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# Thermodynamic and orientational properties of two-dimensional multicomponent hard rectangle fluids

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A molecular statistical model is developed for a two-dimensional multicomponent fluid composed of hard rectangles. The configurational partition function of such a system on a square lattice is evaluated by applying the orientation dependent version of the Flory–Huggins probability method. Unlike earlier treatments of similar problems, the final result for the configurational entropy is independent of the order of placement of the rectangular plate-like particles. The present approach has been extended to enable an analysis of both facewise and edgewise modes of adsorption of rectangular molecules on a planar surface. Further, the limit of infinitesimal lattice size has been considered as the generalized continuous version of the corresponding lattice model. The results obtained within the present continuous approach are compared with those of studies of related one-component hard body fluids.

## 1. Introduction

Two-dimensional (2D) systems composed of hard anisometric particles are a topic of interest in various contexts of condensed matter thermodynamics. Such models, like their 3D counterparts, should be the reference systems used to describe fluids interacting by means of more realistic potentials [1–3]. Also, studying such fluids may be useful in trying to identify the entropy sources contributing to the adsorption properties of rigid molecules on planar surfaces [4–7], as well as to the phase behaviour of thin films of liquid crystalline substances (e.g. cyano derivatives at a water–air interface [8] and on pyrolytic graphite surfaces [9], and lyotropic tubules suspended on the surface of aqueous solutions [10]).

Another reason for this interest is to know the extent to which dimensionality of the system affects the nature of liquid crystalline phase transitions. Recent evidence, both from analytical models [11–14] and from Monte Carlo simulations [3], has indicated that order–disorder transitions in 2D hard body fluids may be either first order or continuous, the character of these transitions being dependent on the shape and aspect ratio of the particles.

Modelling of phase transitions and the structure of monolayers formed by rigid particles requires a treatment of the distribution in surface area of the different molecular configurations. The possible existence of a variety of different orientations of the particles makes the problem significantly more complicated [4–7, 15–19]. However, the theoretical description of such monolayers may be simplified by restricting all the possible modes of adsorption to single representative configurational states. On this view, the problem results in the statistical thermodynamic description of a 2D multicomponent ensemble of anisometric objects even in the case of adsorption of a one-component system.

At present, various methods have been proposed for handling adsorbed anisometric particles. The lattice cluster approach devised by Tovbin [6, 7] is based on the replacement of the calculation of the partition function by solving a set of equations relative to cluster distribution functions, which characterize the probabilities of different local configurations of the particles. In an alternative method, the orientation dependent generalization of the Flory–Huggins statistics [20] is utilized. The earlier studies of adsorbed monolayers composed of semi-flexible [15] and rod-like [16–18] molecules have been carried out by application of the simplest version of Di Marzio's lattice model [21]. In the 2D version of the model [21], each particle is approximated as a rod, which occupies a line of contiguous sites along a single row of a square lattice. The more complicated case concerning the adsorption of plate-like molecules has been studied to a lesser extent. Boehm and Martire developed a mean field analysis of rigid square and

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rectangular plate-like particles on a homogeneous planar surface [19]. In their study, the configurational part of the partition function has been estimated along the same lines as Di Marzio's statistics which has been extended by Shih and Alben [22] to the system of plates placed onto a cubic lattice in restricted, mutually orthogonal orientations. However, the configurational entropy determined in [19] in this manner is dependent upon the sequence of placement of plates and rods onto the lattice.

The problem of packing of squares and rods has been re-examined by Di Marzio *et al.* [23]. The failure of the attempt to solve 'the order of placement problem' led the authors to conclude that for objects other than linear chains a combinatorial lattice method itself breaks down.

It would be desirable, therefore, to have a model of the 2D hard particle mixture in which thermodynamic consistency is obtained by using a rather simple lattice approximation. In the present paper we develop a molecular statistical model of a multicomponent fluid composed of hard rectangles that is continuous in translations and discrete in orientational distribution. Our study comprises two parts. In § 2, the configurational partition function of such a system on a square lattice is evaluated by applying the modified Flory–Huggins configuration counting technique. In § 4, the limit of infinitesimal lattice size is considered as the generalized continuum version of the corresponding lattice model. Also a comparison with some recent 2D models of single component hard body fluids [3, 12, 13, 24] is performed. In § 3, the lattice version of the model is applied to the description of adsorption of rectangular particles on a planar surface.

The procedure used in the present study is based on the method elaborated earlier for a 3D multicomponent fluid of hard rectangular parallelepipeds [25]. As shown in [26], it provides a reasonable description of the tendencies in nematic–isotropic transition parameters in fluids composed of rod- and plate-like particles, which agree with those obtained from other analytical methods and computer simulations [27, 28]. The model derived in [25] proved to be successful in studying the orientational and thermodynamic properties of nematic solutions [29–31] and the stability of biaxial nematic phases [26].

## 2. Configurational statistics for a multicomponent mixture of plate-like rectangular particles placed on a square lattice

In this section, we consider a two-dimensional square lattice with $M$ equivalent cells, each having an area $\Delta u$ equal to $w^2$. Distributed on the lattice are $\{N_\lambda\}$ $(\Sigma_\lambda N_\lambda = N)$ rectangular plate-like particles, their axes being directed along axes $x_1, x_2$ of the quasi-lattice frame. Each component of the mixture is regarded as consisting entirely of rectangles of sort $k$ aligned along a particular direction $\alpha$ $(=1, 2)$. Let the index $\lambda = \alpha k$ label a particle of species $k$ with the orientation $\alpha$; thus, $\lambda$ is assigned values 1, 2 for the particles of sort 1, values 3, 4 for the particles of sort 2, etc. A particle of the $k$th sort is subdivided into $L_\lambda \equiv L_k = A_{1k}\ A_{2k}$ segments, each segment occupying a single lattice site. $N_0\ (= M - \Sigma_\lambda L_\lambda N_\lambda)$ cells are vacant.

Taking into consideration the dependence on the size of a lattice cell [25, 26, 32], the configurational contribution to the Helmholtz free energy of a system of non-attracting anisometric particles placed on a square lattice can be expressed as (see the appendix 1A)

$$F_{\text{latt}} = -kT \ln[g(\{N_\lambda\}; M)\ (\Delta u)^N / n^N] \tag{1}$$

where the combinatorial factor $g(\{N_\lambda\}; M)$ is the total number of ways to arrange $\{N_\lambda\}$ indistinguishable particles on $M$ lattice sites and $n$ is the number of discrete orientations of a particle ($n = 2$, if $A_{1k} \neq A_{2k}$).

As noted in the introduction, the model calculations applied in the earlier studies [19, 23] to a particular case of mixtures of squares and rigid rods on a 2D lattice gave results which were dependent on the sequence of placement of the particles on the array of lattice cells. Thereby the validity of the Flory–Huggins counting method has itself been placed into question for objects other than linear chains. The purpose of this section is to examine the packing problem anew for the case of hard rectangle fluids, retaining the essential features of combinatorial lattice statistics as adapted for 2D and 3D phases with orientational ordering of plate-like and block-like particles [19, 21–23, 25, 26].

In estimating $g(\{N_\lambda\}; M)$, we consider the process where the particles are being placed onto the lattice successively one after another. One has first to evaluate the average number of configurations, $v_\lambda$, available to the $(X_\lambda + 1)$th particle of type $\lambda$, given that $\{X_\lambda\}$ particles have already been placed. This can be estimated as follows:

$$v_\lambda(\{X_\lambda\}; X_\lambda + 1) = X_0 \bar{P}_\lambda(\{X_\lambda\}; L_\lambda - 1) \tag{2}$$

where $X_0$ $(= M - \Sigma_\lambda L_\lambda X_\lambda)$ represents the number of empty lattice cells which can accommodate one corner segment of a rectangle, and $\bar{P}_\lambda$ is defined as the conditional probability that $L_\lambda - 1$ neighbouring cells will be vacant to accommodate the remaining segments of the particle.

In order to approximate $g(\{N_\lambda\}; M)$, we shall seek the numbers $\{v_\lambda\}$ which satisfy relations

$$(\partial \ln v_\lambda / \partial X_\delta)_{T,M.\{X_{\lambda \neq \delta}\}} = \{\partial \ln v_\delta / \partial X_\lambda\}_{T,M.\{X_{\delta \neq \lambda}\}}. \tag{3}$$

Then the combinatorial factor can be calculated as follows:

$$
\begin{aligned}
&\ln g_{\mathrm{d}}(\{N_\lambda\}; M) \\
&= \int_0^{N_1} \ln v_1(X_1)\,\mathrm{d}X_1 + \int_0^{N_2} \ln v_2(N_1; X_2)\,\mathrm{d}X_2 + \ldots \\
&\quad + \int_0^{N_\lambda} \ln v_\lambda(\{N_\beta\}_{\beta<\lambda}; X_\lambda)\,\mathrm{d}X_\lambda;\; g(\{N_\lambda\}; M) \\
&= g_{\mathrm{d}}(\{N_\lambda\}; M) / \prod_\lambda N_\lambda !. \qquad (4)
\end{aligned}
$$

The factorial terms account for indistinguishability of the particles of type $\lambda$.

Such a construction of $g(\{N_\lambda\}; M)$ can be expected to yield the final result, which is independent of the assumed order of molecule placement onto the surface. To show this, we shall represent the term $v_\lambda$, which is introduced in expression (2), as $v_\lambda = g_{\mathrm{d}}(X_1, \ldots, X_\lambda + 1, \ldots; M)/g_{\mathrm{d}}(X_1, \ldots, X_\lambda, \ldots; M)$; it may be interpreted as the average number of placing the $(X_\lambda + 1)$th particle, given that $\{X_\lambda\}$ particles have already been placed. Then the following relations can be obtained:

$$
\begin{aligned}
\ln v_\lambda &\approx \partial \ln g_{\mathrm{d}}(\{X_\lambda\}; M)/\partial X_\lambda \\
&= -\partial(F'_{\mathrm{latt}}/kT)/\partial X_\lambda = -\mu'_\lambda/kT \qquad (5)
\end{aligned}
$$

where in accordance with expressions (1) and (4), $F'_{\mathrm{latt}}(\{X_v\})$ is written for

$$
F_{\mathrm{latt}}(\{X_v\}) + kT\left(\sum_\lambda X_\lambda \ln(\Delta u/2) - \ln \prod_\lambda X_\lambda !\right).
$$

The relationship between $\ln v_\lambda$ and the partial derivation of the combinatorial factor was obtained by Shih and Alben in their treatment of steric interactions of plate-like molecules on a cubic lattice [22].

Taking into consideration expression (5), one can write relations (3) in terms of the chemical potential, $\mu_\lambda$, of particles of type $\lambda$ as

$$
(\partial\mu_\lambda/\partial X_\delta)_{T,A,\{X_\lambda \neq X_\delta\}} = (\partial\mu_\delta/\partial X_\lambda)_{T,A,\{X_\delta \neq X_\lambda\}} \qquad (6)
$$

where $A = M\Delta u$ is the total surface area and $\mu_\lambda = \mu'_\lambda - \ln(\Delta u/2) + \ln X_\lambda$.

Equation (6) is equivalent to the familiar relation in thermodynamics for a 2D multicomponent fluid. Consequently, it is a necessary and sufficient condition of integrability of equation (4), which provides a criterion of the consistency of $g(\{N_\lambda\}; M)$ and the free energy $F_{\mathrm{latt}}$.

Further, we follow ideas of the counting procedure used in [19, 22, 23]. In order to compute the probability $\bar{P}_\lambda$ defined in equation (2), we seek to obtain its mean field approximation by counting the product of the probabilities for placing $L_\lambda - 1$ segments of a plate-like particle as follows:

$$
\bar{P}_\lambda(\{X_\lambda\}; L_\lambda - 1) = \prod_{i=1}^{2} P_i^{(r_\lambda^{(i)} - 1)} \; P_{12}^{(r_\lambda^{(1)} - 1)(r_\lambda^{(2)} - 1)}. \qquad (7)
$$

Here, the first term of the product represents the probability that $r_\lambda^{(i)} - 1$ contiguous cells along directions $\mathbf{e}_i$ $(i = 1, 2)$ from the corner segment of a rectangle are empty, the second term represents the probability that the $(r_\lambda^{(1)} - 1)(r_\lambda^{(2)} - 1)$ contiguous cells needed to build up the rest of the rectangle are empty; $r_\lambda^{(i)}$ denotes the number of lattice cells within an edge constrained along the direction $i$ for a particle of type $\lambda$, $L_\lambda = r_\lambda^{(1)}\ r_\lambda^{(2)}$. The sense of the approach utilized in the cited works is that the probability $P_n$ $(n = 1, 2, 12)$ that a cell in direction $\mathbf{n}$ $(\mathbf{n} = \mathbf{e}_i, \mathbf{e}_1 + \mathbf{e}_2)$ will be empty, given that a neighbour cell in direction $-\mathbf{n}$ is empty, is defined as the fraction of vacant cells in a random distribution of vacant and occupied cells:

$$
P_n = X_0/(X_0 + B_{\mathbf{n}}) \qquad (8)
$$

where $B_{\mathbf{n}}$ is the number of segments which could possibly occupy a cell in direction $\mathbf{n}$.

In the case of a multicomponent mixture, the numbers $B_{\mathbf{n}}$ can be obtained by simple geometrical considerations as

$$
\begin{aligned}
B_i &= \sum_\lambda X_\lambda r_\lambda^{(j)} = \sum_\lambda X_\lambda L_\lambda / r_\lambda^{(i)}, \qquad i \neq j \\
B_{12} &= \sum_\lambda X_\lambda (r_\lambda^{(1)} + r_\lambda^{(2)} - 1). \qquad (9)
\end{aligned}
$$

The number $v_\lambda$ available to the additional $(X_\lambda + 1)$th rectangle may now be estimated from relations (7–9) by substitution into definition (2). However, as shown in appendix 2, the above application of the probability method to the fluid under consideration does not provide its internal consistency.

The main reason for this shortcoming is that the assumption (8) of complete randomness adopted to compute the probability $P_n$ as well as $\bar{P}_\lambda$ of equation (7) neglects the particular steric properties of plate-like particles. In fact, the availability of cells necessary to build up the edges and the interior of the given particle may, due to the effect of blocking of cells by interior segments of the same particle, not be uniform. To overcome this deficiency of a random distribution, while maintaining the ideas of the Flory–Huggins procedure, we have tried to take into consideration the state of neighbouring lattice cells needed for accommodation of $(r_\lambda^{(1)} - 1)(r_\lambda^{(2)} - 1)$ interior segments of the $(X_\lambda + 1)$th particle. For this purpose, we have introduced the relative probability, $P^*_{12}$, of finding the given cell empty given that two adjacent cells along $\mathbf{e}_1$ and $\mathbf{e}_2$ are simultaneously empty, as follows:

$$
P^*_{12} = X_0 P_1 P_2 / X_0 P_{12} = P_1 P_2 / P_{12}. \qquad (10)
$$

According to definition (8), the denominator, $X_0P_{12}$, represents here the average number of two vacant cells, which are in contact as shown in figure 1 (*a*), the cell labelled in figure 1 (*b*) with an asterisk being occupied or empty. The numerator, $X_0P_1P_2$, represents the average number of three vacant adjacent cells which are shown in figure 1 (*b*), the cell (*) now being empty. Thus, the ratio of the products $X_0P_1P_2$ and $X_0P_{12}$ can be interpreted as the relative probability $P^*_{12}$ introduced in equation (10).

Employing equations (8), (9) and (10), for the average number of configurations available to the $(X_\lambda+1)$th particle, one now has:

$$\begin{aligned}
&v^*_\lambda(\{X_\lambda\}; X_\lambda+1)\\
&= X_0 \prod_{i=1}^{2} P_i^{(r_\lambda^{(i)}-1)} \, (P^*_{12})^{(r_\lambda^{(1)}-1)(r_\lambda^{(2)}-1)}\\
&= X_0^{L_\lambda}(X_0+B_{12})^{(r_\lambda^{(1}-1)(r_\lambda^{(2)}-1)}\\
&\quad /[(X_0+B_1)^{(L_\lambda-r_\lambda^{(2)})}(X_0+B_2)^{(L_\lambda-r_\lambda^{(1)})}]. \qquad (11)
\end{aligned}$$

In appendix 2, we demonstrate that the relation (3) is now satisfied. Then, upon applying expression (11) to equation (4), followed by use of Stirling's approximation and the replacement in relations (9) of the values $X_\lambda$ with $N_\lambda$, one obtains the following result for the combinatorial factor:

$$\begin{aligned}
g(\{N_\lambda\}; M) &= \frac{\prod_{i=1}^{2}\left(N_0+\sum_\lambda N_\lambda L_\lambda/r_\lambda^{(i)}\right)!}{\prod_\lambda N_\lambda! N_0!\left[N_0+\sum_\lambda N_\lambda(r_\lambda^{(1)}+r_\lambda^{(2)}-1)\right]!}\\
&= \frac{\prod_{i=1}^{2}(N_0+B_i)!}{\prod_\lambda N_\lambda! N_0!(N_0+B_{12})!}. \qquad (12)
\end{aligned}$$

For the particular case of a mixture of square plates $r\times r$ ($k=1$; $r_{\alpha1}^{(1)}=r_{\alpha1}^{(2)}=r$ for $\alpha=1, 2$) and rods $r\times 1$ ($k=2$; $r_{12}^{(1)}=r$, $r_{12}^{(2)}=1$ for $\alpha=1$, and $r_{22}^{(1)}=1$, $r_{22}^{(2)}=r$ for $\alpha=2$), one has:

$$g_{\mathrm{RS}}(N_1, \{N_{\alpha2}\}; M) = \frac{\prod_\alpha [M-r(r-1)N_1-(r-1)N_{\alpha2}]!}{N_0!N_1!\prod_\alpha N_{\alpha2}![M-(r-1)^2N_1]!}. \qquad (13)$$

When $N_1$ is set to zero, expression (13) leads to

$$\begin{aligned}
g_{\mathrm{R}}(N_1=0, \{N_{\alpha2}\}; M) &= \left[(M-rN_2)!\prod_\alpha N_{\alpha2}!M!\right]^{-1}\\
&\quad \times \prod_\alpha [M-(r-1)N_{\alpha2}]!. \qquad (14)
\end{aligned}$$

Expression (14) corresponds to the familiar Di Marzio result [21] related to rods spread on a 2D lattice.

In another case, for a one-component system of squares consisting of $r^2$ segments, expression (13) is reduced to:

$$\begin{aligned}
&g_{\mathrm{S}}(N_1, N_2=0; M)\\
&\quad = [M-(r^2-r)N_1]!^2\\
&\qquad /\{N!(M-r^2N_1)![M-(r-1)^2N_1]!\}. \qquad (15)
\end{aligned}$$

As shown in §4, in the limit of continuous translations, expression (15) enables one to obtain an equation of state fitting well the result derived by Ree and Hoover [33].

In appendix 3, we have performed an additional test of the lattice statistics developed in this section for a 2D multicomponent fluid. For the particular case of a mixture of squares and rods (squares before rods and rods before squares placements), it is shown, that the final result for the combinatorial factor does not depend on the order of placement of the particles on the lattice.

Finally, one may conclude that the present approach provides an *a priori* basis for studying properties of multicomponent hard rectangle fluids. It may be meaningful for the statistical thermodynamic interpretation of behaviour of monolayers formed by rigid particles. In particular, it may be used for calculation of the adsorbate population distribution in an anisotropic surface ordering.

The limit of infinitesimal lattice cell, which is considered as an approximation of a continuum description of mass centres of particles will be discussed in §4. In the next section, we provide numerical applications of the proposed version of the 2D lattice model.

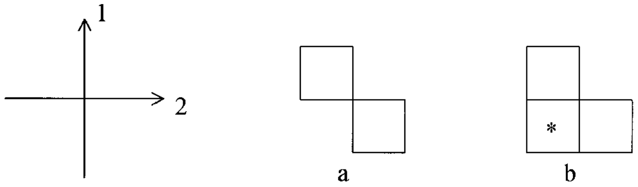


Figure 1. Schematic drawing which explains the definition of the relative probability, $P^*_{12}$, of finding a vacant cell given that two adjacent cells along $\mathbf{e}_1$ and $\mathbf{e}_2$ are simultaneously empty.

## 3. Application of the model to an adsorbed monolayer of plate-like molecules

A treatment of a monolayer adsorption of rectangular molecules on a planar surface may be performed by extension of the methods developed in the studies [6, 7, 19]. Here we apply the Boehm–Martire model

[19], combining it with the above developed results of the packing statistics. We consider a $k$-component mixture of particles with dimensions $A_{1k}\ A_{2k}\ A_{3k}$, which are adsorbed on a square lattice with $M$ sites. In a monolayer of such particles, an infinite number of orientations of molecules with respect to the surface is possible. To simplify the description of the thermodynamic properties of such a monolayer, all the possible projections of each molecule are assumed to be restricted to the states represented with the surface areas arranged in $L_{1k} = A_{1k}\ A_{2k}$, or $L_{2k} = A_{1k}\ A_{3k}$, or $L_{3k} = A_{2k}\ A_{3k}$ adjacent lattice cells. According to this view, for each molecule there are three modes of adsorption, by any of three different faces of a rectangular parallelepiped, the projections of an adsorbed molecule being represented as different species. Thus, on attempting an explanation of the properties of an adsorbed one-component system, one encounters the problem of modelling of a multicomponent mixture.

Let $N_\lambda = N_{\alpha pk}$ denote the number of rectangular particles which are adsorbed along their $L_{pk}$ $(p = 1, 2, 3)$ faces and aligned along direction $\alpha$. Then $N_k = \Sigma_{p=1}^{3} \Sigma_{\alpha=1}^{2} N_{\alpha pk}$, $n = \Sigma N_\lambda / M = \Sigma_\lambda n_\lambda$, and $\theta = \Sigma_k \Sigma_p \Sigma_\alpha L_{pk} n_{\alpha pk}$ represent, respectively, the total number of adsorbed molecules of sort $k$, the surface density of the adsorbate and the surface coverage $(0 \leqslant \theta \leqslant 1)$.

Under the assumption that the molecular segment–surface site adsorption energy, $\varepsilon$, does not depend on a mode of adsorption, the total internal energy, $E$, of a system with non-attracting particles is determined by the surface adsorption energy, $E_\mathrm{a}$, as follows

$$E = E_\mathrm{a} = -|\varepsilon| \sum_k \sum_p \sum_\alpha L_{pk} N_{\alpha pk} = -|\varepsilon| M\theta. \qquad (16)$$

This selection of $E_\mathrm{a}$ is consistent with a chemically homogeneous adsorbate and adsorption surface.

The Helmholtz free energy per lattice cell in units $\beta^{-1} \equiv k_\mathrm{B} T$ may be written as

$$\beta f = \beta F_\mathrm{latt}/M + \beta E_\mathrm{a}/M \qquad (17)$$

where $F_\mathrm{latt}$ is determined with the aid of equation (1) together with an expression (12) for the configurational factor.

To specify the set $\{\bar{N}_\lambda\}$, corresponding to an equilibrium state of an adsorbed monolayer, it is convenient to introduce a chemical potential, $\mu_\lambda$, of an object of type $\lambda$. In this case, such an object corresponds to a face $p_k$ of a molecule of sort $k$, the face being aligned along direction $\alpha$. Taking into account (1), (16) and (17) one gets:

$$\mu_\lambda = [\partial(fM)/\partial N_\lambda]_{M,T,\{N_{\beta\neq\lambda}\}} = \mu_\lambda^* - L_\lambda|\varepsilon| \qquad (18)$$

where a chemical potential, $\mu_\lambda^*$, of an object of type $\lambda$ in an athermal hard rectangle mixture can be obtained from

$$\begin{aligned}\beta\mu_\lambda^* &= \beta(\partial F_\mathrm{latt}/\partial N_\lambda)_{M,T,\{N_{\beta\neq\lambda}\}}\\ &= L_\lambda \sum_i (1 - 1/r_\lambda^{(i)}) \ln\left(\theta^{-1} - 1 + \sum_\lambda \theta_\lambda/\theta r_\lambda^{(i)}\right)\\ &\quad - L_\lambda \ln(\theta^{-1} - 1) - (L_\lambda - r_\lambda^{(1)} - r_\lambda^{(2)} + 1)\\ &\quad \times \ln\left[\theta^{-1} - 1 + \sum_\lambda (r_\lambda^{(1)} + r_\lambda^{(2)} - 1) y_\lambda \Big/ \sum_\lambda L_\lambda y_\lambda\right]\\ &\quad + \ln\left(y_\lambda \Big/ \sum_\lambda L_\lambda y_\lambda\right) + \ln(\Delta u/2). \qquad (19)\end{aligned}$$

Here $y_\lambda = N_\lambda / \Sigma_\lambda N_\lambda = y_{pk} s_{\alpha pk} (\Sigma_{pk=1}^{3} \Sigma_{\alpha=1}^{2} y_{pk} s_{\alpha pk} = 1)$, where $y_{pk}$ represents the fraction of molecules of sort $k$ which have surface area $L_{pk}$; the fraction of the corresponding edgewise adsorbed particles pointing along direction $\alpha$ is $s_{\alpha pk}$.

To obtain the set $\{y_{\alpha pk}\}$ which minimizes the function $f$ at given $T$ and $n$ one needs to solve the following $5k$ simultaneous equations involving any pair of values $y_{pk}$ and a fraction $s_{\alpha pk}$. ($\alpha = 1$ or 2) for each of three modes of adsorption $(p = 1, 2, 3)$:

$$\begin{aligned}(\partial f/\partial s_{\alpha pk})_{T,n,y_{pk}} &= 0\\ (\partial f/\partial y_{pk})_{T,n,s_{p\alpha k}} &= 0.\end{aligned} \qquad (20)$$

In terms of variables $y_{\alpha pk}$, the set (20) is equivalent to the following $5k$ coupled equations, where the index $\alpha$ can be assigned values 1 or 2:

$$\begin{aligned}\mu_{1pk} &= \mu_{2pk}, \quad p = 1, 2, 3\\ \mu_{\alpha 1k} &= \mu_{\alpha 2k}\\ \mu_{\alpha 1k} &= \mu_{\alpha 3k}.\end{aligned} \qquad (21)$$

Once the adsorbate population distribution, $\{y_{\alpha pk}\}$ and $\{s_{\alpha pk}\}$, has been determined, other thermodynamic properties of an adsorbed monolayer can be obtained straightforwardly.

For instance, the spreading pressure, $\Phi_\mathrm{latt}$, of a system with non-attracting particles can be estimated by using equations (1) and (12) to give:

$$\beta\Phi_\mathrm{latt}\Delta u = -\beta\left(\frac{\partial F_\mathrm{latt}}{\partial M}\right)_{T,N} = \ln\frac{\prod_{i=1}^{2}(N_0 + B_i)}{N_0(N_0 + B_{12})}. \qquad (22)$$

Further, we focus on some equilibrium properties of the adsorbed non-attracting square plate molecules consisting of $r\ r\ 1$ cell segments, the possible modes of adsorption being restricted to facewise and edgewise. As noted in the introduction, the statistical thermodynamic analysis of a mixture of squares and rods performed in [19] and in the later study [23] gives different results which depend on the sequence of placement of particles onto a square lattice. The aim of our calculations is to provide a comparison of the results of the present approach with those obtained in [19]. The method labelled in [19] as sequence I is based on the assumption that squares and rods are placed onto the lattice in direct proportion to their final bulk composition. In the other placement sequences denoted as F and E, all facewise (edgewise) adsorbed molecules are introduced onto the surface before edgewise (facewise).

Let $N_1 = Ny_1$ and $N_{\alpha 2} = Ny_2 s_{\alpha 2}$ be the numbers of facewise and edgewise adsorbed particles, respectively; $s_{\alpha 2}$ ($\alpha = 1, 2$) is the fraction of edgewise adsorbed particles aligned along axes $x_1$ and $x_2$ of the coordinate frame. Thus, for the adopted way of labelling the states of adsorbed particles $r^{(1)}_{\alpha 1} = r^{(2)}_{\alpha 1} = r$ for $\alpha = 1, 2$ $(k = 1)$; $r^{(1)}_{12} = r$, $r^{(2)}_{12} = 1$ for $\alpha = 1$, $r^{(1)}_{22} = 1$, $r^{(2)}_{22} = r$ for $\alpha = 2$ $(k = 2)$.

In accordance with equations (20) and (21), equilibrium values of $\{y_{\alpha p}\}$ and $\{s_{\alpha p}\}$ may be located from the following two equations:

$$(\partial f/\partial y_1)_{T,n,s_{12}} = \mu_{12} - \mu_1 = 0 \tag{23}$$

$$(\partial f/\partial s_{12})_{T,n,y_1} = \mu_{12} - \mu_{22} = 0 \tag{24}$$

where the chemical potentials, $\mu_1$ and $\mu_{\alpha 2}$, of facewise and edgewise adsorbed molecules are obtained from equations (18) and (19) to give:

$$\begin{aligned} \mu_1 &= \mu_1^* - r^2|\varepsilon| \\ \beta\mu_1^* &= r(r-1)\sum_{\alpha=1}^{2} \ln[1 - n(r-1)(ry_1 + s_{\alpha 2}y_2)] \\ &\quad + \ln(ny_1) - r^2 \ln(1-\theta) \\ &\quad - (r-1)^2 \ln[1 - n(r-1)^2 y_1] \end{aligned} \tag{25}$$

$$\begin{aligned} \mu_{\alpha 2} &= \mu_{\alpha 2}^* - r^2|\varepsilon| \\ \beta\mu_{\alpha 2}^* &= (r-1)\ln[1 - n(r-1)(ry_1 + s_{\alpha 2}y_2)] \\ &\quad - r\ln(1-\theta) + \ln(ns_{\alpha 2}y_2). \end{aligned} \tag{26}$$

Therefore, equation (24) is always satisfied if $s_{\alpha 2} = 1/2$. It corresponds to the isotropic distribution of rod-like edges on the square lattice.

The spreading pressure for an adsorbed monolayer of square plate-like particles can be estimated upon applying equation (22) and relationships (9) as follows:

$$\begin{aligned} \beta\Phi_{\text{latt}}\Delta u = &\sum_{\alpha=1}^{2} \ln[1 - n(r-1)(ry_1 + s_{\alpha 2}y_2)] \\ &- \ln[1 - n(r-1)^2 y_1] - \ln(1-\theta). \end{aligned} \tag{27}$$

It is seen, that $\Phi_{\text{latt}}$ depends on the surface density, $n$, (or the area per molecule), the surface coverage, $\theta$, and the orientational state of an adsorption layer.

Figures 2 and 3 display, respectively, an adsorbate population distribution (the fraction of edgewise adsorbed molecules, $y_2$) as a function of $rn$ and the $\beta\Phi_{\text{latt}} - n$ isotherms for the system of plate-like particles having dimensions 3 1 1 for some fixed values of $\beta\varepsilon$, along with the data, replotted from [19]. (A variable $rn$ in figure 2 is chosen for comparison with the results of the corresponding $y_2(rn)$ calculations of the cited work.) For the properties investigated, one can see that the inconsistency in estimation of the configurational entropy within the three various methods of [19] is of great consequence numerically. These differences are especially notable in the case of the $\beta\Phi_{\text{latt}} - n$ isotherms. The results of the present calculations are close to those obtained within the method F, but this conformity seems to be fortuitous.

However, for $r = 3$, the qualitative predictions of the behaviour of these properties are the same. It has been revealed, that in this case only isotropic adsorption is possible. All the results exhibit the same tendencies for edgewise adsorption as $rn$ increases, these tendencies being weakened as the values of the molecular segment–surface site adsorption energy increase. Figure 3 shows, that the $\beta\Phi_{\text{latt}}$ curves exhibit the same monotonic increase with $n$, the absence of discontinuities in the slopes of all the isotherms indicating an absence of phase transitions in the monolayer.

Further comparison between the results of the $\beta\Phi_{\text{latt}} - n$ calculations has been made for the case

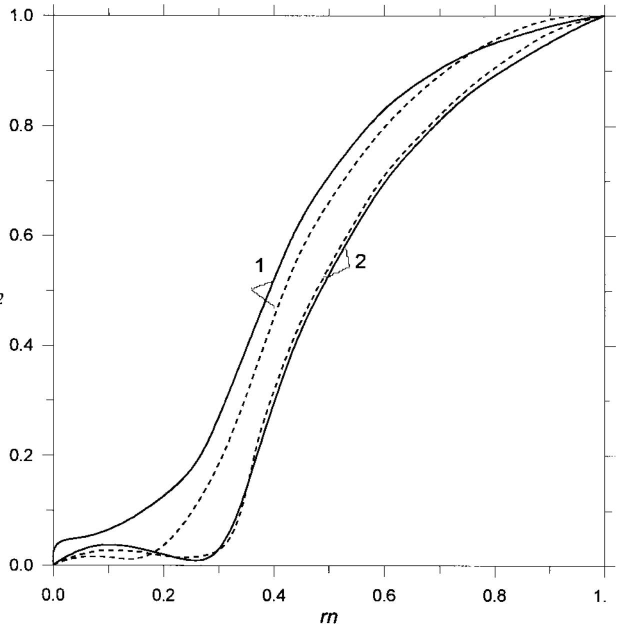


Figure 2. The fraction of edgewise adsorbed plates as a function of $rn$. The curves 1, 2 correspond to $r = 3$ and $\beta\varepsilon = -2/3$; $-2$, respectively. The solid curves are replotted from figure 2 of [19]. The dashed curves show the results obtained within the present model.

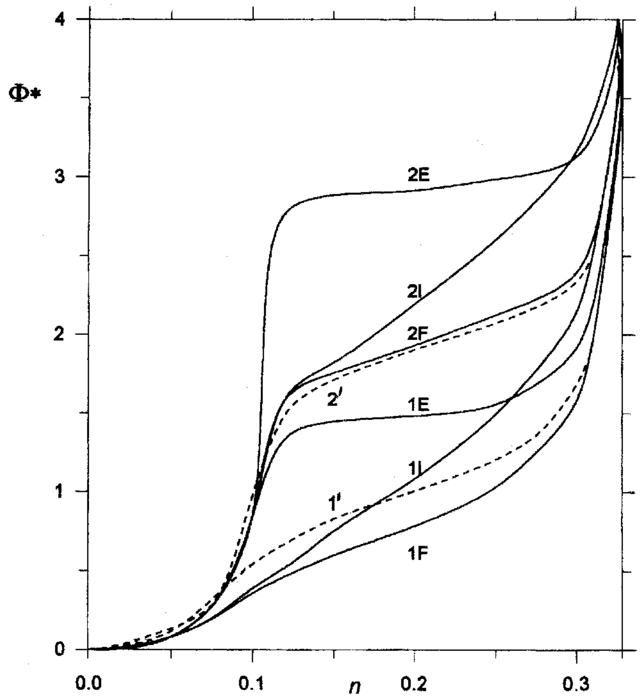


Figure 3. The reduced spreading pressure, $\Phi^* = \beta\Phi_{\text{latt}}/\Delta u$, as a function of $n$ for the adsorbed plates having dimensions 3.3.1 and $\beta\varepsilon = -2/3$ (1); $-2$ (2), respectively. The solid curves are replotted from figure 4 of [19]; symbols F, I, E refer to three different approximations used to evaluate the combinatorial factor (see text). The dashed curves (1′, 2′) show the results obtained within the present model.

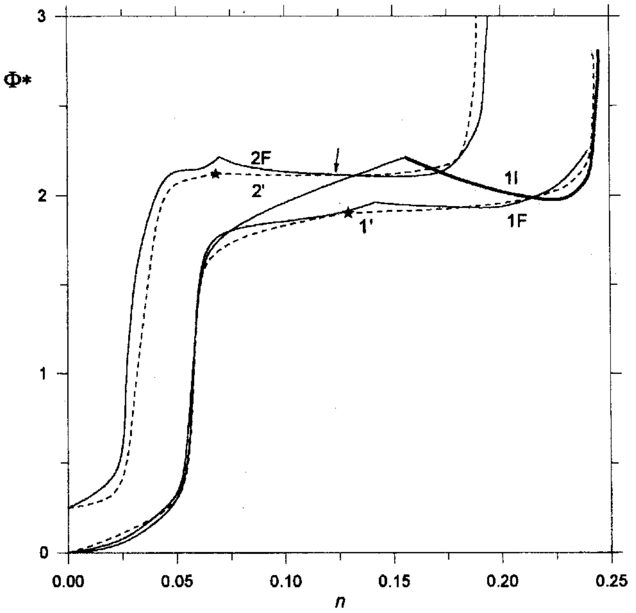


Figure 4. The reduced spreading pressure $\Phi^*$ as a function of $n$ for the adsorbed plates having dimensions 4.4.1 (1) and 5.5.1 (2); $\beta\varepsilon = -2$. The solid curves labelled F are replotted from figure 7, the solid curve labelled I is calculated from equation (31) of [19]; symbols—as in figure 3. The dashed curves (1′, 2′) show the results obtained within the present model; a transition from isotropic to anisotropic ordering of edgewise adsorbed plates is labelled with an asterisk. Location of the minimum on the isotherm 2′ is marked with an arrow. To separate the curves, the $\Phi^*$ scales for the curves 2F and 2′ have been shifted as $\Phi^* + 0.25$.

of plates of edge length 4 and 5 at the fixed value of $\beta\varepsilon = -2$. Figure 4 shows that the isotherms computed in the previous study reveal discontinuities indicating transition from isotropic to anisotropic packing of edgewise adsorbed particles. This discontinuity is more noticeable in the case of the I approximation than that obtained with the aid of approximation F of [19] for the determination of the configurational entropy. Since the states with $\partial\beta\Phi_{\text{latt}}/\partial n < 0$ are unstable, the actual monolayer presumably consists of coexisting isotropic and ordered phases having different densities. In contrast to the results of the former study, discontinuities in the slopes of the isotherms $\beta\Phi_{\text{latt}} - n$ caused by the continuous transition from the isotropic to the nematic state are scarcely detectable. In the case of $r = 5$, the isotherm evaluated within the present approach exhibits a shallow minimum which may indicate a first order transition in a monolayer; however the region with $\partial\beta\Phi_{\text{latt}}/\partial n < 0$ is much less pronounced than in the isotherm obtained in [19].

It may be possible to perform comparisons between the present model and the previous treatments [17–19] on taking into consideration attractive molecular interactions. However, the examples presented seem to provide an adequate sampling. Consideration of molecular attractions in the framework of the Bragg–Williams or quasi-chemical model seems to present no additional problems in principle.

## 4. Continuum version of the 2D lattice model

Generalization of lattice results to a continuum of translation coordinates is possible in a procedure devised previously for a 3D system composed of hard rectangular parallelepipeds [25]. As shown in appendix 1B, the continuum limit of expression (1) for the Helmholtz free energy of the corresponding 2D lattice model is

$$\beta F_{\text{conf}} = \sum_{\lambda} N_{\lambda}\left(-1 + f_{\lambda} b_1 b_2 \frac{\theta}{1-\theta} + \ln\frac{\theta}{1-\theta} + \ln\frac{n'_{\lambda}}{\theta}\right) \tag{28}$$

where $\theta = \Sigma_{\lambda}\, u_{\lambda} N_{\lambda}/A = \Sigma_{\lambda}\, \theta_{\lambda}$ is the fraction of surface area covered by particles, $u_{\lambda}$ is the area per particle, $A$ is the total surface area, $n'_{\lambda} = N_{\lambda}/A$, $b_i = \Sigma_{\lambda}\, \theta_{\lambda}/\theta f_{\lambda}^{(i)}$.

The surface pressure is expressed by

$$\beta \Phi a^2 = -\beta\left(\frac{\partial F_{\text{conf}}}{\partial \tilde{A}}\right)_{T,\{N_\lambda\}} = b_1 b_2 \frac{\theta^2}{(1-\theta)^2} + \frac{n' a^2}{(1-\theta)} \tag{29}$$

where $\tilde{A} = A/a^2$ is a dimensionless surface area, $n' = \Sigma_\lambda n'_\lambda$.

In order to test the validity of the present approach, we have performed the numerical solution of the equation of state for the case of an ordering single component fluid.

Let $N_1$ and $N_2$ be the numbers of rectangles whose long edges are parallel to the axes $x_1$ and $x_2$ of the coordinate frame. In accord with (28) and (29), the free energy, $F^{\text{HR}}$, and the compressibility factor, $Z^{\text{HR}}$, of such a system are given by

$$\begin{aligned}\frac{\beta F^{\text{HR}}}{N} = &-1 + \frac{1}{2\gamma}\frac{\theta}{1-\theta}\left[\frac{\gamma^2+1}{2}(1-S^2) + \gamma(1+S^2)\right] \\ &+ \ln\frac{\theta}{1-\theta} + [(1+S)\ln(1+S) \\ &+ (1-S)\ln(1-S)]/2 - \ln 2 \end{aligned} \tag{30}$$

$$\begin{aligned} Z^{\text{HR}} = \frac{\beta \Phi^{\text{HR}} u}{\theta} = \frac{1}{(1-\theta)^2}\Big\{1 + \frac{\theta}{4}[(\gamma+\gamma^{-1})(1-S^2) \\ + 2(1+S^2) - 4]\Big\}. \end{aligned} \tag{31}$$

Here, $b_1 = (s_1 + \gamma s_2)/\gamma d$, $b_2 = (\gamma s_1 + s_2)/\gamma d$, $u = \gamma d^2$ ($\gamma$ is the length-to-breadth ratio of a rectangle), $s_\lambda = N_\lambda / N$, $(\lambda = 1, 2)$.

The degree of the nematic alignment is given by the order parameter $S = s_1 - s_2$; in our case, the states with $S > 0$ and $S < 0$ are equivalent.

It seems expedient to compare our data on transition characteristics with those of more sophisticated models in which continuous variation of particles is allowed. Expanding $F^{\text{HR}}$ to powers of $S$ yields:

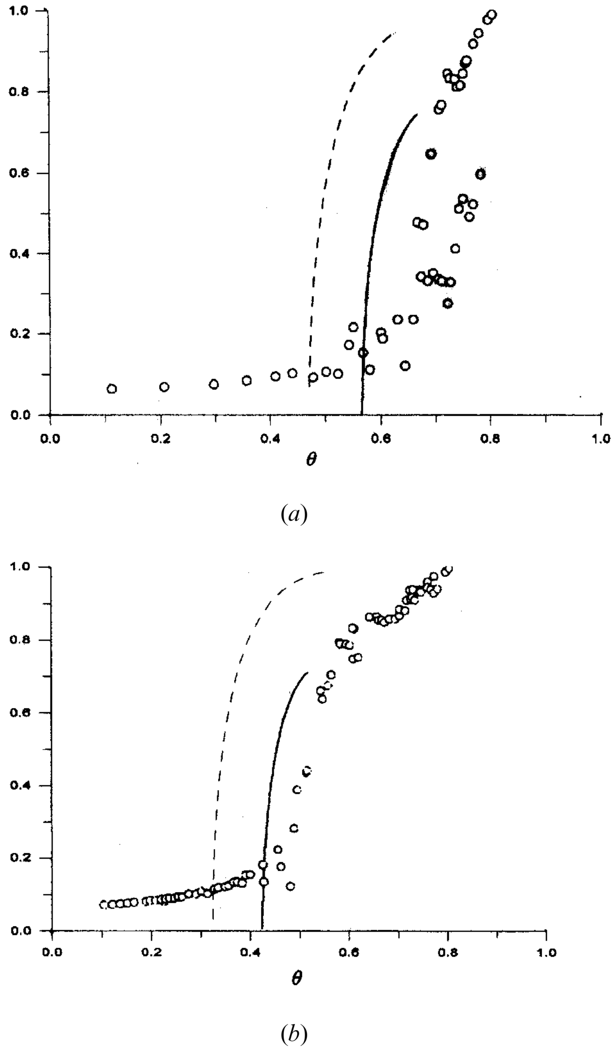
$$\beta F^{\text{HR}}/N = \beta F^{\text{HR}}(S=0)/N + \sum_{n=2}^{4} a_n S^n + o(S^5) \tag{32}$$

where $a_2 = 1/2 - [\theta/(1-\theta)][(\gamma-1)^2/4\gamma]$, $a_3 = 0$, $a_4 = 1/6$.

The fact, that in expansion (32) we have $a_3 = 0$, $a_4 > 0$, indicates that the system under consideration undergoes a continuous transition from isotropic to ordered state. This feature is inherent to the present model due to its symmetry.

Critical surface densities, $\theta^*$, corresponding to a transition to an orientationally ordered state can be calculated from the condition $a_2 = 0$, so that $\theta^* = 2\gamma/(1+\gamma^2)$. For $\gamma = 2$, 4 and 6, the values of $\theta^*$ are 0.8, 0.4706 and 0.3243, respectively. Thus, the values in question are in agreement with the quantities 0.74, 0.49 and 0.38 for hard ellipses with the same aspect ratios, calculated in the framework of the density-functional theory [12].

In figure 5, the order parameters for hard rectangles with elongations 4 and 6 are shown as functions of the surface density, along with the results for hard ellipses with continuous orientations; these data are replotted from [13]. It can be seen that the present model provides conformity in the trends in the order parameters calculated on the basis of the scaled particle theory. However, recent evidence obtained both from analytical theories [11–13] and from computer simulations [3] indicates that in the case of 2D hard rod fluids, the nature of the



(*a*)

(*b*)

Figure 5. Nematic order parameters as a function of the surface density for hard ellipses (solid lines, replotted from [13]) and for hard rectangles (dashes, the present model) with the aspect ratios (*a*) $\gamma = 4$, (*b*) $\gamma = 6$. The circles are MC simulation data for hard ellipses [3].

isotropic–nematic transition is sensitive to the shape and the aspect ratio of the particles. As shown in [13], in the particular case of rectangles having continuous orientations, a system undergoes a continuous transition if $\gamma > 5.44$, while if $2.62 < \gamma < 5.44$ the nematic–isotropic transition is first order. In the case of the ellipses with $\gamma = 4$, this fact is confirmed in [3] by the existence of hysteresis and the jump in the $S - \theta$ plot shown in figure 5.

The numerical results from studying of the equation of state are summarized in figure 6, where the $Z^{\mathrm{HR}} - \theta$ plots are shown for systems of rectangles with several values of $\gamma$. For the isotropic state, these results are compared with an equation of state for an ensemble of disco-rectangles, $Z^{\mathrm{HD}}$, with the same values of $\gamma$, taken as a maximum length to breadth ratio. Values of $Z^{\mathrm{HD}}$ are calculated on the basis of the recent version of an equation of state which reproduces simulation data for 2D isotropic convex body fluids with a great variety of molecular shapes [24]. In accord with the cited model, the compressibility factor, $Z^{\mathrm{HCB}}$, of such fluids is determined by only one non-sphericity parameter $\alpha$ (the shape factor) through equation

$$Z^{\mathrm{HCB}} = 1 + (1/2)(1 + \alpha/2)[(1 + \theta^2/8)(1 - \theta)^{-2} - 1] \tag{33}$$

in the particular case of a disco-rectangle, its shape factor being calculated as $\alpha = [2(\gamma - 1) + \pi]^2 [2\pi(\gamma - 1 + \pi/4)]^{-1}$.

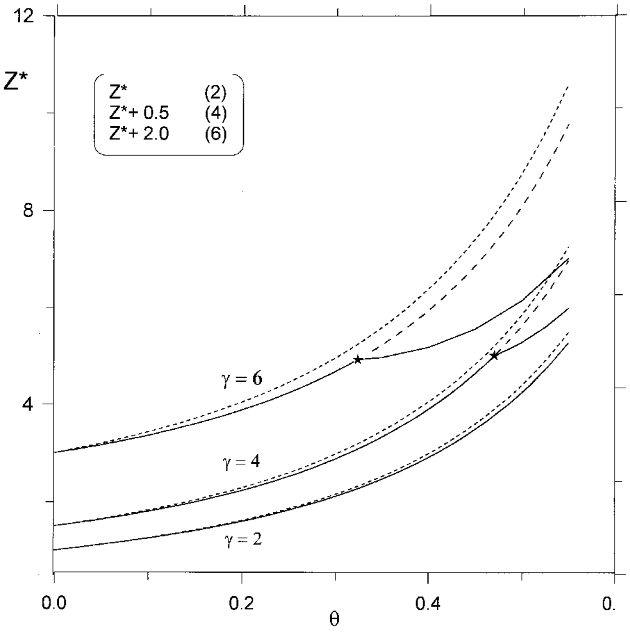


Figure 6. Compressibility factor for hard rectangles and for hard disco-rectangles (with the aspect ratios 2, 4 and 6) as a function of $\theta$. The dashed (short dashes) curves are calculated from equation (32) of [24]. The solid curves correspond to the stable nematic and isotropic phases; the regions of unstable isotropic phases are indicated by the dashed (long dashes) lines (the present model). The branching point on the isotherms is labelled with an asterisk. To separate the curves, the $Z$ scales have been shifted from $Z^*$ ($\gamma = 2$) as $Z^* + 0.5$ ($\gamma = 4$) and $Z^* + 2.0$ ($\gamma = 6$).

As figure 6 shows, equation (33) matches the $Z^{\mathrm{HCB}} - \theta$ data sufficiently well. Also we note that the smaller the value of $\gamma$, the better is the conformity of the data. However, it should be mentioned that equation (33) derived in [24] is accurate only upto the second virial coefficient. At the same time, the 3D version of the present model, as is shown in [26], is identical with the approach based on the third order truncation of the $Y$-series given by Gelbart and Barboy [34].

The continuous transition to the orientationally ordered state (figure 6) starts at the surface density $\theta^*$. For rectangles with continuous orientations, no $Z^{\mathrm{HR}} - \theta$ data in the nematic state are available, but it is evident that for the present discrete orientation model, the system is considerably more ordered than is the hard ellipse fluid with a continuous range of allowed orientations [12]; such a system has been studied within the density-functional theory. This is not surprising since most of the orientational disorder in the latter fluid is due to small deviations from the preferred orientation and such deviations are not permitted in the present approach.

It should be remarked that the effect of discretization in positions and/or orientations of molecules has been recently discussed at length in Sear's treatment of a 3D fluid composed of hard rods or discs [35]. It has been shown, that even for off-lattice particles, restricting their orientations changes their physical behaviour, at least for highly anisometric particles. In particular, lattice versions of off-lattice systems are not suited for studying translational ordering found in translationally ordered liquid crystal phases. For the present model, further work is necessary to examine peculiarities of the phase behaviour of a 2D hard rectangle fluid as a means of studying relevant 2D off-lattice systems.

In conclusion of this section, we compare an equation of state of a gas consisting of parallel squares with that obtained by Ree and Hoover [33]. Using (31) for the compressibility factor, $Z^{\mathrm{HS}}$, of such a fluid, one obtains:

$$Z^{\mathrm{HS}} = (1 - \theta)^{-2} = 1 + 2\theta + 3\theta^2 + 4\theta^3 + \dots$$

while in accordance with [35] it holds that

$$\begin{aligned} Z^{\mathrm{HS}} &= (1 + \theta - 1.5\theta^2)(1 - \theta)^{-2} + \ln(1 - \theta) \\ &= 1 + 2\theta + 3\theta^2 + 3.(6)\theta^3 + \dots \end{aligned}$$

One can see that the present approach provides the factor $Z^{\mathrm{HS}}$ which is accurate up to the third virial coefficient; the values of the fourth virial coefficient differ by less than 10%.

## 5. Conclusion

One of the objectives of this work is to show that a straightforward application of the Flory–Huggins probability method need not lead to inconsistent thermodynamics for a 2D ensemble of particles having the form other than linear chains. The statistics of a multicomponent hard rectangle fluid proposed in this paper is useful by itself, as well as being a meaningful consideration in modelling of an adsorbed monolayer. Such a lattice model offers a plausible frame within which attractive interactions may be included using the Bragg–Williams or quasi-chemical approximations. As to the continuum version of the lattice model, the generalized van der Waals approach which was elaborated for the case of 3D nematic mixtures [36] would seem to treat angle dependent interparticle attractions in the most explicit manner. Addition of other kinds of interactions to hard body fluids under study will presumably result in an approach useful for investigations of monolayers and thin films on a molecular level.

## Appendix 1

*A*. Consider a 2D off-lattice $m$-component system composed of $\{N_k\} = N_1, \dots, N_m$ rectangles constrained on a surface area $A$ at temperature $T$. Let each particle be allowed to point in only $n = 2$ discrete orientations. In the spirit of the treatment of a hard particle 3D fluid elaborated by Zwanzig [36] and Cotter [37], the configurational partition function of the system under consideration may be written as

$$Z_{\{N_k\}} = \left(n^N / \prod_{k=1}^{m} N_k!\right) \sum_{N_{11}} \cdots \sum_{N_{nm}} \prod_{k=1}^{m} \frac{N_k!}{N_{1k}! \dots N_{nk}!} \times \int \mathrm{d}\vec{r}^N \exp(-\beta U_N) \tag{A1}$$

where $\vec{r}^N$ abbreviates the set of all positions, and $U_N$ is the potential energy of interaction of all particles. The sums over all possible orientational distributions $\{N_{11}, N_{21}, \dots, N_{nm}\}$ are restricted by normalization conditions $\Sigma_{\alpha=1}^{2} N_{\alpha k} = N_k$.

The configurational partition function can be approximated by the largest term in the sum. Using the notations of § 2, expression (A1) can be rewritten as

$$Z_{\{N_\lambda\}} = \left(n^N / \prod_{\lambda} \bar{N}_\lambda!\right) \int d\vec{r}^N \exp[-\beta U_N(\vec{r}^N; \{\bar{N}_\lambda\})]. \tag{A2}$$

Here the tildes denote the set $\{N_{11}, N_{21}, \dots, N_{nm}\}$ corresponding to the maximum term in (A1).

Let us view this system on a square lattice of $M = A/\Delta u$ sites. The accuracy of locating a mass centre of a particle equals $\Delta u$, the size of a lattice cell. Then integration over coordinates in $Z_{\{N_\lambda\}}$ reduces to the summation over configurations of a 2D lattice gas, and expression (A2) becomes

$$Z_{\{N_\lambda\}} = (\Delta u)^N / \left(n^N \prod_{\lambda} \bar{N}_\lambda!\right) \sum_{\{U_N\}} g_{\mathrm{d}}(\{\bar{N}_\lambda\}; M) \times \exp(-\beta U_N) \tag{A3}$$

where the summation is carried out over all values of the configurational energy with the most probable orientational distribution $\{\bar{N}_\lambda\}$.

In a system of non-attracting hard particles, the term $g_{\mathrm{d}}(\{\bar{N}_\lambda\}; M)$ in (A3) equals the number of distinguishable ways of arranging $\{\bar{N}_\lambda\}$ particles on a lattice. Thus, (A3) reduces to the expression

$$Z_{\{N_\lambda\}} = (\Delta u)^N \left(n^N \prod_{\lambda} \vec{N}_\lambda!\right)^{-1} g_{\mathrm{d}}(\{\vec{N}_\lambda\}; M). \tag{A4}$$

From equation (A4), the configurational contribution to the Helmholtz free energy for the system under consideration becomes

$$F_{\mathrm{latt}} = -kT \ln[g(\{N_\lambda\}; M)\ (\Delta u)^N / n^N] \tag{A5}$$

where $g(\{N_\lambda\}; M) = g_{\mathrm{d}}(\{N_\lambda\}; M) / \Pi_\lambda N_\lambda!$.

Equation (A5) is essentially equation (1).

*B*. The transition to the continuous translations of the mass centres of particles can be performed by taking the limit ($z = w/a$, $a$ is the unit length):

$$F_{\mathrm{conf}} = \lim_{\Delta u \to 0} F_{\mathrm{latt}} = \lim_{z \to 0} F_{\mathrm{latt}}. \tag{A6}$$

Let us represent the terms $N_0$ and $B_n$ ($n = 1, 2, 12$) of expression (9) in the form

$$N_0 = \left(\sum f_\lambda N_\lambda\right) Z_0 / z^2, \quad N_0 + B_n = \left(\sum f_\lambda N_\lambda\right) Z_n / z^2 \tag{A7}$$

where $f_\lambda = L_\lambda z^2$ is the dimensionless area covered by an object $\lambda$, $Z_0 = \theta^{-1} - 1$, $Z_i = Z_0 = zb_i$ $(i = 1, 2)$, $Z_{12} = Z_0 + z(b_1 + b_2) - z^2 \bar{\bar{Z}}_\lambda(\theta_\lambda / f_\lambda \theta)$, $b_i = \Sigma_\lambda\, \theta_\lambda / \theta f_\lambda^{(i)}$.

Here $f_\lambda^{(i)} = r_\lambda^{(i)} z$ is the dimensionless edge of an object $\lambda$ along the direction $i$, $\theta_\lambda = L_\lambda N_\lambda / M = f_\lambda N_\lambda / \tilde{A}$, $(\tilde{A} = A/a^2)$ is the fraction of the total surface covered with objects $\lambda$.

Combining expression (12) and notations (A7), together with the Stirling formula one can rewrite equation (A6) as follows:

$$\beta F_{\mathrm{conf}} = -\lim_{z\to 0}\left\{\sum_{\lambda} f_{\lambda} N_{\lambda}\left[\sum_{n} h_{n}(Z_{n}\ln Z_{n} - Z_{n})/z^{2}\right]\right\} + \sum_{\lambda} N_{\lambda}(\ln 2N_{\lambda} - 1) - \sum_{\lambda} N_{\lambda}\ln\sum_{\lambda} u_{\lambda} N_{\lambda} \tag{A8}$$

where $h_1 = h_2 = -h_0 = -h_{12} = 1$; $u_{\lambda} = f_{\lambda} a^2$ is the surface area of an object $\lambda$.

Finally, using the L'Hospital rule for the evaluation of the factor $\Sigma_n h_n(Z_n \ln Z_n - Z_n)$ in expression (A8), one gets an expression identical with (28):

$$\beta F_{\mathrm{conf}} = \sum_{\lambda} N_{\lambda}\left(-1 + f_{\lambda} b_1 b_2 \frac{\theta}{1-\theta} + \ln\frac{\theta}{1-\theta} + \ln\frac{n'_{\lambda}}{\theta}\right)$$

where $n'_{\lambda} = N_{\lambda}/A$.

## Appendix 2

Here we verify the Maxwell relations (3) for both the counting procedures for the numbers $v_{\lambda}$ discussed in §2. In the mean field approximations, after substitution of relations (7), (8) and (9) in expression (2) and differentiation, one obtains

$$\frac{\partial \ln v_{\lambda}}{\partial X_{\delta}} = -\frac{L_{\lambda} L_{\delta}}{X_0} + \sum_{i=1}^{2}\frac{(r_{\lambda}^{(i)} - 1)(L_{\delta} - r_{\delta}^{(j)})}{X_0 + B_i} + \frac{\prod_{i=1}^{2}(r_{\lambda}^{(i)} - 1)(r_{\delta}^{(i)} - 1)}{X_0 + B_{12}}. \tag{A9}$$

After permutation of subscripts $\lambda$ and $\delta$ one can see that in this case the relations (3) are not satisfied. However, using expression (10) derived within the proposed version of the Flory–Huggins procedure one gets:

$$\frac{\partial \ln v_{\lambda}^{*}}{\partial X_0} = -\frac{L_{\lambda} L_{\delta}}{X_0} + \sum_{i=1}^{2}\frac{(L_{\lambda} - r_{\lambda}^{(j)})(L_{\delta} - r_{\delta}^{(j)})}{X_0 + B_i} - \frac{\prod_{i=1}^{2}(r_{\lambda}^{(i)} - 1)(r_{\delta}^{(i)} - 1)}{X_0 + B_{12}}. \tag{A10}$$

The derivative (A10) is now symmetric with respect to change of $\lambda$ and $\delta$.

## Appendix 3

In the context of the problem discussed in [19, 23], we show here that expression (13) is independent of the manner of placing the squares and rods onto the square lattice.

First, we determine the combinatorial factor by placing all $N_2 = N_{12} + N_{22}$ rods initially before all $N_1$ square plates are placed. The total number of ways to arrange $N_{12}$ rods in direction 1 and $N_{22}$ rods in direction 2 is given by expression (14). The number of ways of then placing the $N_1$ squares is

$$h_{\mathrm{RS}} = (N_1!)^{-1}\prod_{m=0}^{N_1 - 1} v_{\mathrm{S}}^{\bullet}(m+1, \{N_{\alpha 2}\}) \tag{A11}$$

where $v_{\mathrm{S}}^{\bullet}(m+1, \{N_{\alpha 2}\})$ is the number of cells available to the $(m+1)$th square given that $N_2$ rods and $m$ squares are introduced.

By using expressions (8–11) one gets:

$$v_{\mathrm{S}}^{\bullet} = \frac{(X_0^{\bullet})^{r^2}(X_0^{\bullet} + 2rm + rN_2 - m)^{(r-1)^2}}{\prod_{\alpha=1}^{2}(X_0^{\bullet} + rm + N_{\alpha 2} + rN_{\beta 2})^{r(r-1)}}(\beta \neq \alpha) \tag{A12}$$

where $X_0^{\bullet} = M - r^2 m - rN_2$ is the number of vacant cells.

Upon inserting (A12) and applying standard methods, the product (A11) becomes:

$$h_{\mathrm{RS}} = \frac{M!}{N_0!N_1!}\frac{(M - rN_2)!}{[M - (r-1)^2 N_1]!} \times \frac{\prod_{\alpha}[M - r(r-1)N_1 - (r-1)N_{\alpha 2}]!}{\prod_{\alpha}[M - (r-1)N_{\alpha 2}]!}. \tag{A13}$$

Multiplying $g_{\mathrm{R}}$ from expression (14) with $h_{\mathrm{RS}}$ from (A13) one gets:

$$g_{\mathrm{R}}\ h_{\mathrm{RS}} = \frac{\prod_{\alpha}[M - r(r-1)N_1 - (r-1)N_{\alpha 2}]!}{N_0!N_1!N_{12}!N_{22}![M - (r-1)^2 N_1]!} = g(N_1, \{N_{\alpha 2}\}; M). \tag{A14}$$

Expression (A14) is identical with formula (13).

Further, we calculate the combinatorial factor by introducing $N_1$ squares initially before $N_{12}$ and $N_{22}$ rods are placed.

The total number of ways to place $N_1$ squares on to an empty lattice is given by expression (15). The number of ways of then placing the $N_{12}$ rods in direction 1 is:

$$h_{\mathrm{SR}_1} = (N_{12}!)^{-1}\prod_{m=0}^{N_{12} - 1} v_{\mathrm{R}_1}^{\bullet}(N_1, m+1, N_{22} = 0) \tag{A15}$$

where $v_{\mathrm{R}_1}^{\bullet}$ $(N_1, m+1, N_{22} = 0)$ is the number of cells available to the $(m+1)$th rod in direction 1, given that $N_1$ squares and $m$ rods are introduced.

Upon applying equations (8) and (9) to rods having $r \times 1$ segments, one obtains:

$$v_{\mathrm{R}_1}^{\bullet} = (X_0^{\bullet\bullet})^{r}/(X_0^{\bullet\bullet} + rN_1 + m)^{r-1} \tag{A16}$$

where $X_0^{\bullet\bullet} = M - r^2N_1 - rm$ is the number of empty cells.

From equations (A15) and (A16) there follows:

$$h_{\mathrm{SR}_1} = \frac{(M - r^2N_1)![M - r(r-1)N_1 - (r-1)N_{12}]!}{N_{12}!(M - r^2N_1 - rN_{12})![M - r(r-1)N_1]!}. \tag{A17}$$

Similarly, the number of ways, $h_{\mathrm{SR}_2}$, of placing the remaining $N_{22}$ rods in direction 2 is:

$$h_{\mathrm{SR}_2} = \frac{(M - r^2N_1 - rN_{12})![M - r(r-1)N_1 - (r-1)N_{22}]!}{N_{22}![M - r^2N_1 - r(N_{12} + N_{22})]![M - r(r-1)N_1]!}. \tag{A18}$$

The product of $g_{\mathrm{S}}$, expression (15), $h_{\mathrm{SR}_1}$ and $h_{\mathrm{SR}_2}$ yields again the result, which is identical with expressions (A14) and (13).

Generalization to a multicomponent case can be performed similarly.

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