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Adsorption of square and rectangular plate-like molecules on a planar surface

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A mean-field statistical thermodynamic analysis of monolayer adsorption of rigid square and rectangular plate-like molecules on a homogeneous planar surface is developed. The analysis is simplified by only considering facewise and edgewise modes of adsorption in restricted orthogonal orientations parallel to the surface. The free energy density, adsorbate population distribution and surface spreading pressure are obtained as a function of adsorbate density and compared for square plate molecules using three different sequences of adsorbate molecule placement on the surface to evaluate the configurational degeneracy. It is found that edgewise adsorbed molecules can be anisotropically ordered if the edge length of square and rectangular plate-like molecules exceeds three length units in the absence of anisotropic dispersion interactions. If intermolecular dispersion interactions are present and of sufficient strength, the spreading pressure–density isotherms can exhibit one or two van der Waals loops for square plate molecules with three van der Waals loops possible for rectangular plate adsorbate molecules. The phase transitions for the adsorbed monolayer corresponding to the appearance of these van der Waals loops are discussed.

1. Introduction

Here we develop a statistical thermodynamic analysis of the adsorption of both square and rectangular plate-like molecules on a homogeneous planar surface. Certain aspects of the analysis such as anisotropic surface ordering of adsorbate molecules are probably meaningful for comparison with experimental scanning tunneling microscopy (STM) studies of the packing behaviour of nematogenic molecules such as 4′-*n*-hexyl-4-cyanobiphenyl (6CB) adsorbed on pyrolytic graphite surfaces [1]. The present analysis may also have relevance to the contemplated development of single molecule switching devices which may ultimately involve STM and surface adsorbed molecules which alter their orientation relative to the surface in response to localized changes in applied potential of the scanning tip [2].

The square plate (rectangular plate) molecules are assumed to consist of $r^2 \equiv r \times r \times 1$ ($c \equiv a \times b \times 1$; $a > b$) cubic segments with each face consisting of r^2 (c) segments while the edges possess r segments (either a or b segments). In general an adsorbed plate-like molecule may assume an infinite number of orientations relative to the surface. However an enormous simplification of the configurational aspects of the problem results when the possible modes of adsorption are restricted to facewise (F) and edgewise (E), and the molecular edges parallel to the surface plane for each mode of adsorption are restricted to two mutually orthogonal orientations. In the facewise

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mode of adsorption an adsorbed square (rectangular) molecule is assumed to lie flat on the surface and occupy r^2 ($c \equiv a \times b$) contiguous square surface adsorption sites of unit surface area. In the edgewise mode(s) of adsorption, square (rectangular) plate-like molecules occupy r (a or b) contiguous surface sites directed along either of two preselected mutually orthogonal directions 1 and 2 which are parallel to the surface plane. Thus at any given adsorbate density, the adsorbed molecules are distributed among these possible modes of adsorption. The imposed orientational restrictions simplify the enumeration of the number of accessible non-overlapping configurations and permit the application of the lattice statistics developed by DiMarzio [3, 4] for rigid rod-like molecules and extended by Herzfeld [5] to plate-like and block-like molecules. The assumption of facewise and edgewise adsorption in restricted orientations is consistent with the experimentally observed STM images of the aromatic cores of 6CB adsorbed on graphite [1].

In § 2 we determine the configurational entropy of an adsorbed monolayer of square plate-like molecules using DiMarzio–Herzfeld lattice statistics. The configurational entropy determined in this manner is dependent upon the sequence of placement of the facewise and edgewise adsorbed molecules. Three different orders of placement are explicitly considered and the corresponding configurational entropies are obtained and compared.

In § 3 we determine and compare the statistical thermodynamic behaviour of an adsorbed monolayer of square plate molecules using the three different configurational entropies obtained in § 2. In particular free energy minimization generates the equilibrium molecular population distributions among the possible modes of adsorption as a function of molecular density and temperature for each sequence of adsorbate placement. Also the entropic contribution to the surface spreading pressure is determined and compared for each placement method.

Facewise adsorption is energetically favoured for chemically homogeneous plate-like molecules at low surface coverages when strong attractive surface–molecular segment interactions prevail. However, as the adsorbate density increases, competition for the available surface sites becomes more severe and an enhanced tendency for edgewise molecular adsorption occurs to facilitate packing. Anisotropic ordering of edgewise adsorbed square plate molecules becomes possible provided the edge length is sufficiently large. In the absence of anisotropic dispersion interactions, the appearance of an anisotropically ordered adsorbed phase is entropically driven and theoretical predictions are dependent on the assumed order of placement as indicated in § 3.

Comparison of the statistical thermodynamic behaviours made in § 3 indicate that all placement sequences lead to the same general trends. As a result we conclude § 3 by considering only the case where facewise adsorbed molecules are completely introduced before edgewise adsorbate is accommodated onto the surface. Spreading pressure–density isotherms are determined including pairwise additive intermolecular dispersion interactions in the mean-field approximation [6, 7]. Dispersion interactions which are generally dependent upon the modes of adsorption of the interacting molecular pair can generate one or more van der Waals loops in the spreading pressure–density isotherms [7, 8]. The appearance of such loops suggests the possible occurrences of several distinct types of phase transitions for the adsorbed monolayer and their nature is discussed in § 3.

In § 4 a brief derivation and discussion of the statistical thermodynamic behaviour of adsorbed rectangular plate-like molecules is provided. In particular the adsorption population distribution and the spreading pressure–density isotherm for $3 \times 2 \times 1$

rectangular plate molecules are explicitly determined under conditions where the dispersion interactions are sufficiently attractive to generate three van der Waals loops.

Finally in § 5 possible extensions and applications of the present analysis are suggested.

2. Derivation of the configurational degeneracy for an adsorbed monolayer of square plate-like molecules considering three different methods of molecular placement

Here we consider an adsorbed monolayer of N identical square plate molecules of edgelength, r, adsorbed on a homogeneous planar surface consisting of A equivalent square adsorption sites each of unit area. The analysis is limited to strongly adsorbed monolayers, hence multilayer contributions to the adsorption from molecules hovering above but lacking direct contact with the surface are excluded. It is assumed that there are two possible modes of adsorption, facewise and edgewise, and that all molecular edges are restricted to alignment along either of two mutually orthogonal orientations, 1 and 2, parallel to the surface plane. We let N_c represent the number of facewise adsorbed molecules and N_{ir} $(i=1,2)$ the number of edgewise adsorbed molecules having their edge aligned along direction i. Clearly $N=N_c+N_{1r}+N_{2r}$ and in terms of the total surface density

$$n \equiv N/A = n_c + n_{1r} + n_{2r}, \tag{1}$$

where $0 \leqslant rn \leqslant 1$ and n_c, n_{ir} $(i=1,2)$ represent the individual population densities for each adsorption mode. The fractional surface coverage, θ, is

$$\theta = r^2 n_c + r(n_{1r}+n_{2r}). \tag{2}$$

Consistent with a chemically homogeneous adsorption surface and adsorbate, we assume that each adsorbed molecular segment experiences an attractive surface adhesion energy ϵ $(\epsilon<0)$. Thus at sufficiently low coverages facewise adsorption is energetically favourable, however, as n increases the availability of surface sites diminishes and there is an enhanced tendency for edgewise adsorption to facilitate packing since only single segment—adsorption site occupancy is allowed.

The configurational component of the partition function for the adsorbed monolayer is determined by direct application of the lattice statistics developed by DiMarzio [3, 4] and later extended by Herzfeld [5] to systems of rod-like and plate-like molecules placed on to a regular cubic or square lattice in restricted, mutually orthogonal orientations. The configurational partition function, Ω, is obtained by estimating the number of distinguishable ways of placing the facewise and edgewise adsorbed molecules on the square planar surface such that only one molecular segment occupies an individual adsorption site. We proceed by placing the adsorbed molecules individually on to the surface lattice in such a manner that only single occupancy of an adsorption site by a molecular segment is allowed. The final result for Ω, however, does depend upon the order of placement of facewise and edgewise adsorbed molecules and there is no *a priori* preferred placement sequence.

In this section we shall investigate three different orders of placement and determine the corresponding configurational partition function for each placement sequence and then compare the resulting predicted statistical thermodynamic behaviours. We shall determine $\Omega=\Omega_F$ employing a sequence of placement where all facewise adsorbed molecules are initially introduced on to the surface before all edgewise adsorbed molecules are placed. We shall also determine $\Omega \equiv \Omega_E$ by placing all edgewise adsorbed molecules initially onto the surface before sequentially placing the facewise adsorbed molecules. Finally we shall also obtain $\Omega \equiv \Omega_I$ for an intermediate sequence of adsorbed molecule placement where the probability that a given molecule in the sequence is facewise or edgewise adsorbed is in direct proportion to their respective bulk phase compositions N_c/N, N_{1r}/N or N_{2r}/N.

The number of distinguishable ways of successfully placing N_c facewise absorbed molecules on to the planar surface is given by

$$Y_F \equiv [(N_c)!]^{-1} \prod_{m=0}^{N_c-1} v_{m+1}, \tag{3}$$

where v_{m+1} represents the number of permissible ways of placing the $m+1$th facewise adsorbed molecule on to the surface given that m facewise adsorbed square plate molecules each with $c=r^2$ segments already have been placed successfully. Explicitly

$$v_{m+1}=(A-cm)^c/(A-cm+rm)^{r-1}(A-cm+rm)^{r-1}(A-(c-1)m)^{(r-1)^2} \quad (c\equiv r^2). \tag{4}$$

This result can be deduced as follows. The first segment of the $m+1$th molecule to be placed on the surface is a corner segment (of a square) and there are $A-cm$ available unoccupied sites. The $(r-1)$ edge segments emanating in mutually orthogonal directions 1 and 2 from the corner segment are then sequentially placed on the surface. The probability that there are $r-1$ contiguous empty sites emanating along directions 1 and 2 from the now occupied corner segment is $(\{[A-cm]/[A-cm+rm]\}^{r-1})^2$ where $A-cm$ represents the total number of available unoccupied sites and rm is the number of molecular segments belonging to already successfully placed facewise adsorbed molecules which can interfere with the successive placement of $r-1$ segments along either direction 1 or 2. Finally the probability of successfully placing the remaining $(r-1)^2$ segments of the $m+1$th molecule given that a corner segment and the $2(r-1)$ segments along mutually orthogonal edges emanating from the corner segment have been introduced is $[(A-cm)/(A-(c-1)m)]^{(r-1)^2}$, since only one corner segment of the preceding m molecules on the surface can interfere with the placement of the remaining $(r-1)^2$ segments of the $m+1$th facewise adsorbed molecule.

The product

$$\prod_{m=0}^{N_c-1} v_{m+1},$$

can be evaluated easily by standard methods [3, 4, 9] and equations (3) and (4) give

$$Y_F=(N_c!)^{-1}(A!/(A-r^2N_c)!)[(A-(r^2-1)N_c)!/A!]^{(r-1)/(r+1)}[(A-r(r-1)N_c)!/A!]^{2/r}. \tag{5}$$

This result has been obtained by Shih and Alben [10].

Once the N_c facewise adsorbed molecules have been introduced successfully onto the surface then N_{1r} and N_{2r} edgewise molecules oriented along directions 1 and 2 can be introduced. The familiar DiMarzio lattice statistics [3] for rod-like molecules restricted to mutually orthogonal directions can be applied directly to obtain the total number of possible distinguishable configurations of the adsorbed molecules:

$$\Omega_F = Y_F(N_{1r}!)^{-1}(N_{2r}!)^{-1} \prod_{m=0}^{N_{2r}-1} (A-r^2N_c-rN_{1r}-mr)^r/(A-r^2N_c-rN_{1r} -mr+rN_c+rN_{1r}+m)^{r-1} \times \prod_{k=0}^{N_{1r}-1} (A-r^2N_c-kr)^r/(A-r^2N_c-kr+rN_c+r)^{r-1}.$$

Employing

$$\prod_{k=0}^{N_{1r}-1} (A-r^2N_c-kr)^r/(A-r(r-1)N_c-k(r-1))^{r-1}=(A-r^2N_c)!(A-r(r-1)N_c$$
$$-(r-1)N_{1r})! \times \{(A-r^2N_c-rN_{1r})!(A-r(r-1)N_c)!\}^{-1},$$

and

$$\prod_{m=0}^{N_{2r}-1} (A-r^2N_c-rN_{1r}-mr)^r/(A-r(r-1)N_c-m(r-1))^{r-1}=(A-r^2N_c-rN_{1r})!$$
$$\times (A-r(r-1)N_c-(r-1)N_{2r})! \times \{(A-r^2N_c-r(N_{1r}+N_{2r}))!(A-r(r-1)N_c)!\}^{-1},$$

and equation (5) gives

$$\Omega_{\mathrm{F}}=\Omega_{\mathrm{F}}(N_c, N_{1r}, N_{2r}, A)=(N_c!\, N_{1r}!\, N_{2r}!)^{-1}(A!/(A(1-\theta))!)\left[\prod_{i=1}^{2} (A-r(r-1)N_c\right.$$
$$\left.-(r-1)N_{ir})!\right](A!)^{-2} \times \{(A-(r^2-1)N_c)!/A!\}^{(r-1)/r+1}$$
$$\times \{(A-r(r-1)N_c)!/A!\}^{-2+2/r}. \tag{6}$$

If however, the edgewise adsorbed square plate molecules are completely introduced on to the surface before the facewise adsorbed molecules, then the number of distinguishable ways of placing the edgewise adsorbed molecules is

$$Y_{\mathrm{E}}=[A!(A-rN_{1r}-rN_{2r})!]^{-1} \prod_{i=1}^{2} \{(A-(r-1)N_{ir})!/N_{ir}!\}, \tag{7}$$

which follows from equation (6) by setting $N_c=0$. The number of distinguishable ways of then placing N_c facewise adsorbed square plate-like molecules onto the surface given that $N_r \equiv N_{1r}+N_{2r}$ edgewise molecules have already been introduced is

$$Z_{\mathrm{E}}=(N_c!)^{-1} \prod_{m=0}^{N_c-1} g_{m+1},$$

where

$$g_{m+1}=(A-rN_r-r^2m)^{r^2}\left(\prod_{i=1}^{2} (A-(r-1)N_{ir}-r(r-1)m)^{r-1}\right)^{-1}$$
$$\times (A-(r-1)N_r-(r^2-1)m)^{-(r-1)^2}, \tag{8}$$

represents the number of ways of placing the $m+1$th facewise adsorbed molecule onto the lattice given that $N_r \equiv N_{1r}+N_{2r}$ edgewise and m facewise adsorbed molecules have been introduced. The factor $(A-rN_r-r^2m)$ represents the number of empty sites available for the placement of a corner segment of the $m+1$th molecule. The factors

$$(A-rN_r-r^2m)^{r-1}/[A-rN_r-r^2m+N_{1r}+rN_{2r}+rm]^{r-1},$$

and

$$(A-rN_r-r^2m)^{r-1}/[A-rN_r-r^2m+rN_{1r}+N_{2r}+rm]^{r-1},$$

respectively, represent the probabilities of finding $r-1$ empty contiguous lattice sites directed along lines parallel to directions 1 and 2, respectively, and emanating from the initially placed corner segment of the $m+1$th facewise adsorbed molecule. The factors

$$A-rN_r-r^2m+N_{1r}+rN_{2r}+rm \equiv A-(r-1)N_{1r}-r(r-1)m,$$

and

$$A-rN_r-r^2m+rN_{1r}+N_{2r}+rm \equiv A-(r-1)N_{2r}-r(r-1)m,$$

represent the sums of the number of empty sites and number of segments of previously placed molecules, along directions 1 and 2, respectively, which can interfere with the placement of an edge segment of the $m+1$th facewise adsorbed molecule. Finally the factor $(A-rN_r-r^2m)^{(r-1)^2}/(A-(r-1)N_r-(r^2-1)m)^{(r-1)^2}$ represents the probability of placing the remaining $(r-1)^2$ segments of the $m+1$th facewise adsorbed molecule after a corner segment and $2(r-1)$ edge segments along directions 1 and 2 have been placed successfully.

Explicit evaluation of Z_{E} gives

$$Z_{\mathrm{E}}=(N_c!)^{-1}(A-rN_r)!((A-(1-\theta))!)^{-1}[(A-(r-1)N_r-(r^2-1)N_c)!/$$
$$(A-(r-1)N_r)!]^{(r-1)/(r+1)}\prod_{j=1}^{2}[(A-(r-1)N_{jr}-r(r-1)N_c)!/(A-(r-1)N_{jr})!]^{1/r}, \quad (9)$$

and from equations (7) and (9)

$$\begin{aligned}\Omega_{\mathrm{E}}\equiv\Omega_{\mathrm{E}}(N_c,N_{1r},N_{2r},A)=&(N_{1r}!\,N_{2r}!\,N_c!(A(1-\theta))!A!)^{-1}\\ &\times[(A-(r-1)N_r-(r^2-1)N_c)!/(A-(r-1)N_r)!]^{(r-1)/(r+1)}\\ &\times\prod_{j=1}^{2}\{[(A-(r-1)N_{jr}-r(r-1)N_c)!]^{r^{-1}}\\ &\times[(A-(r-1)N_{jr})!]^{r^{-1}-1}\},\end{aligned} \quad (10)$$

represents the total number of distinguishable ways of placing N_{1r} and N_{2r} edgewise and N_c facewise adsorbed molecules on a square lattice of A equivalent adsorption sites.

Another method for placing the adsorbate molecules on the surface involves introducing them sequentially in either facewise or edgewise modes in direct proportion to their final bulk adsorbed phase composition. Let ϕ $(0\leqslant\phi\leqslant1)$ represent the fraction of edgewise adsorbed molecules irrespective of their surface orientation and the order parameter, S $(-1\leqslant S\leqslant1)$ represent the relative difference $(N_{1r}-N_{2r})/(N_{1r}+N_{2r})$, in the number of edgewise adsorbed square plate-like molecules aligned along directions 1 and 2, then $N_c=N(1-\phi)$, $N_{1r}=N\phi(1+S)/2$ and $N_{2r}=N\phi(1-S)/2$, respectively, represent the number of facewise and edgewise adsorbed molecules aligned along directions 1 and 2. It is assumed that after m molecules $(0\leqslant m\leqslant N)$ have been placed on the surface that $m(1-\phi)$ facewise and $m\phi(1+S)/2$ and $m\phi(1-S)/2$ edgewise adsorbed molecules along directions 1 and 2, respectively, are present. Hence the number of ways of placing the $m+1$th molecule which has probabilities $1-\phi$, $\phi(1+S)/2$ or $\phi(1-S)/2$ of being in the corresponding allowed facewise and edgewise modes is

$$\begin{aligned}h_{m+1}=&(A-r^2(1-\phi)m-r\phi m)^{r^2(1-\phi)+r\phi(1+S)/2+r\phi(1-S)/2}\\ &\times(A-r^2(1-\phi)m-r\phi m+r(1-\phi)m+\tfrac{1}{2}r\phi(1-S)m\\ &+\tfrac{1}{2}\phi(1+S)m)^{-(r-1)(1-\phi+1/2\phi(1+S))}\\ &\times(A-r^2(1-\phi)m-r\phi m+r(1-\phi)m+\tfrac{1}{2}r\phi(1+S)m\\ &+\tfrac{1}{2}\phi(1-S)m)^{-(r-1)(1-\phi+1/2\phi(1-S))}\\ &\times(A-r^2(1-\phi)m-r\phi m+(1-\phi)m+\phi m)^{-(r-1)^2(1-\phi)}.\end{aligned} \quad (11)$$

The justification for the individual factors in this expression should be apparent from the previous discussion accompanying the development of the expressions for Ω_F and Ω_E (see equations (4) and (8)).

The total number of distinguishable ways of introducing $N_c = N(1-\phi)$ facewise and $N_{1r} = N\phi(1+S)/2$ and $N_{2r} = N\phi(1-S)/2$ edgewise adsorbed molecules aligned along 1 and 2 is

$$\begin{aligned}\Omega_I = \Omega_I(N,\phi,S,A) &= ((N(1-\phi))!(N\phi(1+S)/2)!(N\phi(1-S)/2)!)^{-1}\prod_{m=0}^{N-1} h_{m+1}\\ &= ((N(1-\phi))!(N\phi(1+S)/2)!(N\phi(1-S)/2)!)^{-1}[A!/(A(1-\theta))!]\\ &\quad\times[(A-r(r-1)(1-\phi)N-(r-1)\phi N(1+S)/2)!/A!]^{[1-\phi+\phi(1+S)/2][r(1-\phi)+\phi(1+S)/2]^{-1}}\\ &\quad\times[(A-r(r-1)(1-\phi)N-(r-1)\phi N(1-S)/2)!/A!]^{[1-\phi+\phi(1-S)/2][r(1-\phi)+\phi(1-S)/2]^{-1}}\\ &\quad\times[(A-(r^2-1)N+r(r-1)\phi N)!/A!]^{(r-1)(1-\phi)(1+r(1-\phi))^{-1}}. \qquad (12)\end{aligned}$$

Clearly when $S=0$, $N_{1r}=N_{2r}=N\phi/2$ and the edgewise adsorbate is isotropically distributed between the allowed orientations.

In the limit $N_{1r}\to 0$, $N_{2r}\to 0$ (or $\phi\to 0$) $\Omega_F \Rightarrow \Omega_E \Rightarrow \Omega_I = (N!)^{-1}(A!/(A-r^2N)!)((A-r(r-1)N)!/A!)^{2/r}((A-(r^2-1)N)!/A!)^{(r-1)/(r+1)}$ and also in the limit $N_c\to 0$ ($\phi\to 1$) $\Omega_F \Rightarrow \Omega_E \Rightarrow \Omega_I = (N_{1r}!N_{2r}!)^{-1}(A-(r-1)N_{1r})!(A-(r-1)N_{2r})!/A!(A-rN_r)!$ which is the DiMarzio result for rod-like molecules restricted to two orthogonal orientations. In general, however, for equal values of A, N, ϕ and S the configurational degeneracies Ω_F, Ω_E and Ω_I are different and corresponding variations in the predicted statistical thermodynamic behaviours are anticipated and is the subject of investigation in the next section.

3. Statistical thermodynamic behaviour of square plate-like molecules adsorbed on a homogeneous planar surface

Here we investigate and compare the statistical thermodynamic behaviour of an adsorbed monolayer of square plate-like molecules formed on a chemically homogeneous planar surface. The configurational degeneracies, Ω_α (α = F, E, I) and hence configurational entropies, $S_\alpha \equiv k_B \ln \Omega_\alpha$, depend upon the assumed order of adsorbate placement and since the Ω_α (α = F, E, I) in general differ, differences in the statistical thermodynamic behaviours are anticipated.

For simplicity the internal energy, βE, in units of $\beta^{-1} \equiv k_B T$ is assumed to be independent of the order of adsorbate placement and given by

$$\beta E = -N[r^2(1-\phi)\beta|\epsilon| + r\phi\beta|\epsilon|] - (Nn/2)\{\beta w_1 + \beta(w_1-w_2)[3\phi^2 - 4\phi + \phi^2 S^2]/2\}, \qquad (13)$$

where $|\epsilon|$ is the absolute value of the molecular segment–surface adhesion energy and w_1 ($w_1 \geqslant 0$) and w_2 ($w_2 \geqslant 0$) are, respectively, intermolecular pair dispersion interaction energies averaged over all internuclear separations between any pair of molecules in the same and different states of surface adsorption [7, 8]. If $w_1 = w_2$ the dispersion interaction energy reduces to $-Nn\beta w_1/2$.

The Helmholtz free energy density in units of $\beta^{-1} \equiv k_B T$ for the αth mode of adsorbate placement is

$$\beta f_\alpha \equiv \beta F_\alpha/A = \beta E/A - \ln \Omega_\alpha/A, \quad \alpha \equiv \text{F, E, I}. \qquad (14)$$

Employing equations (6), (10), (12) and (13) and Stirling's approximation generates the following explicit results for the surface free energy densities

$$\begin{aligned}\beta f_{\mathrm{F}}=&\,p+q_{+}+q_{-}+\beta e+2(1-r^{-1})(1-r(r-1)n(1-\phi))\ln(1-r(r-1)n(1-\phi))\\&-[(r-1)/(r+1)][1-(r^{2}-1)n(1-\phi)]\ln[1-(r^{2}-1)n(1-\phi)],\end{aligned}\tag{15}$$

$$\begin{aligned}\beta f_{\mathrm{E}}=&\,p+(q_{+}+q_{-})/r+\beta e+(r-1)(r+1)^{-1}(1-(r-1)n\phi)\ln(1-(r-1)n\phi)\\&-(r-1)(r+1)^{-1}(1-(r-1)n\phi-(r^{2}-1)n(1-\phi))\ln[1-(r-1)n\phi\\&-(r^{2}-1)n(1-\phi)]-(1-r^{-1})\{(1-(r-1)n\phi(1+S)/2)\ln(1-(r-1)n\phi(1+S)/2)\\&+(1-(r-1)n\phi(1-S)/2)\ln(1-(r-1)n\phi(1-S)/2)\},\end{aligned}\tag{16}$$

and

$$\begin{aligned}\beta f_{\mathrm{I}}=&\,p+(1-\phi+\phi(1+S)/2)(r(1-\phi)+\phi(1+S)/2)^{-1}q_{+}+(1-\phi+\phi(1-S)/2)\\&\times(r(1-\phi)+\phi(1-S)/2)^{-1}q_{-}+\beta e-(r-1)(1-\phi)(1+r(1-\phi))^{-1}[1-(r-1)n\\&\times(1+r(1-\phi))]\ln[1-(r-1)n(1+r(1-\phi))],\end{aligned}\tag{17}$$

where

$$\begin{aligned}p\equiv p(n,\phi,S)=&\,n(1-\phi)\ln(n(1-\phi))+[n\phi(1+S)/2]\ln[n\phi(1+S)/2]\\&+[n\phi(1-S)/2]\ln[n\phi(1-S)/2]+(1-r^{2}n+r(r-1)n\phi)\\&\times\ln(1-r^{2}n+r(r-1)n\phi),\end{aligned}\tag{18}$$

$$\begin{aligned}q_{\pm}\equiv q_{\pm}(n,\phi,S)=&-[1-(r-1)n[r(1-\phi)+\phi(1\pm S)/2]]\ln[1-(r-1)n\\&\times[r(1-\phi)+\phi(1\pm S)/2]],\end{aligned}\tag{19}$$

with

$$\begin{aligned}q_{+}(S=0)=q_{-}(S=0)\equiv q=&-[1-(r-1)n(r(1-\phi)+\phi/2)]\ln[1-(r-1)n\\&(r(1-\phi)+\phi/2)]\end{aligned}$$

and

$$\beta e\equiv\beta E/A=-n[r^{2}(1-\phi)+r\phi]\beta|\epsilon|-(n^{2}/2)\{\beta w_{1}+\beta(w_{1}-w_{2})[3\phi^{2}-4\phi+\phi^{2}S^{2}]/2\}.\tag{20}$$

When $r=1\,\beta f_{\mathrm{F}}=\beta f_{\mathrm{E}}=\beta f_{\mathrm{I}}=p+q_{+}+q_{-}+\beta e=n\ln n+(1-n)\ln(1-n)-n\beta|\epsilon|-n^{2}\beta w_{1}/2$ ($\phi=S=0$ when $r=1$). It is also easily verified that $\beta f_{\mathrm{F}}\Rightarrow\beta f_{\mathrm{E}}\Rightarrow\beta f_{\mathrm{I}}$ in the limits $n\rightarrow 0$, $\phi\rightarrow 0$, $S=0$ and as $n\rightarrow 1$, $\phi\rightarrow 1$.

For given values of n and $\beta^{-1}=k_{\mathrm{B}}T$, the values of ϕ and S are determined by the requirement that they minimize the corresponding free energy densities. The relationships which evolve from these minimization conditions are from equation (15)

$$\begin{aligned}\partial\beta f_{\mathrm{F}}/\partial\phi=0=&\,t+\beta n^{-1}\partial e/\partial\phi+2(r-1)^{2}\ln[1-r(r-1)n(1-\phi)]\\&-(r-1)^{2}\ln[1-(r^{2}-1)n(1-\phi)]-(r-1)(r-(1+S)/2)\\&\times\ln[1-r(r-1)n(1-\phi)-(r-1)n\phi(1+S)/2]-(r-1)(r-(1-S)/2)\\&\times\ln[1-r(r-1)n(1-\phi)-(r-1)n\phi(1-S)/2],\end{aligned}\tag{21}$$

and

$$\begin{aligned}\partial\beta f_{\mathrm{F}}/\partial S=0=&\ln[(1+S)/(1-S)]+(r-1)\ln[1-r(r-1)n(1-\phi)\\&-(r-1)n\phi(1+S)/2]-(r-1)\ln[1-r(r-1)n(1-\phi)\\&-(r-1)n\phi(1-S)/2]-n\phi\beta(w_1-w_2)S,\end{aligned}\tag{22}$$

$$\begin{aligned}\partial\beta f_{\mathrm{E}}/\partial\phi=0=&t+\beta n^{-1}\partial e/\partial\phi-(r-1)^2(r+1)^{-1}\ln(1-(r-1)n\phi)\\&-r(r-1)^2(r+1)^{-1}\ln[1-(r-1)n\phi-(r^2-1)n(1-\phi)]\\&+((r-1)^2/2r)\{(1+S)\ln[1-(r-1)n\phi(1+S)/2]+(1-S)\\&\times\ln[1-(r-1)n\phi(1-S)/2]\}+(r^{-1}-1)\{(r-(1+S)/2)\\&\times\ln[1-r(r-1)n(1-\phi)-(r-1)n\phi(1+S)/2]\\&+(r-(1-S)/2)\ln[1-r(r-1)n(1-\phi)\\&-(r-1)n\phi(1-S)/2]\},\end{aligned}\tag{23}$$

and

$$\begin{aligned}\partial\beta f_{\mathrm{E}}/\partial S=0=&\ln[(1+S)/(1-S)]+(r-1)^2r^{-1}\ln[(1-(r-1)\\&\times n\phi(1+S)/2)/(1-(r-1)n\phi(1-S)/2)]+(1-r^{-1})\\&\times\ln[(1-r(r-1)n(1-\phi)-(r-1)n\phi(1+S)/2)/(1-r(r-1)n(1-\phi)\\&-(r-1)n\phi(1-S)/2)]-n\phi S\beta(w_1-w_2),\end{aligned}\tag{24}$$

and

$$\begin{aligned}\partial\beta f_{\mathrm{I}}/\partial\phi=0=&t+\beta n^{-1}\partial e/\partial\phi+(r-1)[n^{-1}(1+r(1-\phi))^{-2}\\&-(r-1)]\ln[1-(r-1)n(1+r(1-\phi))]-(1/2)(r-1)[(1+S)n^{-1}\\&\times[r(1-\phi)+\phi(1+S)/2]^{-2}+1-S]\ln[1-(r-1)n[r(1-\phi)\\&+\phi(1+S)/2]]-(1/2)(r-1)[(1-S)n^{-1}[r(1-\phi)\\&+\phi(1-S)/2]^{-2}+1+S]\ln[1-(r-1)n[r(1-\phi)\\&+\phi(1-S)/2]]+r(r-1)(2-\phi)(1+r(1-\phi))^{-1}\\&-(r-1)(1-\phi+\phi(1+S)/2)(r-(1+S)/2)\{r(1-\phi)+\phi(1+S)/2\}^{-1}\\&-(r-1)(1-\phi+\phi(1-S)/2)(r-(1-S)/2)\{r(1-\phi)+\phi(1-S)/2\}^{-1},\end{aligned}\tag{25}$$

and

$$\begin{aligned}\partial\beta f_{\mathrm{I}}/\partial S=0=&\ln[(1+S)/(1-S)]+(r-1)^2\phi(1-\phi)S\{(r(1-\phi)+\phi/2)^2-\phi^2S^2/4\}^{-1}\\&+(r-1)[1-n^{-1}(1-\phi)(r(1-\phi)+\phi(1+S)/2)^{-2}]\ln[1-(r-1)\\&\times n[r(1-\phi)+\phi(1+S)/2]]-(r-1)[1-n^{-1}(1-\phi)(r(1-\phi)\\&+\phi(1-S)/2)^{-2}]\ln[1-(r-1)n[r(1-\phi)+\phi(1-S)/2]]\\&-n\phi S\beta(w_1-w_2),\end{aligned}\tag{26}$$

where

$$\begin{aligned}t\equiv t(n,\phi,S)=&-\ln(1-\phi)+(1/2)(1+S)\ln[\phi(1+S)/2]+(1/2)(1-S)\\&\times\ln[\phi(1-S)/2]+r(r-1)\ln(1-r^2n+r(r-1)n\phi),\end{aligned}\tag{27}$$

and

$$\beta n^{-1}\partial e/\partial\phi \equiv r(r-1)\beta|\varepsilon| - n(3\phi/2-1)\beta(w_1-w_2) - n\phi S^2\beta(w_1-w_2)/2. \qquad (28)$$

It can be verified easily that $S=0$ always satisfies equations (22), (24) and (26), and these solutions correspond to isotropic edgewise adsorption. In the absence of anisotropic dispersion interactions (i.e. $\beta(w_1-w_2)=0$), the appearance of anisotropic edgewise adsorption requires that $r>3$ [7], where $S\neq 0$ solutions become possible for equations (22), (24) and (26) at sufficiently large densities n, $r^{-1}\geqslant n>r^{-2}$. Also the conditions $\partial^2\beta f_\alpha/\partial\phi^2>0$, $\partial^2\beta f_\alpha/\partial S^2>0$ and $(\partial^2\beta f_\alpha/\partial S^2)(\partial^2\beta f_\alpha/\partial\phi^2)-(\partial^2\beta f_\alpha/\partial S\partial\phi)^2>0$ $(\alpha\equiv \mathrm{F,I,E})$ must be satisfied by the solutions, ϕ and S, which satisfy equations (21) and (22) or (23) and (24) or (25) and (26) in order that the corresponding βf_α represent minima.

In the limit of strong adsorption ($\beta\epsilon\ll -1$), $r^2n(1-\phi)+rn\phi\simeq 1$ or $\phi\simeq(nr^2-1)/(r(r-1)n)$ and equations (22), (24) and (26) can be solved directly for S as a function of prescribed values of r, n ($n\geqslant r^{-2}$) and $\beta(w_1-w_2)$. Some examples of the $S-(rn)$ dependence calculated from equations (22), (24) and (26) appear in figure 1 for $r=4$ and $r=5$ and $\beta(w_1-w_2)=0$ in the full coverage limit. An anisotropic $S\neq 0$ solution appears for a given r at lower densities for the $\alpha=\mathrm{F}$ case where the facewise adsorbed molecules are introduced first on to the lattice. This perhaps suggests that initial placement of the facewise adsorbate may bias anisotropic ordering of the edgewise adsorbate at lower densities due to the greater depletion in the accessible surface area which accompanies

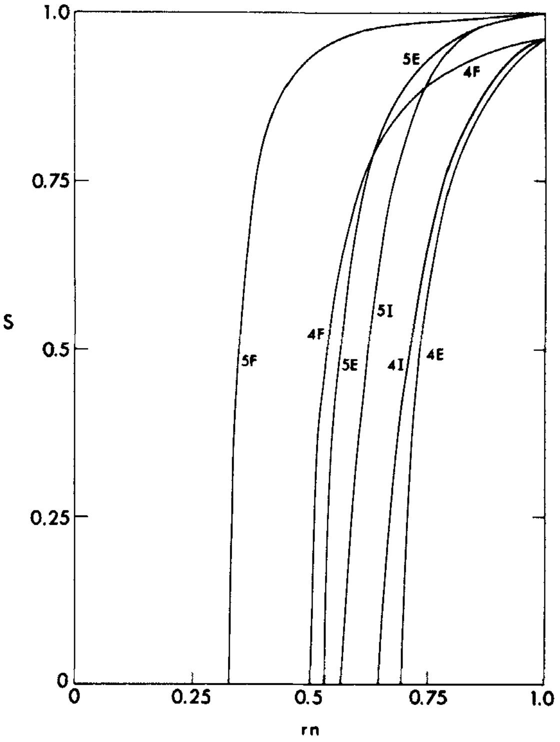

Figure 1. $S-rn$ curves evaluated from equations (22), (24) and (26) in the full coverage limit. The curves labelled 4α $\alpha=\mathrm{F}$, I, E and 5α $\alpha=\mathrm{F}$, I, E correspond to adsorbed square plate molecules with $r=4$ and $r=5$.

facewise adsorption. The $S-n$ results determined from equations (24) and (26) ($\alpha = \mathrm{E}$ and $\alpha = \mathrm{I}$) exhibit relatively slight deviation from one another throughout the relevant density range compared to the $\alpha = \mathrm{F}$ case. For every case S exhibits a typical monotonic increase with n. For any given n where anisotropic edgewise adsorption is possible one must compare free energy densities for anisotropic and isotropic edgewise adsorption to ascertain the thermodynamically more stable state of lowest free energy.

When $r \leqslant 3$ and $\beta(w_1 - w_2) = 0$ only isotropic edgewise adsorption is possible for all n ($0 \leqslant n \leqslant 1/r$) and equations (21), (23) and (25) (with $S = 0$ and $\beta(w_1 - w_2) = 0$) can then be solved to obtain ϕ as a function of n for fixed values of r and $\beta|\epsilon|$. The values of ϕ which satisfy these equations for given r, $\beta|\epsilon|$ and n minimize the corresponding free energy density and determine the equilibrium distribution of adsorbed molecules in the facewise and edgewise modes of adsorption. Equations (21), (23) and (25) generally predict a monotonic increase of ϕ with n (r and $\beta|\epsilon|$ fixed) indicating a greater tendency for edgewise adsorption as n increases. Some results of $\phi - n$ calculations obtained from equations (21), (23) and (25) for $r = 2$ and $r = 3$ for various selections of $\beta|\epsilon|$ are presented in figure 2. For the larger values of $\beta|\epsilon|$ employed the strong adsorption limit is approached and $\phi \simeq 0$ for $0 \leqslant n < r^{-2}$, and ϕ increases monotonically with n for $r^{-2} \leqslant n = r^{-1}$. Thus facewise adsorption dominates for $0 \leqslant n \leqslant r^{-2}$ and only for $n > r^{-2}$ does

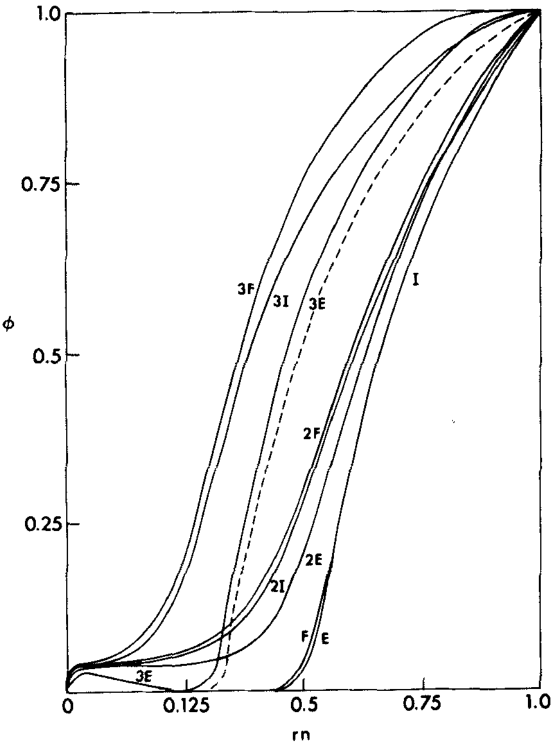

Figure 2. $\phi - rn$ curves evaluated from equations (21), (23) and (25) with $\beta w_1 = \beta(w_1 - w_2) = 0$. The curves labelled F, I, E correspond to $r = 2$ and $\beta\epsilon = -5$ and are virtually indistinguishable. The curves labelled 2α ($\alpha \equiv \mathrm{F}, \mathrm{I}, \mathrm{E}$) correspond to $r = 2$ and $\beta\epsilon = -2$. The curves labelled 3α ($\alpha \equiv \mathrm{F}, \mathrm{I}, \mathrm{E}$) correspond to $r = 3$ and $\beta\epsilon = -2/3$. When $r = 3$ and $\beta\epsilon = -2$ the corresponding $\phi - rn$ curves for $\alpha \equiv \mathrm{F}$, I, E all merge between the curve 3E and the dashed curve.

Table 1.

r	$\beta\lvert\epsilon\rvert$	βf_{F}	βf_{I}	βf_{E}
2	2	$0 \leqslant n < 0{\cdot}1$	$0{\cdot}1 < n < 0{\cdot}375$	$0{\cdot}375 < n \leqslant 0{\cdot}5$
2	5	$0 \leqslant n < 0{\cdot}1$	$0{\cdot}1 < n < 0{\cdot}275$	$0{\cdot}275 < n \leqslant 0{\cdot}5$
3	0·667	$0 \leqslant n < 0{\cdot}05$ $0{\cdot}175 < n \leqslant 0{\cdot}333$	$0{\cdot}05 < n < 0{\cdot}175$	—
3	2	$0 \leqslant n < 0{\cdot}05$	$0{\cdot}05 < n < 0{\cdot}2$	$0{\cdot}2 < n \leqslant 0{\cdot}33$

edgewise adsorption become appreciable in order to facilitate packing. The $\phi-n$ results are rather insensitive to the model free energy density employed (i.e. βf_{F}, βf_{E} or βf_{I}) in the strong adsorption limit although for the smaller values of $\beta|\epsilon|$, greater model variations in the $\phi-n$ dependences appear.

For given values of r, $\beta|\epsilon|$ and n the minimum values of the βf_α ($\alpha=\mathrm{F, E, I}$) can be determined by inserting the values of ϕ which satisfy equations (21), (23) or (25) into the corresponding equations (15), (16) or (17) with $S=0$ and $\beta(w_1-w_2)=0$. A summary of the results of some free energy calculations are listed in table 1 where the lowest free energy and corresponding density range are indicated for the chosen values of r and $\beta|\epsilon|$.

Generally βf_{F} represents the lowest free energy density for all the cases considered in the low density region while βf_{I} represents the lowest free energy for intermediate surface densities where the transition from predominantly facewise to edgewise adsorption occurs. In the high density range where edgewise adsorption dominates, βf_{E} gives the lowest free energy density except for the relatively weak surface adsorption case with $r=3$ and $\beta|\epsilon|=0{\cdot}667$ where βf_{F} actually gives the lowest free energy density. It should be added that for $\beta|\epsilon|\geqslant 2$ the relative differences between the values of βf_{F}, βf_{I} and βf_{E} for any n usually are less than 1 per cent.

The dimensionless spreading pressure multiplied by the unit area per adsorption site in units of $\beta^{-1}=k_{\mathrm{B}}T$, $\beta\Phi_\alpha$, can be determined from the relationship

$$\beta\Phi_\alpha \equiv -\beta f_\alpha + n(\partial\beta f_\alpha/\partial n)_\beta, \quad (\alpha \equiv \mathrm{F, I, E}). \tag{29}$$

Employing equations (15), (16) and (17) in equation (29) leads to the following explicit results:

$$\begin{aligned}\beta\Phi_{\mathrm{F}} = {} & \ln\,[(1-r(r-1)n(1-\phi)-(r-1)n\phi(1+S)/2)(1-r(r-1)n(1-\phi) \\ & -(r-1)n\phi(1-S)/2)]-\ln\,(1-\theta)+2(r^{-1}-1)\ln\,(1-r(r-1)n(1-\phi)) \\ & +(r-1)(r+1)^{-1}\ln\,[1-(r^2-1)n(1-\phi)]-n^2\beta w_1/2 \\ & -n^2\beta(w_1-w_2)[3\phi^2-4\phi+\phi^2S^2]/4,\end{aligned} \tag{30}$$

$$\begin{aligned}\beta\Phi_{\mathrm{I}} = {} & (r-1)(1-\phi)(1+r(1-\phi))^{-1}\ln\,[1-(r^2-1)n+r(r-1)n\phi]-\ln\,(1-\theta) \\ & +[1-\phi+\phi(1+S)/2]\{r(1-\phi)+\phi(1+S)/2\}^{-1}\ln\,[1-r(r-1)n(1-\phi) \\ & -(r-1)n\phi(1+S)/2]+[1-\phi+\phi(1-S)/2]\{r(1-\phi)+\phi(1-S)/2\}^{-1} \\ & \times\ln\,[1-r(r-1)n(1-\phi)-(r-1)n\phi(1-S)/2]-\eta^2\beta w_1/2 \\ & -n^2\beta(w_1-w_2)[3\phi^2-4\phi+\phi^2S^2]/4,\end{aligned} \tag{31}$$

and

$$\begin{aligned}\beta\Phi_{\rm E}={}&(1-r^{-1})\ln[(1-(r-1)n\phi(1+S)/2)(1-(r-1)n\phi(1-S)/2)]-\ln(1-\theta)\\&-n^2\beta w_1/2+(r-1)(r+1)^{-1}\ln[(1-(r-1)n\phi-(r^2-1)n(1-\phi))/(1-(r-1)n\phi)]\\&+r^{-1}\ln[(1-r(r-1)n(1-\phi)-(r-1)n\phi(1+S)/2)(1-r(r-1)n(1-\phi)\\&-(r-1)n\phi(1-S)/2]-n^2\beta(w_1-w_2)[3\phi^2-4\phi+\phi^2S^2]/4.\end{aligned}\qquad(32)$$

Spreading pressure–density curves calculated from equations (30), (31) and (32) for isotropic edgewise adsorption with $\beta(w_1-w_2)=0$ and $\beta w_1=0$ are displayed in figures 3 and 4 for $r=2$, $\beta|\epsilon|=2$, and $\beta|\epsilon|=5$ and $r=3$, $\beta|\epsilon|=0{\cdot}667$ and $\beta|\epsilon|=2$. The differences in the $\beta\Phi_\alpha-n$ $\alpha=\mathrm{F,I,E}$ isotherms predicted for the different models of adsorbate placement become more apparent for $r=3$ as $n>r^{-2}$ and edgewise adsorption becomes significant. At low and very high surface coverages, however, $\beta\Phi_{\rm F}\leftrightarrow\beta\Phi_{\rm I}\leftrightarrow\beta\Phi_{\rm E}$, that is, the $\beta\Phi_\alpha$ are essentially identical for each placement model.

In general, $\beta\Phi_\alpha-n$ $(\alpha\equiv\mathrm{F,I,E})$ isotherms determined for an adsorbed monolayer of square plate-like molecules exhibit the following behaviour in the strong adsorption limit $(\epsilon\ll 0)$. At low densities, $0\leqslant n<r^{-2}$, nearly all the molecules are adsorbed facewise on the surface and behave as a two dimensional adsorbed gas. Condensation of the gas to a two dimensional liquid of facewise adsorbed molecules may occur as the density increases in the range $0\leqslant n<r^{-2}$ if the reduced dispersion interaction energy $-\beta w_1/2$ $(w_1\geqslant 0)$ is sufficiently attractive (i.e. the temperature is low enough).

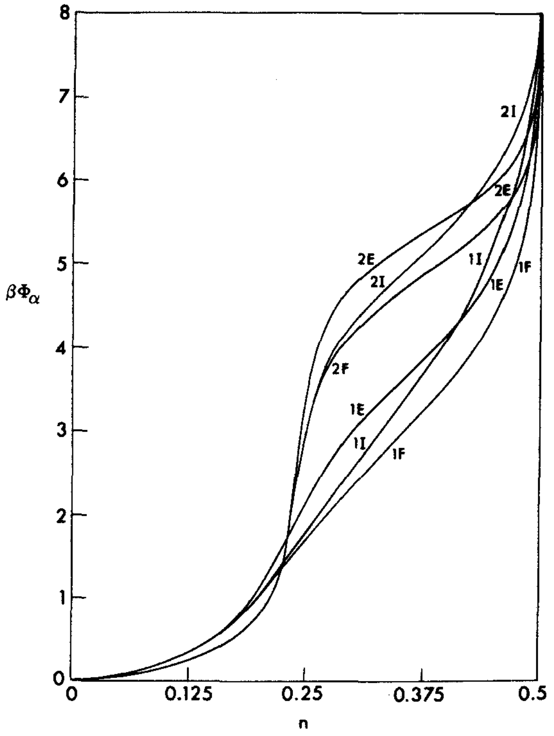

Figure 3. $\beta\Phi_\alpha-n$ isotherms evaluated from equations (30), (31) and (32) for $r=2$, $\beta w_1=\beta(w_1-w_2)=0$. The isotherms labelled 1α and 2α $(\alpha\equiv\mathrm{F,\ I,\ E})$ correspond to $\beta\epsilon=-2$ and $\beta\epsilon=-5$, respectively.

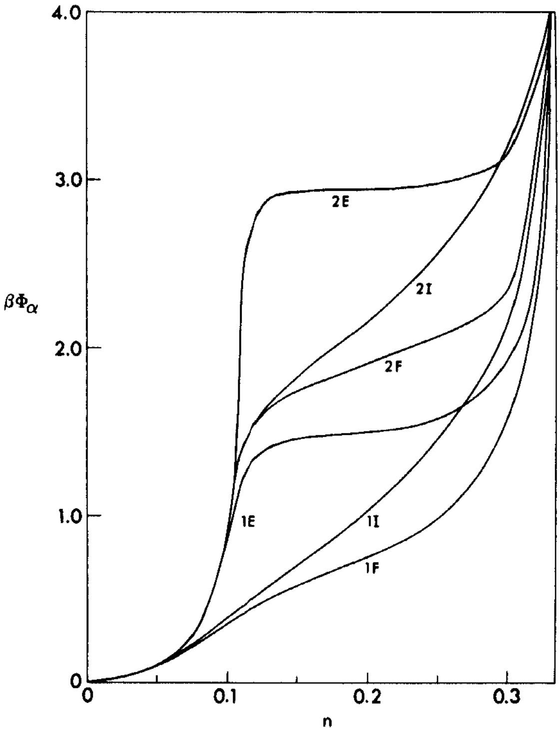

Figure 4. $\beta\Phi_\alpha - n$ isotherms evaluated from equations (30), (31) and (32) for $r=3$, $\beta w_1 = \beta(w_1 - w_2) = 0$. The isotherms labelled 1α and 2α ($\alpha \equiv$ F, I, E) correspond to $\beta\epsilon = -2/3$ and $\beta\epsilon = -2$, respectively.

When n increases in the region $r^{-2} < n \leqslant r^{-1}$ more and more square plate-like molecules must adsorb edgewise to facilitate packing. If attractive intermolecular forces of sufficient strength persist other phase transitions may occur with coexisting surface adsorbed phases possessing both different densities and perhaps order parameters if anisotropic edgewise adsorption is possible. In general the lower density phase possesses the larger fraction of facewise adsorbed molecules (i.e. lower ϕ).

The three placement models utilized here predict the same general trends for the density dependences of ϕ, S and $\beta\Phi_\alpha$ $\alpha =$ F, I, E although there are numerical differences. The intermediate placement model ($\alpha \equiv$ I) is perhaps the most conceptually satisfying since the order of placement of adsorbate molecules is consistent with the bulk composition of the adsorbed monolayer. For sufficiently strong adsorption table 1 reveals that the free energy densities βf_F, βf_I and βf_E each have density ranges over which they represent the lowest free energy and no particular choice of placement order generates the lowest free energy over the entire density range. The predicted free energies, βf_F, βf_I and βf_E differ only slightly (less than one per cent) over the entire density range and probably should not be used as the sole criterion for selecting a preferred order of placement. The statistical thermodynamic results obtained from βf_F are mathematically and computationally simpler than those obtained from βf_I and βf_E. Hence, further aspects of the statistical thermodynamic behaviour of adsorbed square plate and, in §4, rectangular plate-like molecules will be considered using βf_F exclusively.

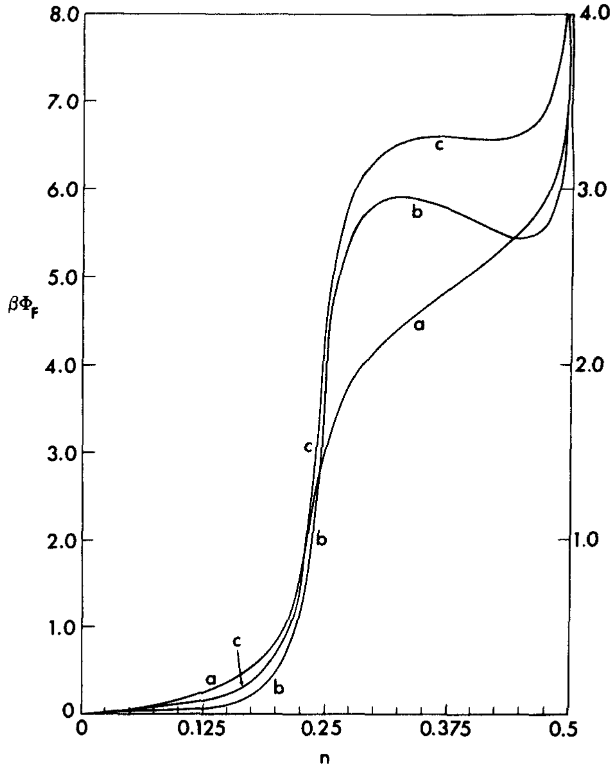

Figure 5. $\beta\Phi_F - n$ isotherms evaluated from equation (30) for $r=2$, $\beta\epsilon = -5$, $\beta(w_1 - w_2) = 0$ and (*a*) $\beta w_1 = 0$, (*b*) $\beta w_1 = 28$ and (*c*) $\beta w_1 = 22$. The left hand ordinate scale gives $\beta\Phi_F$ for case (*a*) while the right hand ordinate scale gives $\beta\Phi_F$ for cases (*b*) and (*c*).

In figure 5 $\beta\Phi_F - n$ isotherms calculated from equation (30) are exhibited for square plate-like molecules with $r=2$, $\beta|\epsilon| = 5$, $\beta(w_1 - w_2) = 0$ and the following dispersion interaction energies $\beta w_1 = 0$, $\beta w_1 = 22$ and $\beta w_1 = 28$. When dispersion interactions are present, condensation between a facewise adsorbed gas and liquid occurs if the temperature is low enough to render $\beta w_1 < \beta_c w_1$ where $\beta_c^{-1} \equiv k_B T_c$ is a critical temperature for adsorbed gas–liquid condensation which depends on r and the corresponding critical density, $n_c \equiv n_c(r)$. If strong adsorption prevails ($\beta\epsilon \ll 0$) then for $0 < n < r^{-2}$, $\phi \sim 0$ and to an excellent approximation equation (30) reduces to

$$\beta\Phi_F = (2/r)\ln[1 - r(r-1)n] + (r-1)(r+1)^{-1}\ln[1-(r^2-1)n]$$
$$-\ln(1-r^2 n) - n^2\beta w_1/2. \qquad (30a)$$

The critical density, n_c, and critical reduced temperature, $(\beta_c w_1)^{-1}$ can be determined by locating the critical point (i.e. point of inflection) by simultaneously solving the equations $\partial\beta\Phi_F/\partial n_c = \partial^2\beta\Phi_F/\partial n_c^2 = 0$. Some results for n_c and $\beta_c w_1/2r^2$ as functions of r are recorded in table 2.

If $\beta w_1 < \beta_c w_1$ a van der Waals loop appears in the $\beta\Phi_F - n$ isotherm not only in the density region $0 < n < r^{-2}$ but also in the density region $r^{-2} < n < r^{-1}$ where edgewise adsorption becomes significant. The appearance of a second van der Waals loop for $r^{-1} > n > r^{-2}$ suggests a phase separation between coexisting adsorbed liquid phases. The higher density phase possesses a larger fraction of edgewise adsorbed molecules

Table 2. Critical constants n_c and $\beta_c w_1/2r^2$ for $\beta\Phi_F-n$ isotherms for facewise adsorbed square plate-like molecules as a function of r.

r	$\beta_c w_1/2r^2$	$n_c r^2$	$\beta_c^* w_1/2r^2$	$n_c^* r$
1	2·00	0·500	—	—
2	3·39	0·356	2·61	0·785
3	4·00	0·313	0·686	0·715
4	4·32	0·294	0·535	0·652
5	4·52	0·285		
6	4·65	0·278		
7	4·75	0·274		
8	4·82	0·271		
9	4·88	0·268		
10	4·92	0·266		
12	4·99	0·264		
20	5·11	0·258		
100	5·29	0·252		
1000	5·33	0·250		

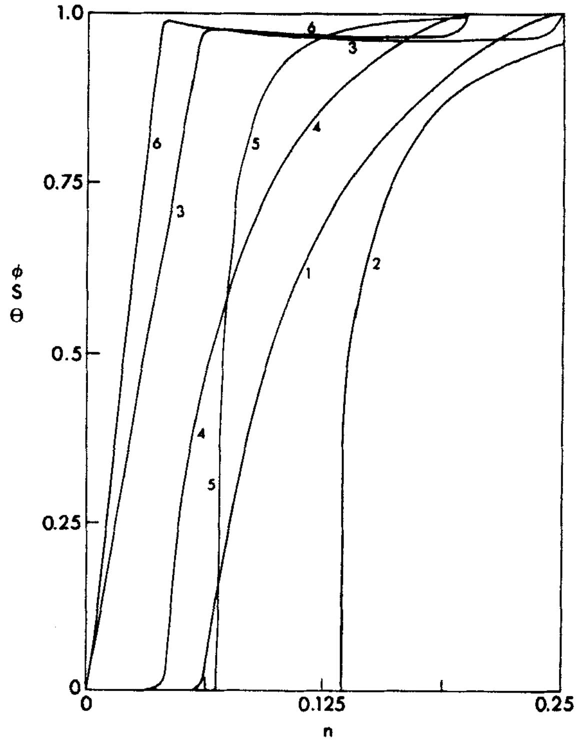

Figure 6. $\phi-n$, $S-n$ and $\theta-n$ curves calculated from equation (21) and (22) for $r=4$ and $r=5$ with $\beta\epsilon=-2$, $\beta w_1=\beta(w_1-w_2)=0$. Curve 1, $\phi-n$, $r=4$; curve 2, $S-n$, $r=4$; curve 3, $\theta-n$, $r=4$; curve 4, $\phi-n$, $r=5$; curve 5, $S-n$, $r=5$; curve 6, $\theta-n$, $r=5$.

while the lower density phase has a larger fraction of facewise adsorbed molecules. For isotropic edgewise adsorption, the critical density, n_c^* and critical reduced temperature, $\beta_c^* w_1$, for this adsorbed liquid–liquid phase separation can be estimated for sufficiently small r ($r < 5$) in the strong adsorption limit by first employing equations (21) and (27) in equation (30) with $S = 0$ to eliminate the $\ln(1-\theta) \equiv \ln(1-r^2n(1-\phi)-rn\phi)$ term in $\beta\Phi_F$ and using $\phi = (r-(rn)^{-1})/(r-1)$ (corresponding to full coverage) and then determining the inflection point in the region $r^{-2} < n < r^{-1}$. The results for n_c^* and $\beta_c^* w_1$ for $r = 2$, 3 and 4 are also listed in table 2. Comparison of $\beta_c w_1$ and $\beta_c^* w_1$ for a given r reveals that $\beta_c w_1 > \beta_c^* w_1$. Hence if $\beta w_1 > \beta_c w_1$ (i.e. $T < T_c$), two van der Waals loops will appear in the $\beta\Phi_F - n$ isotherm, one located in the density range $0 < n \leqslant r^{-2}$ and the other in the range $r^{-2} \leqslant n \leqslant r^{-1}$. This situation is illustrated by curve (*b*) in figure 5. If, however, $\beta_c w_1 > \beta w_1 > \beta_c^* w_1$ only a single van der Waals loop appears in the density region $r^{-2} \leqslant n \leqslant r^{-1}$, and this behaviour is illustrated by curve (*c*) in figure 5. When $\beta < \beta_c^* < \beta_c$ (i.e. $T > T_c^* > T_c$), $\beta\Phi_F$ becomes a monotonically increasing function of n if isotropic edgewise adsorption prevails for $r^{-2} < n \leqslant r^{-1}$ (see for example, curve (*a*) in figure 5).

For $r > 3$, anisotropic edgewise adsorption is possible for $r^{-2} < n \leqslant r^{-1}$ even when anisotropic dispersion interactions are absent. When $\beta(w_1 - w_2) = 0$, equations (21) and (22) can be simultaneously solved with relative ease for ϕ and S ($S \neq 0$) as a function of n and $\beta|\epsilon|$ for $r > 3$. Explicit calculations of the density dependence of ϕ and S for $r = 4$ and

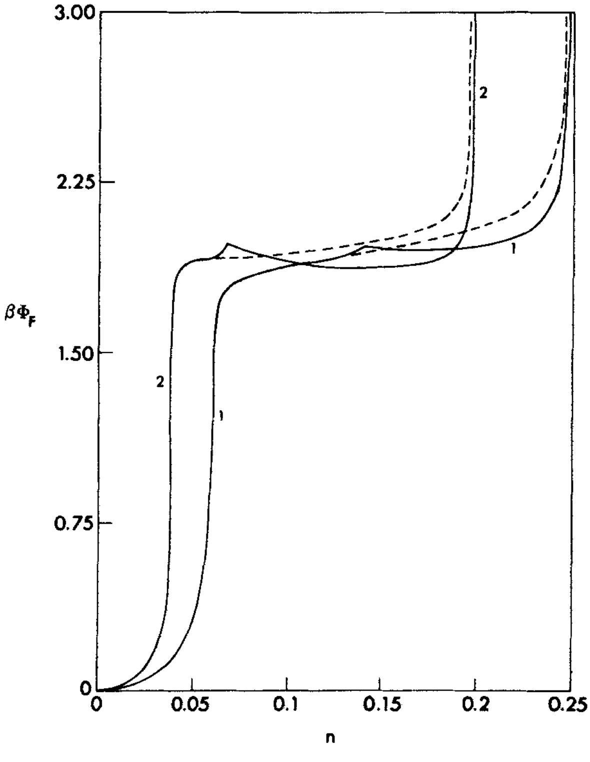

Figure 7. $\beta\Phi_F - n$ isotherms evaluated from equation (30) for $\beta\epsilon = -2$ and $\beta w_1 = \beta(w_1 - w_2) = 0$ with $r = 4$ (curve 1) and $r = 5$ (curve 2). The required values of ϕ and S for each n are determined from equations (21) and (22). The dotted lines represent the portion of the $\beta\Phi_F - n$ isotherms which would result if $S = 0$ over the indicated density ranges.

$r=5$ with $\beta|\varepsilon|=2$ appear in figure 6. Anisotropic edgewise adsorption is found to be possible and represents the states of lowest free energy for $0{\cdot}25 \geqslant n > 0{\cdot}135$ when $r=4$ and $\beta\varepsilon=-2$ and for $0{\cdot}2 \geqslant n > 0{\cdot}0685$ when $r=5$ and $\beta\varepsilon=-2$. Figure 6 reveals that both S and ϕ monotonically increase with n while the surface coverage, θ, increases monotonically with n for $0 \leqslant n \leqslant r^{-2}$ and then passes through a minimum for $r^{-2} < n < r^{-1}$ before approaching $\theta \to 1$ as $rn \to 1$.

In figure 7 the corresponding $\beta\Phi_F - n$ isotherms for $r=4$ and $r=5$ calculated from equation (30) (with ϕ and S determined from equations (21) and (22) for each n) are exhibited for the case $\beta w_1 = 0$. A discontinuity in the slope of the isotherms appears at the density, $n \equiv n_t > r^{-2}$, where a transition from isotropic to anisotropic edgewise adsorption occurs. The $\beta\Phi_F - n$ isotherms exhibit shallow minima in the density range $r^{-2} < n < r^{-1}$ and $\partial\beta\Phi_F/\partial n < 0$ for $n_t < n < n_m$ where n_m is the density at the minimum. Since $\partial\beta\Phi_F/\partial n < 0$ corresponds to a thermodynmically unstable adsorbed state, this result suggests that a single homogeneous adsorbed phase is thermodynamically unstable for $n_t < n < n_m$ and the actual adsorbed monolayer consists of coexisting adsorbed phases with different densities and order parameters for the edgewise adsorbate. The lower density adsorbed state possesses a larger fraction of facewise adsorbed molecules and the edgewise adsorbed molecules are isotropically distributed between the allowed orientations. The higher density coexisting adsorbed phase has a larger fraction of edgewise adsorbed molecules which are anisotropically distributed among the allowed orientations. This prediction of coexisting adsorbed phases appears even in the absence of attractive intermolecular dispersion interactions.

4. Brief discussion of the adsorption of rectangular plate-like molecules

Here we briefly consider an adsorbed monolayer of N identical homogeneous rectangular plate-like molecules of dimensions $a \times b \times 1$ $(a > b)$ adsorbed on a homogeneous planar surface of A equivalent square adsorption sites of unit area. It is assumed that there are three possible modes of adsorption, facewise and edgewise, along either the longer a edge or the b edge, and that in each mode there are two possible mutually orthogonal orientations for each edge. If N_{ia} and N_{ib} respectively denote the numbers of rectangular plate-like molecules which are edgewise adsorbed along their a and b edges (either edge) and aligned along direction i $(i=1,2)$ and N_{ic} where $c \equiv a \times b$ denotes the number of facewise adsorbed molecules with their longest edge (edge a) aligned along i, then $(i=1,2;\ \lambda=a,b,c)$ $N=\Sigma_{i=1}^{2}\Sigma_{\lambda=a}^{c} N_{i\lambda}$, $n \equiv N/A = \Sigma_{i=1}^{2}\Sigma_{\lambda=a}^{c} n_{i\lambda}$ where $n_{i\lambda} \equiv N_{i\lambda}/A$ and $\theta = \Sigma_{i=1}^{2}\Sigma_{\lambda=a}^{c} \lambda n_{i\lambda}$ respectively represent the total number of adsorbed molecules, the surface density of adsorbate and the surface coverage $(0 \leqslant \theta \leqslant 1)$.

The configurational partition function, Ω_R for rectangular plate-like molecules is again determined from the number of distinguishable ways of placing the facewise and edgewise adsorbed molecules onto the square planar surface such that only one molecular segment can occupy an individual adsorption site. The result obtained for Ω_R does depend upon the order of placement of the adsorbed molecules, as anticipated from the previous analysis of square plate molecular adsorption. Here we restrict the discussion to the case where the facewise adsorbed molecules are introduced first onto the square planar surface lattice. The analysis for determining Ω_{RF} proceeds in essentially an identical manner to that employed to obtain Ω_F for square plate molecules and will only be briefly outlined here.

The number of distinguishable ways of placing the $N_c \equiv \Sigma_{i=1}^{2} N_{ic}$ facewise adsorbed rectangular plate-like molecules on to the surface is

$$Y_{\mathrm{RF}} = (N_{1c}!N_{2c}!)^{-1} \prod_{m=0}^{N_c-1} v_{m+1}, \tag{33}$$

where v_{m+1} represents the number of permissible ways of placing the $m+1$th facewise adsorbed molecule onto the surface, given that $(N_{1c}/N_c)m$ and $(N_{2c}/N_c)m$ molecules having their longer a edges aligned along directions 1 and 2 respectively have been successfully introduced. Explicitly

$$\begin{aligned} v_{m+1} = {} & (A-cm)^c/\{(A-cm+(bN_{1c}+aN_{2c})m/N_c)^{a-1}(A-cm+(aN_{1c}+bN_{2c})m/N_c)^{b-1} \\ & \times (A-(c-1)m)^{(a-1)(b-1)}\}. \end{aligned} \tag{34}$$

This result for rectangular plate molecules represents the generalization of equation (4) obtained for square plate molecules. Equation (34) reduces to equation (4) when $a=b=r$ and can be derived by the same arguments which led to equation (4).

The product

$$\prod_{m=0}^{N_c-1} v_{m+1},$$

can be evaluated in the same manner as equation (5) and

$$\begin{aligned} Y_{\mathrm{RF}} = {} & \left(\prod_{i=1}^{2} N_{ic}!\right)^{-1} (A!/(A-cN_c)!)[(A-(c-1)N_c)!/A!]^{(a-1)(b-1)/(c-1)} \\ & \times [(A-(c-b)N_{1c}-(c-a)N_{2c})!/A!]^{(a-1)N_c\{(c-b)N_{1c}+(c-a)N_{2c}\}^{-1}} \\ & \times [(A-(c-a)N_{1c}-(c-b)N_{2c})!/A!]^{(b-1)N_c\{(c-a)N_{1c}+(c-b)N_{2c}\}^{-1}}, \end{aligned} \tag{35}$$

which is the corresponding generalization of equation (5) to rectangular plate molecules. When $a=b=r$ equation (35) reduces to equation (5). Also note that equation (35) is invariant upon interchange of labels 1 and 2.

Once the facewise adsorbed molecules have been introduced successfully, then the

$$N_a \equiv \sum_{i=1}^{2} N_{ia},$$

and

$$N_b \equiv \sum_{i=1}^{2} N_{ib},$$

edgewise adsorbed molecules are introduced and direct application of the familiar DiMarzio lattice statistics [3] for rod-like molecules restricted to two mutually orthogonal directions leads to

$$\begin{aligned} \Omega_{\mathrm{RF}} = {} & \left(\prod_{i=1}^{2} \prod_{\lambda=a}^{c} N_{i\lambda}!\right)^{-1} (A!/(A(1-\theta))!)[(A-(c-1)N_c)!/A!]^{\omega}[(A-(c-b)N_{1c} \\ & -(c-a)N_{2c})!/A!]^{\alpha} \times [(A-(c-a)N_{1c}-(c-b)N_{2c})!/A!]^{\gamma} \times [(A-(c-b)N_{1c} \\ & -(c-a)N_{2c}-(a-1)N_{1a}-(b-1)N_{1b})!] \times [(A-(c-a)N_{1c}-(c-b)N_{2c} \\ & -(a-1)N_{2a}-(b-1)N_{2b})!](A!)^{-2}, \end{aligned} \tag{36}$$

where $\omega \equiv (a-1)(b-1)/(c-1)$, $\alpha \equiv (a-1)N_c((c-b)N_{1c}+(c-a)N_{2c})^{-1}-1$ and $\gamma \equiv (b-1)N_c((c-a)N_{1c}+(c-b)N_{2c})^{-1}-1$. When $a=b=r$, $N_{ia}=N_{ib}=N_{ir}/2$, $i=1,2$, $N_{1c}=N_{2c}=N_c/2$ and equation (36) reduces to equation (6). The configurational degeneracies, Ω_{RE} and Ω_{RI}, which generalize Ω_{E} (see equation (10)) and Ω_{I} (see equation (12)) to rectangular plate-like molecules can also be obtained by similar methods but are not reproduced here.

Both the total surface–adsorption energy, E_{a}, and the total dispersion energy, E_{d}, between all interacting pairs of adsorbed molecules contribute to the total internal energy

$$E = E_{\text{a}} + E_{\text{d}}.$$

We assume that in general

$$E_{\text{a}} = -\sum_{i=1}^{2} \sum_{\lambda=a}^{c} N_{i\lambda}\lambda|\epsilon_\lambda|, \tag{37}$$

and in the mean-field approximation

$$E_{\text{d}} = -(2A)^{-1} \sum_i \sum_j \sum_\lambda \sum_{\lambda'} N_{i\lambda}N_{j\lambda'}w_{ij\lambda\lambda'}, \tag{38}$$

where the $|\epsilon_\lambda| \lambda = a, b, c$ represent the absolute values of the molecular segment–surface site adsorption energy for an adsorbed molecule in state λ and the $w_{ij\lambda\lambda'}$ represent the total pair interaction energy between a pair of adsorbed molecules in orientations and states $i\lambda$ and $j\lambda'$ averaged over all non-overlapping intermolecular separations [7]. If for simplicity, we set $|\epsilon_\lambda| = |\epsilon|$ for all $\lambda = a, b, c$ then

$$E_{\text{a}} = -\sum_i \sum_\lambda N_{i\lambda}\lambda|\epsilon| = -A\theta|\epsilon|. \tag{37 a}$$

This selection for E_{a} is consistent with a chemically homogeneous adsorbate and adsorption surface. Also for isotropically adsorbed molecular systems where $N_{1\lambda} = N_{2\lambda} = N_\lambda/2$ $\lambda = a, b, c$, it is reasonable to assume a two parameter interaction potential

$$w_{ij\lambda\lambda'} \equiv w_{\lambda\lambda'} \equiv w_1\delta_{\lambda\lambda'} + w_2(1-\delta_{\lambda\lambda'}),$$

and

$$E_{\text{d}} = -(2A)^{-1}\left[N^2 w_2 + \sum_\lambda N_\lambda^2(w_1 - w_2)\right], \tag{38 a}$$

where $\delta_{\lambda\lambda'}$ is the Kronecker delta function. If $w_1 = w_2$, the dispersion interaction energy is independent of the modes of adsorption of the interacting molecular pair.

In the maximum term approximation, the free energy density becomes for rectangular plate-like molecules

$$\beta f_{\text{RF}} \equiv -A^{-1}\ln\Omega_{\text{RF}} - \beta \sum_i \sum_\lambda n_{i\lambda}\lambda|\epsilon_\lambda| - (\beta/2)\sum_i \sum_j \sum_\lambda \sum_{\lambda'} n_{i\lambda}n_{j\lambda'}w_{ij\lambda\lambda'}, \tag{39}$$

where Ω_{RF} is explicitly given by equation (36). If equations (36), (37 *a*) and (38 *a*) are utilized for chemically homogeneous and isotropically adsorbed molecules, equation (39) becomes

$$
\begin{aligned}
\beta f_{\mathrm{RF}} = {} & -A^{-1}\ln\Omega_{\mathrm{RF}} - \beta\theta|\epsilon| - (\beta/2)\left[n^2 w_2 + \sum_{\lambda} n_\lambda^2 (w_1 - w_2)\right] \\
= {} & \sum_{\lambda}\,[n_\lambda \ln(n_\lambda/2)] + (1-\theta)\ln(1-\theta) - (a-1)(b-1)(c-1)^{-1}(1-(c-1)n_c) \\
& \times \ln(1-(c-1)n_c) - 2[1-(1/2)\{(a-1)n_a + (b-1)n_b + (2c-a-b)n_c\}] \\
& \times \ln[1-(1/2)\{(a-1)n_a + (b-1)n_b + (2c-a-b)n_c\}] \\
& + 4(c+1-a-b)(2c-a-b)^{-1} \\
& \times [1-(2c-a-b)n_c/2]\ln[1-(2c-a-b)n_c/2] \\
& - \beta|\epsilon|\theta - (\beta/2)\left[n^2 w_2 + \sum_{\lambda} n_\lambda^2 (w_1 - w_2)\right].
\end{aligned}
\tag{39 a}
$$

For a given density, *n*, the state of the adsorbed monolayer as specified by the set $\{n_\lambda\}(\lambda = a, b, c)$ is determined by free energy minimization subject to the constraint

$$
n = \sum_{\lambda'} n_{\lambda'} \quad (0 \leqslant n \leqslant b^{-1}): \quad \partial\left(\beta f_{\mathrm{RF}} - v \sum_{\lambda'} n_{\lambda'}\right)\Big/\partial n_\lambda = 0 \quad \lambda = a, b, c, \tag{40}
$$

where *v* is a Lagrange multiplier. For isotropic surface adsorption the free energy minimization generates a pair of coupled transcendental equations involving any pair of the surface densities, n_a, n_b, n_c, since application of the constraint eliminates one surface density of the set $\{n_\lambda\}$. In the strong adsorption limit solution of these coupled equations is usually facilitated by taking advantage of the knowledge that at least one of the adsorption modes is negligibly populated for any surface density.

Once the populations $\{n_\lambda\}$ have been determined as functions of *n* and *T*, other statistical thermodynamic functions can be obtained. For instance, the spreading pressure × (unit surface area) in units of $k_{\mathrm{B}}T$, $\beta\Phi_{\mathrm{RF}}$ becomes for isotropically adsorbed rectangular plate-like molecules

$$
\begin{aligned}
\beta\Phi_{\mathrm{RF}} \equiv {} & -\beta(f_{\mathrm{RF}} - n\partial f_{\mathrm{RF}}/\partial n) = \ln[(1-(2c-a-b)n_c/2 - (a-1)n_a/2 - (b-1)n_b/2)^2/(1-\theta)] \\
& + (a-1)(b-1)(c-1)^{-1}\ln[1-(c-1)n_c] + 4(a+b-c-1)(2c-a-b)^{-1} \\
& \times \ln[1-(2c-a-b)n_c/2] - (\beta/2)\left[n^2 w_2 + (w_1 - w_2)\sum_{\lambda} n_\lambda^2\right].
\end{aligned}
\tag{41}
$$

When $a = b = r$, $c = r^2$, $n_a = n_b = n\phi/2\; n_c = n(1-\phi)$, equation (41) reduces to equation (30) with $S = 0$, which is the result for square plate-like molecules isotropically adsorbed edgewise.

The adsorption population distribution and $\beta\Phi_{\mathrm{RF}}$ for rectangular plate-like molecules with $a = 3$, $b = 2$, $c = a \times b = 6$ as a function of surface density, *n*, were determined for $\beta\epsilon = -2$ and $\beta w_1 = +48$ and $\beta w_2 = 0$. This selection for the dispersion energies favours interaction between molecular pairs which are in identical adsorption modes, be it facewise or edgewise. The critical density and temperature for complete facewise adsorption of the 3 × 2 rectangular plate molecules is $n_c = 0{\cdot}055$ and $\beta_c w_1 = +45{\cdot}12$ (i.e. $\beta_c w_1/c^2 = \beta_c w_1/36 = 1{\cdot}25$).

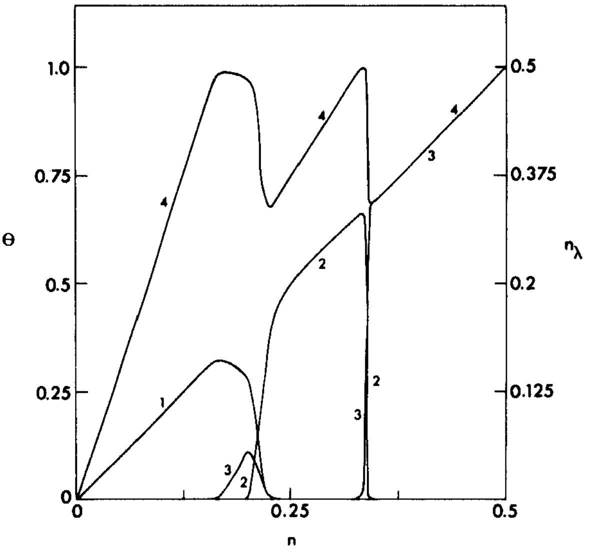

Figure 8. Curves 1, 2, 3 respectively give the population densities n_c, n_a and n_b obtained as a function of n for 3 × 2 × 1 rectangular plate molecules with $\beta\epsilon = -2$, $\beta w_1 = 48$ and $\beta w_2 = 0$. Curve 4 represents the total surface coverage $\theta \equiv 3n_a + 2n_b + 6n_c$ as a function of $n = n_a + n_b + n_c$.

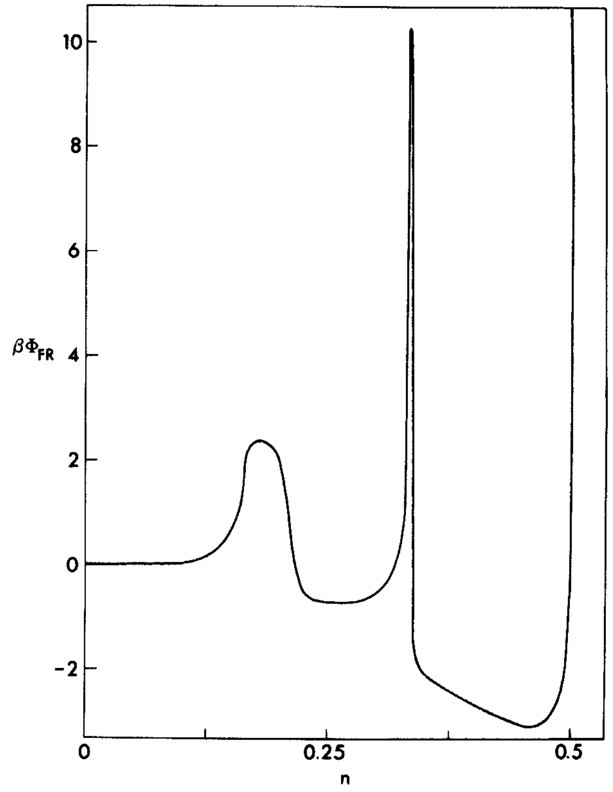

Figure 9. $\beta\Phi_{FR} - n$ isotherm calculated from equation (41) for $3 \times 2 \times 1$ rectangular plate molecules with $\beta\epsilon = -2$, $\beta w_1 = +48$ and $\beta w_2 = 0$ using the n_λ $\lambda = a, b, c$ exhibited in figure 8.

The population distribution, $\{n_\lambda\}$, and coverage, θ, as a function of n for 3×2 rectangular plate molecules are presented in figure 8. Note the sawtooth-like variation at θ with n which results in the strong adsorption limit in the immediate vicinities of the transition densities $n\simeq c^{-1}$ and $n\simeq a^{-1}$. The corresponding $\beta\Phi_{\mathrm{FR}}-n$ isotherm is displayed in figure 9 and it exhibits three distinct van der Waals loops, one in each of the respective density ranges $0<n<(c^{-1}\equiv 1/6)$, $1/6<n<(a^{-1}\equiv 1/3)$, and $1/3<n<(b^{-1}\equiv 1/2)$. The phase transitions represented by these loops correspond to a gas–liquid condensation of facewise adsorbed molecules in the density range $0<n<c^{-1}$; and liquid–liquid phase separations in the density ranges $c^{-1}<n<a^{-1}$ and $a^{-1}<n<b^{-1}$. The phase separation in the density range $c^{-1}<n<a^{-1}$ occurs between two adsorbed liquid phases with the lower density phase dominated by facewise adsorbed molecules while the higher density phase essentially consists of edgewise adsorbed molecules with the longer edge of length a in contact with the surface. In the region $a^{-1}<n<b^{-1}$, the phase separation corresponds to edgewise adsorbed liquid phases with the lower (higher) density phase dominated by molecules adsorbed along their long (short) edge. Thus the sequence of phase transitions with increasing density is facewise adsorbed gas↔facewise adsorbed liquid↔edgewise adsorbed liquid (long edge)↔edgewise adsorbed liquid (short edge). The 3 x 2 dimensions of the rectangular plate-like molecules considered here are sufficiently small to guarantee an isotropic distribution of orientations for all modes of adsorption in the absence of anisotropic dispersion interactions [7].

5. Concluding remarks

The present analysis provides a tractable mean-field theory of the adsorption of plate-like molecules which by suitable modifications can be generalized and extended to describe the statistical thermodynamics behaviour of a wide variety of related adsorption systems. These include adsorbed mixtures of plate-like, rod-like and/or chain-like molecules, multilayer adsorption of plate-like molecules, and adsorption of chemically heterogeneous plate-like molecules on homogeneous or heterogeneous surfaces where perhaps intermolecular and/or molecule–surface hydrogen bonding effects may exist.

A worthwhile extension of this analysis is an investigation of the conditions where anisotropic ordering may occur for both facewise and edgewise modes of adsorption of rectangular plate-like molecules. Determination of spreading pressure–density isotherms and the corresponding phase diagrams is also of interest for rectangular plate molecules capable of anisotropic ordering in one or more adsorption modes.

A plethora of selections of the effective intermolecular dispersion interactions between adsorbed molecules can be adopted to generate considerable variety in the adsorption behaviour. For example, pairwise dispersion interactions which are most favourable to nearest neighbour facewise–edgewise molecular pairs may produce an adsorbed monolayer with alternate rows of facewise and edgewise adsorbed molecules at sufficiently high surface coverage. This may be consistent with the pronounced positional order observed from STM images of 6CB adsorbed on pyrolitized graphite [1]. Addition of flexible or semiflexible chain-like tail segments to the rigid plate-like cores may be required to more closely simulate the molecular structure of adsorbed alkylcyanobiphenyls [1].

The present analysis was restricted to homogeneous one phase states of adsorption although this limitation is unnecessary. Generalization to spatially non-uniform adsorbed states would permit investigation of density, population distribution and order parameter fluctuations and interfacial properties between coexisting adsorbed mesophases. Extension of the analysis to investigate smectic mesophase behaviour in adsorbed monolayers of nematogenic or anisotropic plate-like molecules may also require consideration of spatially inhomogeneous adsorption.

Implementation of the analysis is simplified considerably because of the orientational restrictions imposed on the adsorbate molecules relative to the surface. This feature probably exaggerates the variation of the statistical thermodynamic behaviour in the vicinity of $n \sim 1/r^2$ or $n \sim 1/c$ where a transition from predominately facewise to edgewise adsorption occurs in the strong adsorption limit. Inclusion of more intermediate orientations would tend to mollify the adsorption behaviour somewhat in these transition regions.

Finally three different sequential methods of adsorbed molecule placement on the surface have been utilized for comparison to estimate the configurational degeneracy. All three methods predict similar trends in the statistical thermodynamic behaviour of adsorbed square plate molecules but differ quantitatively. While there is no firm *a priori* basis for selecting a placement sequence, the intermediate mode (I) is perhaps the most intellectually satisfying. The facewise before edgewise method (F method) of adsorbate placement, however, leads to somewhat simpler expressions for the free energy density, free energy minimization conditions and the spreading pressure and, as a result, was employed exclusively in the latter parts of §§3 and 4. The experimental method of preparation of the surface adsorbed monolayer or film may also motivate the selection of the placement method most appropriate for theoretical simulation of the actual adsorbed system.

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