$
$$- (1-y)\mu_A - y\mu_B = 0.$$

The derivative should be equal to 0 at equilibrium, i.e.

$$\partial(\Omega_c/N_0)/\partial y = T[\ln y - \ln(1-y)] - W_A(0) + W_B(0)$$
$$+ [(y-1)\hat{U}_{AA}(R_0) + (1-2y)\hat{U}_{BA}(R_0) + y\hat{U}_{BB}(R_0)]$$
$$+ \mu_A - \mu_B = 0.$$

Elimination of μ_A between (28) and (C1) yields

$$[T/(1+6p)] \ln[1 - (1+6p)(1-x)] - \tfrac{1}{2}(1-p)(1-x)^2$$
$$\times (\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i) + \tfrac{1}{2}\hat{U}_{BB}^i = \mu_B.$$

Combining this with the corresponding formula for the commensurable phase

$$T \ln y + (1-y)\hat{U}_{AB} - \tfrac{1}{2}(1-y)^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c) + \tfrac{1}{2}\hat{U}_{BB}^c + W_B(0) = \mu_B$$

one finds

$$-W_B(0) = \tfrac{1}{2}\hat{U}_{BB}^c - \tfrac{1}{2}\hat{U}_{BB}^i - \tfrac{1}{2}(1-y)^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c)$$
$$+ [(1-p)/2](1-x)^2(\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i)$$
$$- T \ln[1 - (1+6p)(1-x)]^{1/(1+6p)}/y. \tag{C2}$$

Similarly, elimination of μ_B between (28) and (C1) yields

$$[-6pT/(1+6p)] \ln[1 - (1+6p)(1-x)] + T \ln(1-x)$$
$$- \tfrac{1}{2}[(1-p)x^2 + p](\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i) + \tfrac{1}{2}\hat{U}_{AA}^i = \mu_A.$$

Combining this with the corresponding equation for the C phase:

$$T \ln(1-y) - \tfrac{1}{2}y^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c) + \tfrac{1}{2}\hat{U}_{AA}^c + W_A(0) = \mu_A$$

one obtains

$$-W_A(0) = \tfrac{1}{2}\hat{U}_{AA}^c - \tfrac{1}{2}\hat{U}_{AA}^i - \tfrac{1}{2}y^2(\hat{U}_{AA}^c - 2\hat{U}_{AB}^c + \hat{U}_{BB}^c)$$
$$+ \tfrac{1}{2}[(1-p)x^2 + p](\hat{U}_{AA}^i - 2\hat{U}_{AB}^i + \hat{U}_{BB}^i) - T \ln(1-x)/(1-y)$$
$$- [6pT/(1+6p)] \ln[1 - (1+6p)(1-x)]. \tag{C3}$$

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