

Oriental correlations in the lattice gas of angular trimers on the square lattice

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys. A: Math. Gen. 29 485

(<http://iopscience.iop.org/0305-4470/29/3/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.71

The article was downloaded on 02/06/2010 at 04:08

Please note that [terms and conditions apply](#).

Orientalional correlations in the lattice gas of angular trimers on the square lattice

Klaus Froböse, Frank Bonnemeier and Josef Jäckle

Universität Konstanz, Fakultät für Physik, Postfach 5560 M 680, D-78434 Konstanz, Germany

Received 6 September 1995, in final form 6 November 1995

Abstract. The ordering tendency of a lattice gas of angular trimers on the square lattice is investigated by calculating the entropy, the density and two static orientational susceptibilities, using transfer matrix methods and a Bethe–Peierls approximation. It is concluded that an order–disorder phase transition does not occur, and only weak orientational order exists. The lattice gas of angular trimers is proposed as a two-dimensional model for a glass-forming molecular liquid like liquid ortho-terphenyl.

1. The model

The tendencies of molecular liquids to form both liquid crystals and glasses depends crucially on the geometric shape of the constituent molecules. A non-spherical molecular shape may facilitate the formation of an ordered non-crystalline structure, as occurs in liquid–crystalline phases. On the other hand, it may impede the process of crystallization so much that a stable glass can be formed. While a complicated shape of the molecules generally suppresses the crystallization of a molecular liquid, the question of ordering requires a special investigation. In this paper such an investigation is carried out theoretically on the level at which molecular liquids are modelled by lattice gases with units occupying more than one lattice site.

The classic example of such a model is the lattice gas of dimers on the square lattice [1–9]. Here we examine a lattice gas on the same two-dimensional lattice with units of more complicated shape, angular trimers (figure 1). The angular trimers represent molecules of angular shape like ortho-terphenyl (which consists of three benzene rings) [10]. Liquid ortho-terphenyl is a good glass former because the interlocking of molecules impedes crystallization. Whether our lattice gas can be considered as a (two-dimensional) model of such a glass-forming liquid depends on the amount of ordering which occurs in it. A phase transition into a phase with orientational order at high packing density would disqualify the model for this purpose. We therefore investigate the tendency for ordering in this lattice gas by calculating various static quantities which are sensitive to ordering, namely the entropy, the activity and two different static orientational susceptibilities.

The paper is organized as follows. In section 2 we determine the configurational entropy at maximum concentration $c_{\max} = \frac{1}{3}$ by calculating for strips of width W the number of ways in which the molecules may be arranged in the completely filled lattice. Both periodic ($2 \leq W \leq 18$) and fixed boundary conditions ($2 \leq W \leq 16$) are considered.

The rest of the paper is devoted to systems with varying concentration c between 0 and c_{\max} . The calculation of the concentration c as a function of the activity z and the entropy per lattice site s as a function of the concentration is performed by two different

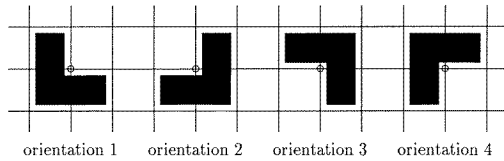


Figure 1. The four orientations of angular trimers. The circles denote the position of the centres of the molecules.

methods: (i) the transfer matrix method (section 3), and (ii) an extension of the Bethe–Peierls approximation (section 4). Using the transfer matrix method, in addition two static susceptibilities with respect to different types of orientation-dependent external fields are calculated (section 3.3). Section 5 contains the conclusion.

2. The entropy of the full lattice

In this section we calculate the configurational entropy per particle s for close-packed infinitely long strips of width W . The value for the infinite lattice is obtained by extrapolation of the entropy to the limit $W \rightarrow \infty$.

Following a method due to Fowler and Rushbrooke [11, 12], which they applied to the dimer problem, we count the number of ways a strip of width W can be filled completely by molecules. We consider the first $(L - 1)$ rows of the strip to be completely filled already. Since the triangular molecules extend over two rows, in general some of the molecules occupying sites in row $(L - 1)$ stick out into row L and occupy some sites there. We denote the configuration of empty and occupied sites in row L by a . Since it is possible that no molecule sticks out into row L , the ‘all-empty’ configuration, which we denote by a_0 , must also be taken into account. It is also possible that the molecules sticking into the L th row fill this row completely, producing the ‘all-occupied’ configuration of that row. Let the number of ways in which a general state can be generated be $N(W, L; a)$. For $L = 1$ we have

$$N(W, 1; a) = \delta_{a, a_0} \quad (2.1)$$

since it is not possible for the molecules to occupy only sites in one row.

By filling all empty sites in the L th row, a certain configuration of empty and occupied sites is generated in row $(L + 1)$. We denote this configuration of empty and occupied sites by a' . The number of ways in which configuration a' in row $(L + 1)$ can be generated by filling molecules on the empty sites in configuration a in the L th row defines a transfer matrix $T(a', a)$. If a is the ‘all-occupied’ configuration, no molecule can be added so that row $(L + 1)$ remains in the ‘all-empty’ configuration a_0 . This must be counted as one way. Formally, therefore, if a is the ‘all-occupied’ configuration,

$$T(a', a) = \delta_{a', a_0} \quad (2.2)$$

holds. The number of ways $N(W, L + 1; a')$ in which the first L rows of the strip can be completely filled with configuration a' of empty and occupied sites on row $(L + 1)$ (and no occupied sites on row $(L + 2)$), can now be expressed by $N(W, L; a)$ and the transfer matrix as

$$N(W, L + 1; a') = \sum_a T(a', a) N(W, L; a). \quad (2.3)$$

For a rectangle of length L we therefore get

$$N(W, L; a') = \sum_a (T^{L-1})_{a', a} \delta_{a, a_0} \quad (2.4)$$

where T is a matrix in the space of vacancy distributions of a row with elements $T(a', a)$. It can be shown that the largest eigenvalue of the matrix T determines the configurational entropy per line in the limit $L \rightarrow \infty$.

For the cases $W = 2$ and $W = 3$ the eigenvalue problem can be solved analytically, for larger values of W the matrix T and its largest eigenvalue were determined by a computer program. In this program a configuration a of empty and occupied sites is mapped to a pattern of 0-bits (empty) and 1-bits (occupied) in a computer word A . Interpreting the bit pattern as a number, it may be used for the enumeration of the configurations. The filling procedure starts with image A of configuration a in the L th row and image $A' = 0$ of the configuration a' in the $(L + 1)$ th, which is empty at the beginning. A particle is inserted by replacing in A either a 0-bit by a 1-bit or a pair of adjacent 0-bits by a pair of 1-bits, according to the orientation of the inserted molecule. In the same way that part of the molecule which belongs to the next row is inserted into A' . The filling is performed in all possible distinct ways. For each filled A , i.e. a sequence of W 1-bits in A , the resulting A' is recorded, which gives a contribution of 1 to $T(a', a)$. The largest eigenvalue of $T(a', a)$ is determined by repeated multiplication of an arbitrary starting vector by $T(a', a)$.

The numerical results for the entropy per lattice site in the case of *periodic* boundary conditions are presented in the second column of table 1. The values show oscillations with decreasing amplitude when the width increases. For widths $W > 13$ the oscillations are so small that we may take the value for $W = 18$ as the limiting value for $W \rightarrow \infty$. Thus we get

$$s_{\infty} = 0.27693150 \pm 0.00000005 \quad (2.5)$$

where the error is estimated from the variation for the five largest W values.

In order to extrapolate the results for the entropy per lattice site for *fixed* boundary conditions to the case of strips of infinite width, we assume that the total entropy contains two contributions: one, which is proportional to the volume, and a second one, which is

Table 1. Entropy per site for completely filled strips of width W with periodic and fixed boundary conditions.

Width	Periodic boundaries	Fixed boundaries
2	0.34657359	0.1155245
3	0.29862658	0.1155245
4	0.28200180	0.1565662
5	0.27589960	0.1676508
6	0.27864780	0.1917545
7	0.27681051	0.2004126
8	0.27697965	0.2105052
9	0.27697335	0.2177875
10	0.27693779	0.2236694
11	0.27692921	0.2284793
12	0.27693544	0.2325368
13	0.27693116	0.2359397
14	0.27693162	0.2388696
15	0.27693162	0.2414068
16	0.27693151	0.2436270
17	0.27693148	—
18	0.27693150	—

proportional to the surface, i.e. the length L of the strip:

$$S_W = s_\infty L W + \beta L \quad (2.6)$$

where s_∞ is the entropy per lattice site for a strip of infinite width, and the constant β has the meaning of a specific surface entropy. Thus we expect that the entropy per lattice site s_W for strips of finite width W depends on W according to

$$s_W = s_\infty + \frac{\beta}{W}. \quad (2.7)$$

The validity of (2.7) is tested by plotting the values for the entropy per lattice site versus $1/W$ in figure 2. Taking for s_∞ the value obtained from periodic boundary conditions (2.5) and using only the data for the six largest W values, we find for the surface entropy per row

$$\beta = -0.5329 \pm 0.0001. \quad (2.8)$$

This contribution is negative, because the surface imposes some orientational order in the arrangement of the molecules.

For comparison, we calculate the entropy per lattice site $s_{\text{ideal}}(c)$ of an ideal lattice gas of molecules with four different independent orientations, which is given by

$$s_{\text{ideal}}(c) = -c \ln(c) - (1 - c) \ln(1 - c) + c \ln(4). \quad (2.9)$$

For $c = c_{\text{max}}$ we obtain

$$s_{\text{ideal}}(c_{\text{max}}) = \ln(3) = 1.099 \quad (2.10)$$

where the contribution of the entropy of mixing is 0.637 and the orientational entropy is 0.462. The actual s_∞ is smaller than either contribution and is only about a quarter of their sum. Interestingly, s_∞ is close to the entropy per site for a square lattice filled with dimers, which is 0.29 [3, 4]. In view of these similar entropy values we expect that an order–disorder transition does not occur as for the dimer lattice gas.

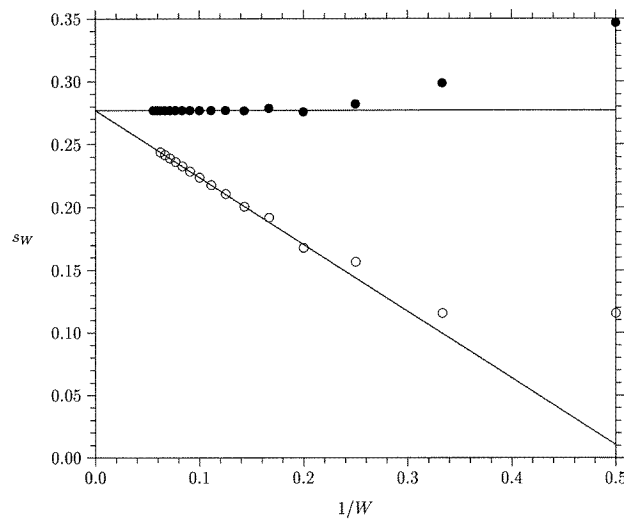


Figure 2. Entropy per site for the completely filled lattice as a function of $1/W$ for periodic (●) and fixed boundary (○) conditions. The horizontal line represents s_∞ . The other line has slope β as given by equation (2.8).

3. The transfer matrix method in general

3.1. The method

In the preceding section we determined the configurational entropy of the full lattice by a transfer matrix method similar to that used by Fowler and Rushbrooke [11]. Here we develop a more general transfer matrix method, which admits the calculation of the entropy for arbitrary densities lower than c_{\max} . Furthermore, this method allows the computation of susceptibilities with respect to external fields, which depend on the orientation of the molecules. A molecule can have four different orientations (figure 1).

We calculate the grand canonical partition function for strips of width W with periodic boundary conditions. The molecules have activities $z_i = e^{\beta\mu_i}$ according to their four orientations i , where μ_i is the corresponding chemical potential.

As in the previous section we consider the first L rows of the strip and assume in the L th row a certain configuration a of empty and occupied sites to be present. The partition function for such a part of the strip is denoted by $Z(W, L; a)$.

Now we extend the rectangle by one row with configuration a' of empty and occupied sites in the $(L + 1)$ th row. All molecular configurations in this larger rectangle are obtained from all molecular configurations of the shorter rectangle with all possible configurations a of empty and occupied sites in the L th row, by filling in trimers on sites of the L th and $(L + 1)$ th row, such that the configuration a' of empty and occupied sites is obtained in the $(L + 1)$ th row.

If $p(n_1, n_2, n_3, n_4; a', a)$ is the number of different ways in which n_i particles with orientation i ($i = 1, 2, 3, 4$) may be inserted into a lattice with the configuration of empty and occupied sites a in the L th row in order to get the configuration of empty and occupied sites a' in the $(L + 1)$ th row, the transfer matrix $T(a', a)$ is given by

$$T(a', a) = \sum_{n_1, n_2, n_3, n_4} p(n_1, n_2, n_3, n_4; a', a) z_1^{n_1} z_2^{n_2} z_3^{n_3} z_4^{n_4}. \quad (3.1)$$

If a' is the 'all-empty' configuration a_0 , no particles must be added, so that

$$T(a_0, a) = 1 \quad \text{for all } a. \quad (3.2)$$

If a is the 'all-occupied' configuration, relation (2.2) holds again. In computational work it is convenient to determine the $p(n_1, n_2, n_3, n_4; a', a)$ only once and to store them for the computation of $T(a', a)$ according to equation (3.1).

The partition function $Z(W, L; a)$ obeys the recursion relation

$$Z(W, L + 1; a') = \sum_a T(a', a) Z(W, L; a). \quad (3.3)$$

Since for $L = 1$ the only configuration is the 'all-empty' configuration, we get

$$Z(W, 1; a) = \delta_{a, a_0}. \quad (3.4)$$

Because of the periodic boundary conditions, some of the configurations of empty and occupied sites are obtained from one another by cyclic permutations. The corresponding partition function is not affected by such a transformation. Selecting from each set of configurations of empty and occupied sites, which are obtained from one another by cyclic permutations, a representative \bar{a} , and denoting the corresponding set of configurations of empty and occupied sites by $\mathcal{S}(\bar{a})$, one can write equation (3.3) as

$$Z(W, L + 1; \bar{a}') = \sum_{\bar{a}} \left(\sum_{a \in \mathcal{S}(\bar{a})} T(\bar{a}', a) \right) Z(W, L; \bar{a}). \quad (3.5)$$

Defining the matrix

$$\mathcal{T}(\bar{a}', \bar{a}) = \sum_{a \in \mathcal{S}(\bar{a})} T(\bar{a}', a) \quad (3.6)$$

the recursion relation (3.3) may be rewritten as

$$Z(W, L + 1; \bar{a}') = \sum_{\bar{a}} \mathcal{T}(\bar{a}', \bar{a}) Z(W, L; \bar{a}). \quad (3.7)$$

The total partition function is given by

$$Z(W, L) = \sum_{\bar{a}'} \sum_{a' \in \mathcal{S}(\bar{a}')} Z(W, L; a'). \quad (3.8)$$

In the limit $L \rightarrow \infty$ we get

$$Z(W, L) = A \lambda(z_1, z_2, z_3, z_4)^L \quad (3.9)$$

where A is a constant and $\lambda(z_1, z_2, z_3, z_4)$ is the largest eigenvalue of the matrix $\mathcal{T}(\bar{a}', \bar{a})$. Hence we obtain in the thermodynamic limit

$$\frac{p}{k_B T} = \lim_{L \rightarrow \infty} \frac{\ln(Z(W, L))}{W L} = \frac{\ln(\lambda(z_1, z_2, z_3, z_4))}{W}. \quad (3.10)$$

3.2. Calculation of the concentration and the entropy

From the expression (3.10) the concentration c_i of the particles with orientation i can be calculated by numerical differentiation:

$$c_i = \lim_{L \rightarrow \infty} z_i \frac{\partial \ln(Z(W, L))}{\partial z_i} \frac{1}{W L} = z_i \frac{\partial \ln(\lambda(z_1, z_2, z_3, z_4))}{\partial z_i} \frac{1}{W}. \quad (3.11)$$

However, the concentration can also be derived in a different way, if the eigenvector belonging to the largest eigenvalue is available. This is the case in our calculation. Since $\mathcal{T}(\bar{a}', \bar{a})$ is not a symmetric matrix, there are in fact two eigenvectors, a right one $v_R(\bar{a})$ and a left one $v_L(\bar{a}')$ for the same largest eigenvalue λ , which fulfil the relations

$$\lambda v_R(\bar{a}') = \sum_{\bar{a}} \mathcal{T}(\bar{a}', \bar{a}) v_R(\bar{a}) \quad (3.12)$$

$$\lambda v_L(\bar{a}) = \sum_{\bar{a}'} \mathcal{T}(\bar{a}', \bar{a}) v_L(\bar{a}'). \quad (3.13)$$

The eigenvectors are supposed to be normalized, so that

$$\sum_{\bar{a}} v_L(\bar{a}) v_R(\bar{a}) = 1. \quad (3.14)$$

With this assumption we get

$$\begin{aligned} z_i \frac{\partial}{\partial z_i} \ln(\lambda(z_1, z_2, z_3, z_4)) &= z_i \frac{\partial}{\partial z_i} \sum_{\bar{a}', \bar{a}} v_L(\bar{a}') \mathcal{T}(\bar{a}', \bar{a}) v_R(\bar{a}) \\ &= \sum_{\bar{a}, \bar{a}'} v_L(\bar{a}) \left(z_i \frac{\partial}{\partial z_i} \mathcal{T}(\bar{a}, \bar{a}') \right) v_R(\bar{a}') \end{aligned} \quad (3.15)$$

where the remaining terms cancel to 0 because of the relations (3.12)–(3.14). According to equation (3.1) the derivative $z_i \frac{\partial}{\partial z_i} \mathcal{T}(\bar{a}', \bar{a})$ can be performed analytically. Since the probabilities $p(n_1, n_2, n_3, n_4; \bar{a}', a)$ are purely combinatorial and do not depend on the activities z_i , we get

$$z_i \frac{\partial}{\partial z_i} \mathcal{T}(\bar{a}', \bar{a}) = \sum_{a \in \mathcal{S}(\bar{a})} \sum_{n_1, n_2, n_3, n_4} p(n_1, n_2, n_3, n_4; \bar{a}', a) z_1^{n_1} z_2^{n_2} z_3^{n_3} z_4^{n_4} n_i. \quad (3.16)$$

The concentration c as a function of $u = z/(1+z)$ with $z = z_1 = z_2 = z_3 = z_4$ has been calculated for strips of width W from 3 to 11. The result for $W = 11$ is shown in figure 3. Within the resolution of the figure the results for $W = 9$ and $W = 10$ cannot be distinguished. So we may take this figure also for the limiting case $W \rightarrow \infty$.

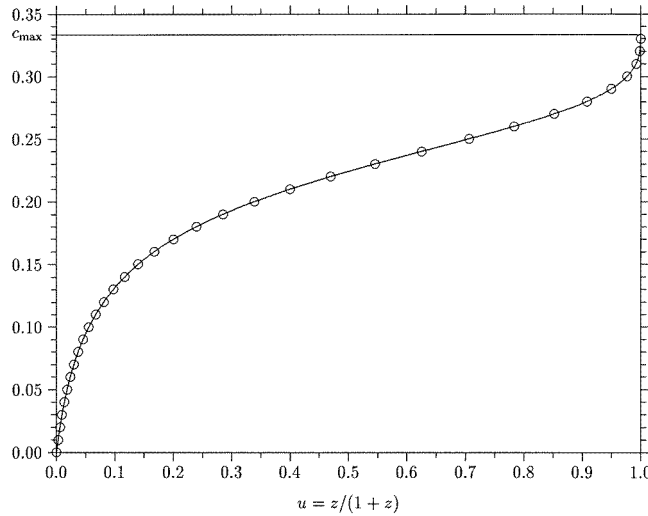


Figure 3. Concentration as a function of $u = z/(z+1)$ calculated by the transfer matrix method for a strip of width $W = 11$. Within the resolution of the graph there is no difference to the results for $W = 9$ and $W = 10$. The results from the Bethe–Peierls approximation (section 4) are represented as circles. They also coincide within the resolution of the graph.

Note that the slope of the curves at $u = 1$ is ∞ . Near to this singularity we find

$$\frac{1}{3} - c(u) \propto (1-u)^{1/3}. \quad (3.17)$$

As can be seen from figure 3 the curves agree remarkably well with the data, which are obtained from the Bethe–Peierls approximation (see section 4), which are drawn as circles.

The entropy per lattice site $s(c)$ is related to the largest eigenvalue by

$$s = k_B \left(\frac{1}{W} \ln(\lambda(z_1, z_2, z_3, z_4)) \Big|_{z_1=z_2=z_3=z_4=z} - c \ln(z) \right) \quad (3.18)$$

which is obtained from equation (3.10). The entropy per lattice site as a function of the concentration c of a strip of width $W = 11$ is shown in figure 4. For low densities the entropy is an increasing function of the concentration. Above $c \approx 0.22$ the entropy decreases with increasing concentration and drops to its final value at $c = c_{\max}$, which was calculated independently in section 2. Again, there is no visible difference to the cases $W = 9$ and $W = 10$, so that we take this figure again as the limiting case $W \rightarrow \infty$. In order to compare this result to the entropy of an ideal lattice gas in which the molecules may have four independent orientations (equation (2.9)) we show the reduced entropy $s_{\text{red}} = s/s_{\text{ideal}}$ in the inset. As is expected this function starts with 1 at low densities. It drops to about $\frac{1}{4}$ at the maximum concentration. As was already stated in the previous section this value implies an appreciable degree of disorder, so that we do not expect an ordering phase transition.

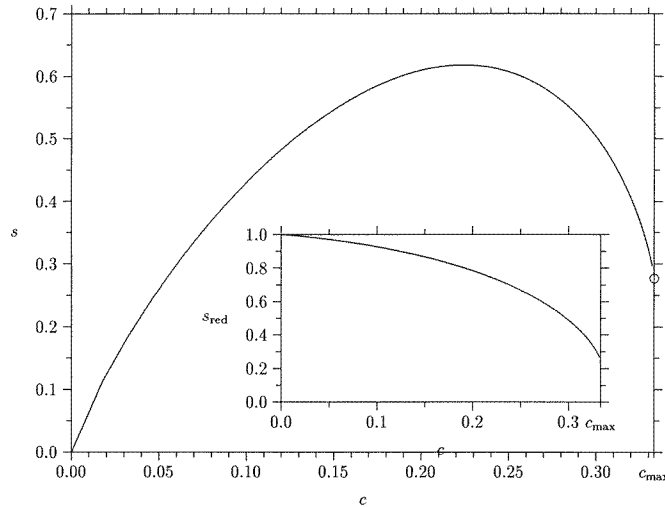


Figure 4. Entropy per lattice site as a function of c calculated by the transfer matrix method for a strip of width $W = 11$. Within the resolution of the graph there is no difference between the results for $W = 9$ and $W = 10$. The circle at c_{\max} marks $s(c_{\max})$ as derived in section 2. The inset shows the reduced entropy $s_{\text{red}}(c)$, which is explained in the text.

3.3. Calculation of the susceptibilities

More reliable information about a tendency towards an ordering phase transition is available from the susceptibilities. They are calculated by applying weak external fields A_i to the molecules according their orientation i . The response of the densities of the corresponding particles, due to the changes of the potential energy, determines the susceptibility. However, there is the constraint that the total density must not be changed.

Among the various possibilities of defining susceptibilities two special cases are selected:

(i) The molecules are considered as acting like electric dipoles in an electric field. The particles with one specified orientation (e.g. orientation 1) experience a rise of energy A , when the external field is applied, whereas the energy of the particles with opposite orientation (orientation 3) is decreased by the same amount. The energy of the remaining particles is not affected.

In this case the total density is not changed to linear order of the perturbing field. The quantity $M_1 = c_1 - c_3$ plays the role of the ‘magnetization’ per volume, so that the susceptibility per particle is given by

$$k_B T \chi_1 = \frac{1}{c} \left(\frac{\partial M_1}{\partial A} \right)_{A=0}. \quad (3.19)$$

In figure 5 we present the results for $\chi_1(c)$ for a strip of width $W = 11$. The curves for $W = 9$ and $W = 10$ differ only slightly from those for the case $W = 11$.

We may attribute an orientation variable $\sigma_n^{(1)}$ to the sites n which is 0 for empty sites, 1 if the site is occupied by a molecule of orientation 1, -1 if it is occupied by a molecule of orientation 3, and 0 otherwise. In terms of this orientational variable the activity of a particle at site n may be expressed as

$$z(n) = z e^{-\beta \sigma_n^{(1)} A}. \quad (3.20)$$

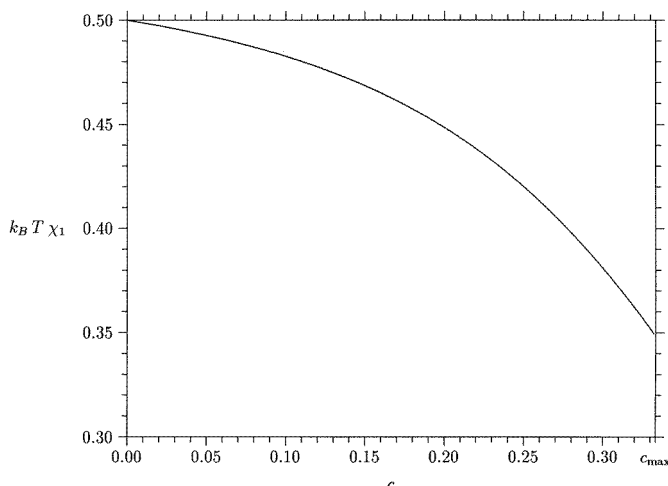


Figure 5. χ_1 as a function of c calculated by the transfer matrix method for a strip of width 11.

In this case the susceptibility χ_1 can be expressed as

$$k_B T \chi_1 = \frac{1}{c V} \sum_{n,m} \langle \sigma_n^{(1)} \sigma_m^{(1)} \rangle = \frac{1}{2} + \frac{2}{c V} \sum_{n>m} \langle \sigma_n^{(1)} \sigma_m^{(1)} \rangle. \quad (3.21)$$

Here the first term $\langle (\sigma_n^{(1)})^2 \rangle = \frac{1}{2}$ represents $k_B T \chi_1$ in the absence of orientational correlations. The second term is due to correlations. Since it is negative, the correlations are predominantly negative. In the case of close packing the reduction is largest and amounts to about 30%. Assuming that orientational correlations decrease rapidly with molecular distance, we conclude that pairs of antiparallel molecules with nearest neighbour (figure 6a) and next-nearest neighbour position of their centres occur more frequently than pairs of parallel molecules with next-nearest neighbour position of their centres (figure 6b). At the maximum concentration pairs of antiparallel molecules with next-nearest neighbour position of their centres do not exist.

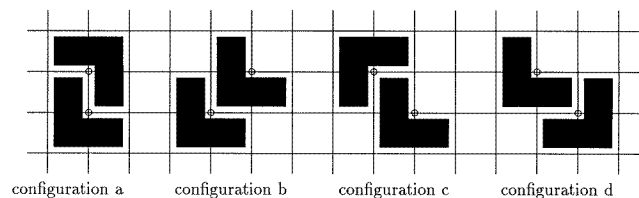


Figure 6. Nearest (a) and next-nearest neighbour configurations (b, c, d) of angular trimers. In configuration a the molecules are antiparallel, in configuration b they are parallel.

(ii) We assume that molecules with either of two opposite orientations (e.g. orientations 1 and 3) gain the energy A in an external field, so that we have

$$z_1 = z_3 = z_2 e^{-\beta A} \quad z_2 = z_4. \quad (3.22)$$

This perturbation is analogous to the interaction of electric quadrupoles with an electric field gradient.

In order to keep the total density fixed, the activity z must be appropriately chosen. With

$$z_1 = z_3 = z e^{-\beta A/2} \quad z_2 = z_4 = z e^{A/2} \quad (3.23)$$

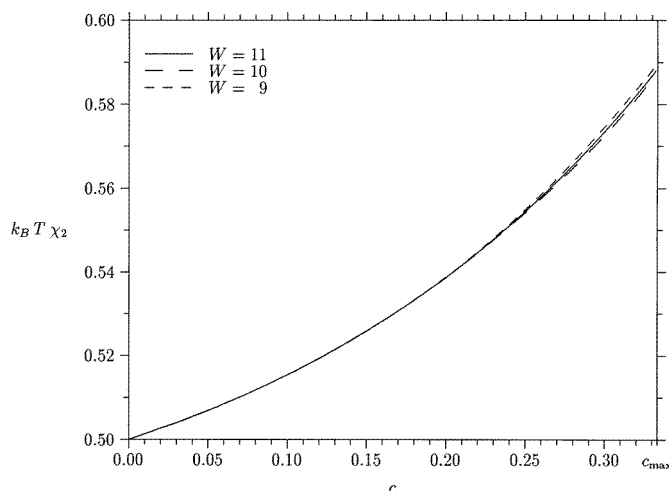


Figure 7. χ_2 as a function of c calculated by the transfer matrix method for strips of width $W = 9, 10, 11$.

there is no change in the concentration to first order in A . The ‘magnetization’ M_2 per volume in terms of the partial concentrations is defined as $M_2 = c_1 + c_3 - c_2 - c_4$. The susceptibility χ_2 per particle is thus obtained as

$$k_B T \chi_2 = \frac{1}{c} \left(\frac{\partial M_2}{\partial A} \right)_{A=0}. \quad (3.24)$$

In figure 7 we present the results for $k_B T \chi_2(c)$ for strips of width $W = 9, 10$ and 11 . A small dependence on the width is observable, indicating that the susceptibility is a more sensitive quantity than the concentration or entropy. For the interpretation of this result we attribute to a site n a second ‘orientational’ variable $\sigma_n^{(2)}$, which is 0 for unoccupied sites, 1 if there is a molecule with either orientation 1 or 3, and -1 otherwise. In terms of this orientational variable the activity of a particle at site n may be expressed as

$$z(n) = z e^{-\beta \sigma_n^{(2)} A/2}. \quad (3.25)$$

For the susceptibility per particle we then obtain

$$k_B T \chi_2 = \frac{1}{2c} \frac{1}{V} \sum_{n,m} \langle \sigma_n^{(2)} \sigma_m^{(2)} \rangle = \frac{1}{2} + \frac{1}{cV} \sum_{n>m} \langle \sigma_n^{(2)} \sigma_m^{(2)} \rangle. \quad (3.26)$$

The first term $\langle (\sigma_n^{(2)})^2 \rangle$ gives $k_B T \chi_2$ in the absence of correlations. Here $k_B T \chi_2$ is enhanced as a result of positive orientational correlations. The enhancement amounts to a maximum of about 20% at close packing. Again we assume that the orientational correlations are appreciable only for nearest and next-nearest neighbour molecules. Now both configurations figure 6a and b yield positive contributions. Negative contributions are obtained from the next-nearest neighbour configurations shown in figures 6c and d. We conclude from the result for χ_2 that configurations a and b have larger statistical weight than configurations c and d. From case (i) we already know that configuration 6a is more frequent than configuration b. The predominance of configuration a is also confirmed by direct inspection of randomly generated configurations.

4. The Bethe–Peierls approximation

In this section we use quite a different approach for the determination of $c(z)$ than in the previous ones. We apply a mean-field method, which is a generalization of the Bethe–Peierls approximation. (For a similar treatment of a simpler problem without an orientational degree of freedom see [13].)

The possible positions of the centres of the molecules, which are indicated in figure 1, also form a square lattice. From this lattice we consider an arbitrary 3×3 cluster. To each site we attribute an activity, which may also depend on the orientation of the occupying molecule, and determine the grand canonical partition function for this cluster by summing over all allowed configurations.

The centre site is attributed the true activity $z_0 = z$. For the rest of the cluster sites we assume that the effective activity deviates from this value because of the influence of the surrounding lattice. Since the influence of the surrounding lattice depends on the position within the cluster, we assume different effective activities for all sites and orientations which are not symmetrically equivalent. We therefore are led to introduce five different effective activities: two for the nearest-neighbour sites and three for the next-nearest neighbour sites.

The partition function Z_{cl} can be expressed in terms of z and the as yet unknown effective activities z_1, \dots, z_5 . The result is a polynomial of degree 4 in the six activities consisting of 105 additive terms.

From the thermodynamic relation

$$\langle n_i \rangle = \frac{z_i}{Z_{\text{cl}}} \frac{\partial Z_{\text{cl}}}{\partial z_i} \quad \text{for } i \in \{0, 1, 2, 3, 4, 5\} \quad (4.1)$$

the average number of particles in the cluster corresponding to the effective activity z_i can be calculated. Since the lattice is homogeneous, the concentration of the particles of any orientation should be equal for all sites. Applying this requirement to the sites of the cluster, is the basic idea of the Bethe–Peierls approximation. With this condition $\langle n_i \rangle$ is related to the concentration by

$$\langle n_i \rangle = \gamma_i \frac{c}{4} \quad (4.2)$$

where $\gamma_0 = 1$, $\gamma_1 = \gamma_2 = 2$, $\gamma_3 = \gamma_4 = 1$ and $\gamma_5 = 2$ are the number of symmetrically equivalent sites and orientations in the cluster. From the equations (4.1) and (4.2) we get six independent equations from which the effective potentials and $z_0 = z$ can be determined self-consistently for a given c . Thus the equations (4.1) and (4.2) establish the relation $c(z)$. The results for the concentration as a function of $u = z/(z+1)$ are presented in figure 3 as circles. Within the resolution of the graph they are equal to those obtained by the transfer matrix method. The entropy per lattice site may be derived from $c(z)$ by the thermodynamic relation

$$s(z) = k_B \left(\int_0^z dz' \frac{c(z')}{z'} - c(z) \ln(z) \right). \quad (4.3)$$

Because of the good agreement between the curves for $c(z)$ from the transfer matrix method and the Bethe–Peierls approximation in figure 3, the curves for $s(c)$ are also the same.

Since mean-field theories neglect long-range correlations, the good agreement of the results implies that long-range correlations are not relevant for the thermodynamics of the system.

5. Conclusion

In this paper we calculated by transfer matrix methods various static quantities characterizing the short-range order in the lattice gas of angular trimers on the square lattice (sections 2 and 3). As an alternative method a Bethe–Peierls approximation is also applied (section 4). Quantities calculated are the entropy per lattice site as a function of concentration, the concentration as a function of the activity, and two static susceptibilities for orientational ordering of dipolar and quadrupolar type. The results obtained by the different methods are in very good agreement with one another and with Monte Carlo data. They show that the ordering tendency is but weak. No indication of an order–disorder phase transition is observed. The existing short-range order is dominated by the occurrence of pairs of antiparallel trimers in nearest-neighbour positions, which form close-packed rectangular units (figure 6, configuration a). For the full lattice the entropy per site is found to be close to the corresponding value for the dimer problem, where an order–disorder phase transition is known to be absent [8, 9].

We conclude that the lattice gas of angular trimers may be considered as a model of a glass-forming liquid composed of molecules of angular shape like liquid ortho-terphenyl. It would be of interest to extend the model to three dimensions and to study dynamic properties.

References

- [1] Fisher M E and Temperley H N V 1960 *Rev. Mod. Phys.* **32** 1029
- [2] Temperley H N V and Fisher M E 1961 Dimer problem in statistical mechanics—an exact result *Phil. Mag.* **6** 1061
- [3] Fisher M E 1961 Statistical mechanics of dimers on a plane lattice. *Phys. Rev.* **124** 1664
- [4] Kasteleyn P W 1963 Dimer statistic and phase transition *J. Math. Phys.* **4** 287
- [5] Fisher M E and Stephenson J 1963 Statistical mechanics of dimers on a plane lattice II. Dimer correlations and monomers *Phys. Rev.* **132** 1411
- [6] Nagle J F 1966 New series expansion method for the dimer problem *Phys. Rev.* **152** 190
- [7] Baxter R J 1968 Dimers on a rectangular lattice *J. Math. Phys.* **9** 650
- [8] Gaunt D S 1969 Exact series-expansion study on the monomer-dimer-problem *Phys. Rev.* **179** 174
- [9] Runnels L K 1970 Exact finite method of lattice statistics III. Dimers on the square lattice *J. Math. Phys.* **11** 842
- [10] Lewis L J and Wahnström G 1994 Molecular-dynamics study of supercooled ortho-terphenyl *Phys. Rev. E* **50** 3865
- [11] Fowler R H and Rushbrooke G S 1937 An attempt to extend the statistical theory of perfect solutions *Trans. Faraday Soc.* **33** 1272
- [12] Bonnemeier F 1992 *Diploma Thesis* Konstanz (unpublished)
- [13] Froböse K and Jäckle J 1985 Static correlations of higher order and diffusion in an interacting lattice gas *J. Stat. Phys.* **42** 551