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Entropy of hard hexagons

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Abstract. Metcalf and Yang have obtained the numerical estimate $0{\cdot}3333k$ for the entropy per site of hard hexagons. They therefore conjecture that the exact value is $k/3$. We have used the corner transfer matrix method to obtain a more accurate numerical estimate, namely $0{\cdot}333\,242\,721\,976\,k$, which contradicts the conjecture. The problem is a good example of the numerical accuracy of the method.

1. Introduction

Baxter (1968) developed a sequence of variational approximations for the monomer–dimer system on the square lattice. Numerically they were found to converge very well: at least six significant figures could be obtained from the first few approximations.

This method has been generalised (Kelland 1976, Baxter 1978) to the Potts model, and to square lattice models with a face (e.g. nearest-neighbour, next-nearest neighbour, and 'four-spin' interactions). For an isotropic model it gives equations for the free energy and for two matrices A and F. In the limit when these matrices have infinite size, the equations are exact and A is the 'corner transfer matrix' of the model, while F is the 'half-row' transfer matrix. The equations can be given a simple graphical interpretation in terms of building up a lattice out of quadrants and half-rows and half-columns.

For the zero-field Ising model the infinite-size matrix equations have been solved exactly (Baxter 1977, Tsang 1977). The results, notably that for the magnetisation, of course agree with Onsager's solution (Onsager 1944, Yang 1952).

If the matrices are restricted to finite (even small) size, then quite good approximations are obtained, and the approximation increases in accuracy as the size is increased. The rate of convergence should be least at a critical point, and very fast at low or high temperatures.

For the zero-field Ising model these properties have been explicitly verified by Tsang (1979). They have been used by Baxter and Enting (1979) to obtain the first 23 terms in the low-temperature series expansion of the Ising model in a field. To do this it was only necessary to take A and F to be 15×15 matrices.

2. Variational approximation for the triangular lattice

This method can be applied to the triangular lattice. Let the number of sites be N; at each site i let there be a 'spin' σ_i, with value + or −, and let the total energy be

$$E=\sum_{(i,j,k)}\epsilon(\sigma_i,\sigma_j,\sigma_k), \tag{1}$$

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where the sum is over all the $2N$ triangular faces (i, j, k) of the lattice and $\epsilon(\sigma_i, \sigma_j, \sigma_k)$ is the energy of interaction of the three spins on a triangle. Let us further take the model to be isotropic, so that $\epsilon(a, b, c)$ is unchanged by permuting a, b, c.

The partition function is then

$$Z = \sum_{\{\sigma\}} e^{-E/kT} = \sum_{\{\sigma\}} \prod_{(i,j,k)} w(\sigma_i, \sigma_j, \sigma_k), \tag{2}$$

where the summation is over all 2^N values of $\{\sigma_1, \ldots, \sigma_N\}$, and

$$w(a, b, c) = \exp[-\epsilon(a, b, c)/kT]$$

is the Boltzmann weight of a triangle of spins a, b, c.

Let κ be the partition function per site in the thermodynamic limit, i.e.

$$\kappa = \lim_{N\to\infty} Z^{1/N}. \tag{3}$$

Then the variational approximation for κ is

$$\sum_b F(a, b)A^2(b)F(b, a) = \xi A^4(a), \tag{4a}$$

$$\sum_c w(a, b, c)F(a, c)A(c)F(c, b) = \eta^{1/2}A(a)F(a, b)A(b), \tag{4b}$$

$$\kappa = \eta/\xi, \tag{4c}$$

$$A^T(a) = A(a), \qquad F^T(a, b) = F(b, a). \tag{4d}$$

Here a, b, c have possible values + and −; each of $F(+, +)$, $F(+, -)$, $F(-, +)$, $F(-, -)$, $A(+)$, $A(-)$ is a matrix; and ξ and η are positive real numbers.

3. Graphical interpretation

The equations (4) can be interpreted graphically. Consider the lattice segments of r rows shown in figure 1. Let λ denote all the spins on the left-hand edges other than the spin a at the top; similarly, let μ denote all the right-hand spins other than a or b. Let $A_{\lambda\mu}(a)$ be the combined Boltzmann weight of segment $1(a)$, summed over all interior spins; and let $F_{\lambda\mu}(a, b)$ be the corresponding weight for segment $1(b)$.

Now let $A(a)$ be the matrix with elements $A_{\lambda\mu}(a)$ in position (λ, μ); similarly for $F(a, b)$. Then the equations (4a) and (4b) have the graphical representation given in figure 2, where each figure represents the combined Boltzmann weight of a section of

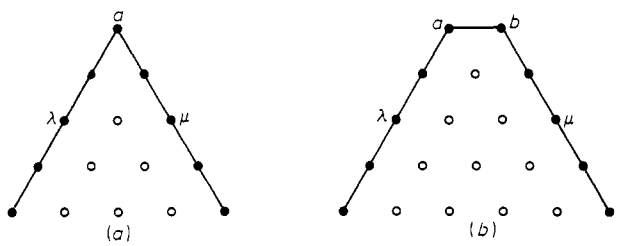

Figure 1. Lattice segments corresponding respectively to the matrices $A(a)$ and $F(a, b)$. An appropriate boundary condition should be applied to the spins on the bottom row.

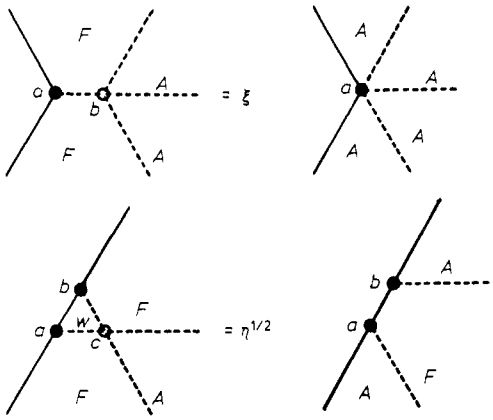

Figure 2. Graphical interpretation of equations (4*a*) and (4*b*), the summations over spins on broken lines being performed in anti-clockwise order.

the lattice, further subdivided into A- and F-segments. Spins on solid circles or lines are free to take any allowed values (the same on each side of an equation). The Boltzmann weight is to be summed over all spins to the right of the solid lines, including those on open circles or broken lines.

In each equation in figure 2, the LHS and RHS differ only in the number of sites to the right of the solid lines: in the first (second) equation there are $2r-1$ (r) more sites on the LHS than the RHS. When r is large we expect these extra sites merely each to contribute a factor κ, independent of the values of the free spins on the solid circles and on nearby sites on the solid lines. Thus in this sense equations (4*a*) and (4*b*) will be satisfied, with

$$\xi = \kappa^{2r-1}, \qquad \eta^{1/2} = \kappa^{r}, \tag{5}$$

so that equation (4*c*) is also satisfied.

The A and F matrices can be renormalised to ensure that their elements tend to finite limits as $r \to \infty$. From equations (4), this will affect ξ and η, but not η/ξ. Thus κ will still be given by equation (4*c*). For any value of r, the symmetry relations (4*d*) are satisfied.

The equations (4) are unaffected by the transformations

$$A(a) \to P^{\mathrm{T}}(a)A(a)P(a), \qquad F(a,b) \to P^{\mathrm{T}}(a)F(a,b)P(b), \tag{6}$$

where $P(+)$ and $P(-)$ are arbitrary orthogonal matrices. Thus one can always arrange that $A(+)$ and $A(-)$ are diagonal matrices.

We pre-multiply equation (4*a*) by $A^2(a)$, and equation (4*b*) by $A(b)F(b,a)A(a)$; then summing, taking traces, and using equation (4*c*), we obtain

$$\kappa = \frac{\Sigma_a \operatorname{Tr} A^6(a)[\Sigma_{a,b,c}\, w(a,b,c) \operatorname{Tr} A(b)F(b,a)A(a)F(a,c)A(c)F(c,b)]^2}{[\Sigma_{a,b} \operatorname{Tr} A^2(a)F(a,b)A^2(b)F(b,a)]^3}. \tag{7}$$

This is a variational principle for κ, in that the RHS is stationary when equations (4) are satisfied.

To summarise this section: we can in principle construct infinite matrices $A(a)$, $F(a,b)$ such that equations (4) are satisfied exactly. Thus we expect that if we solve (4) for finite-size matrices, and then let the size tend to infinity, we shall obtain a sequence of successively more accurate approximations to κ.

4. Specialisation to hard hexagons

From now on we specialise to hard hexagons with activity z, i.e. the triangular lattice gas with infinite nearest-neighbour repulsion. Let $\sigma_i = +$ if site i is empty, $-$ if it contains a particle. Two particles cannot be adjacent, so spins on adjacent sites cannot both have value $-$. Each negative spin contributes a factor z. Sharing out this factor between the six surrounding triangles, it follows that

$$w(a, b, c) = \begin{cases} 1 & \text{if } a = b = c = +, \\ z^{1/6} & \text{if one of } a, b, c \text{ is } -, \text{ the other two being } +, \\ 0 & \text{if any two of } a, b, c \text{ are } -. \end{cases} \tag{8}$$

Taking $a = b = -$ in equation (4b), it follows at once that

$$F(-, -) = 0. \tag{9}$$

The density ρ is given by

$$\rho = z \frac{\partial}{\partial z} \ln \kappa. \tag{10}$$

Differentiating equation (7) with respect to z, using equation (8) and the fact that the RHS is stationary with respect to the $A(a)$ and $F(a, b)$, and then using equation (4), we obtain

$$\rho = \frac{\operatorname{Tr} A^6(-)}{\operatorname{Tr}(A^6(+) + A^6(-))}. \tag{11}$$

(This equation has a very simple graphical representation: slice the lattice like a cake into six segments about a central point i. Each segment has Boltzmann weight $A(\sigma_i)$. The denominator in equation (11) is the sum over all spin configurations on the lattice, while the numerator is the sum over configurations with $\sigma_i = -$. This ratio is of course the density.)

5. The 'Kramers–Wannier' approximation

It is helpful to start by considering the case when the matrices $A(a)$, $F(a, b)$ are 1×1. (For the square lattice Ising model the corresponding approximation is equivalent to that of Kramers and Wannier (1941).)

We can then choose

$$A(+) = 1, \qquad A(-) = b, \qquad F(+, +) = 1, \qquad F(+, -) = F(-, +) = g, \tag{12}$$

and the equations (4) become

$$1 + gb^2g = \xi, \qquad g^2 = \xi b^4, \qquad 1 + z^{1/6} gbg = \eta^{1/2}, \qquad z^{1/6} g = \eta^{1/2} bg. \tag{13}$$

For a given value of b, these equations can easily be solved for z, g, ξ, and η. If we then introduce a variable x such that

$$b^6 = x/(1 + x), \tag{14a}$$

then, using equations (4*c*) and (11), we obtain

$$z=\frac{x}{(1-x)^5(1-x^2)}, \qquad \kappa=\frac{1}{(1-x)(1-x^2)}, \qquad \rho=\frac{x}{1+2x}. \tag{14b}$$

The density must lie between 0 and the close-packed value of $\frac{1}{3}$, so x lies between 0 and 1. For any positive value of z there is just one such value for x.

This approximation is really very good at low activities and densities. (To obtain a good high-density approximation the equations must be modified to take account of the spontaneous breaking of the translation symmetry of the lattice.) It can be used to expand κ in a Taylor series in z, giving

$$\kappa_{\text{approx}}=1+z-3z^2+16z^3-106z^4+789z^5-6319z^6+\ldots . \tag{15a}$$

To this order, the correct expansion can be obtained from the triangular Ising model results of Sykes *et al* (1965), by setting $\mu u^3=z$ and letting $\mu\to 0$, $u\to\infty$, keeping z fixed. It is

$$\kappa_{\text{exact}}=1+z-3z^2+16z^3-106z^4+789z^5-6318z^6+\ldots . \tag{15b}$$

Thus even the 1×1 approximation gives κ correctly to order z^5, and in the coefficient of z^6 is in error only by one! For $z=1$ it gives $\ln\kappa=0{\cdot}333\,050$, and as we shall see later, this number is accurate to three significant figures.

6. Higher approximations

It is useful to define four further matrices $U(+)$, $U(-)$, $R(+)$, $R(-)$ by

$$U(a)=\begin{pmatrix} w(+,a,+)F(+,+) & w(+,a,-)F(+,-) \\ w(-,a,+)F(-,+) & w(-,a,-)F(-,-)\end{pmatrix} \tag{16}$$

$$R(a)=\xi^{-1/2}\begin{pmatrix} A(+)F(+,a)A^{-2}(a)\\ A(-)F(-,a)A^{-2}(a)\end{pmatrix} \tag{17}$$

where $a=+$ or $-$. Then equations (4*a*) and (4*b*) (interchanging a and b in the latter equation) can be written

$$R^{\mathrm{T}}(a)R(a)=\mathrm{I}, \tag{18}$$

$$U(a)R(a)=R(a)(\eta^{1/2}A(a)), \tag{19}$$

where again $a=+$ or $-$.

The matrices $U(+)$ and $U(-)$ are symmetric. Let us use the representation in which $A(+)$ and $A(-)$ are diagonal. Then it is obvious from equation (19) that the columns of $R(a)$ are the eigenvectors of $U(a)$. Equation (18) merely states that eigenvectors of the same matrix should be chosen to be orthonormal.

As for the square lattice (Baxter 1978, Baxter and Enting 1979), we find the following iterative procedure converges for sufficiently small z, given a reasonable initial guess at ξ, η, $A(a)$, $F(a,b)$, where $A(+)$ is $m\times m$ and $A(-)$ is $n\times n$.

(i) Calculate $U(+)$ and $U(-)$ from equation (16). Ensure they are symmetric by setting the bottom-left elements equal to the top-right.

(ii) Obtain their eigenvalues, arranged in numerically decreasing order, and the corresponding normalised eigenvectors.

(iii) Set $\eta^{1/2}$ equal to the largest eigenvalue of $A(+)$. Divide all eigenvalues by $\eta^{1/2}$. Set the diagonal elements of $A(+)(A(-))$ equal to the first $m(n)$ eigenvalues of $U(+)(U(-))$.

(iv) Calculate the matrices $F(a, b)$ from equation (17), choosing ξ so that the top-left element of $F(+, +)$ is unity.

Repeat steps (i) to (iv) until sufficient accuracy is obtained.

Given the solution for particular values of m and n, this procedure can also be used to obtain a reasonable guess at the solution for larger values. At stage (iii) one merely keeps not just the eigenvalues of $U(+)$ and $U(-)$ corresponding to the original $A(+)$ and $A(-)$, but also the next largest of all the eigenvalues (or group of close-together next-largest eigenvalues), and modifies m or n accordingly. It is *not* necessary to keep all the eigenvalues, as has been previously suggested (Baxter 1978). This has been made clear by the series-expansion results of Baxter and Enting (1979).

Starting from the Kramers-Wannier solution, with $m = n = 1$, and following this procedure, we can calculate each matrix element and eigenvalue to leading order in an expansion in powers of z. Regarding two eigenvalues as 'close together' if they agree to leading order, or differ only by a factor $z^{1/6}$, we obtain the sequence of approximations shown in table 1. In the fourth approximation, the elements of the matrices $F(a, b)$ (to leading order in a z expansion) are given by

$$F(+,+)=\begin{pmatrix} 1 & -z^{2\frac{1}{2}} & -z^{5\frac{1}{2}} & -z^{8\frac{1}{2}} \\ -z^{2\frac{1}{2}} & z^2 & -z^3 & -z^6 \\ -z^{5\frac{1}{2}} & -z^3 & -z^3 & z^4 \\ -z^{8\frac{1}{2}} & -z^6 & z^4 & z^4 \end{pmatrix}$$

$$F(-,+)=z^{1/3}\begin{pmatrix} 1 & z^{1\frac{1}{2}} & z^{4\frac{1}{2}} & z^{7\frac{1}{2}} \\ z^{6\frac{1}{2}} & -z^3 & -z^3 & z^4 \\ z^{9\frac{1}{2}} & -z^6 & z^4 & z^4 \end{pmatrix} \tag{20}$$

$$F(+,-)=F^{\mathrm{T}}(-,+), \qquad F(-,-)=0.$$

Table 1. Values of m, n and the diagonal elements of $A(+)$, $A(-)$ (to leading order in a z expansion) for the first six approximations for hard hexagons.

Approxn	m	n	$A(+)$	$z^{-1/6}A(-)$
1	1	1	1	1
2	2	1	$1, -z$	1
3	3	2	$1, -z, z^2$	$1, z^2$
4	4	3	$1, -z, z^2, -z^3$	$1, z^2, -z^3$
5	6	4	$1, -z, z^2, -z^3, z^4, z^4$	$1, z^2, -z^3, z^4$
6	8	5	$1, -z, z^2, -z^3, z^4, z^4, -z^5, -z^5$	$1, z^2, -z^3, z^4, -z^5$

To leading order each matrix element is independent of the size of the approximation, so long as the approximation is big enough to include it. (For instance, $F_{11}(-, +)$ has leading term $z^{1/3}$ in every approximation. Numerically, we find that the individual elements converge rapidly to their values for infinite matrices.) Thus to leading order the matrices $F(a, b)$ for approximations 1, 2 and 3 can be obtained by appropriately truncating the matrices in equations (20).

7. Numerical results for $z = 1$

Metcalf and Yang (1978) have estimated the entropy of systems of particles with nearest-neighbour exclusion on various lattices. For the triangular lattice this is the hard-hexagon problem with $z = 1$, and the entropy per site is

$$S = N^{-1}k \ln Z = k \ln \kappa. \tag{21}$$

By considering $m \times \infty$ lattices, with $m = 2, \ldots, 9$, and diagonalising the transfer matrix numerically, they obtained the estimate

$$S/k = \ln \kappa = 0{\cdot}3333 \ldots . \tag{22}$$

On the basis of this they conjectured that S/k might be exactly $\frac{1}{3}$. If this were so it would be very interesting, for it would suggest that the problem could be solved exactly.

We have therefore used the equations (4) and the above iterative procedure to obtain a better numerical estimate of $\ln \kappa$ for $z = 1$. Since this value is much less than the estimated critical value of 11 (Runnels and Combs 1966), we are well inside the low-density phase, and we expect the successive approximations to converge to the exact infinite-matrix solution.

For each approximation, the iteration procedure converged reasonably rapidly, and the final solution had the general structure of table 1 and equation (20). (In fact it was approximately the same, but with z in table 1 and equation (20) replaced by an 'effective' z of 0·255: presumably this effective z approaches 1 near the critical point.) This makes us confident that we have converged on the correct solution of the equations.

We used double precision arithmetic and iterated until each individual element of the matrix equations (4) was satisfied to relative accuracy 10^{-12}. Since κ is only weakly sensitive to most of the elements, and not highly sensitive to any, we are therefore confident that in each approximation κ is correct to at least this accuracy.

In each approximation we calculated not only the diagonal elements of $A(+)$ and $A(-)$ used in stage (iii), but also those not used, coming from the extra eigenvalues. Let A_{rem} be the largest of those not used.

If the used ones were independent of the approximation (i.e. had their exact values for infinite matrices), then the effect of truncating the matrices to finite size would be to introduce an error into $\mathrm{Tr}(A^6(+)+A^6(-))$ of approximately A^6_{rem}. Since this trace is of order unity, this is also the relative error. From equation (7) we might expect this to be approximately the relative error in κ. For the square-lattice Ising model, Baxter and Enting (1979) found the corresponding assertion to be valid.

Table 2. Values of $\ln \kappa$ for the first five approximations, together with their differences from the fifth value, A^6_{rem}, and ρ. Digits 13 to 16 are suspect, but their differences fit well enough with A^6_{rem} to suggest that 13 and 14 in $\ln \kappa$ may be correct.

Approxn	$\ln \kappa$	Diff	A^6_{rem}	ρ
1	0·333 050 27	$1{\cdot}9\times10^{-4}$	$1{\cdot}9\times10^{-4}$	0·161 984
2	0·333 242 657 00	$6{\cdot}5\times10^{-8}$	$5{\cdot}6\times10^{-8}$	0·162 432 600
3	0·333 242 721 958 27	$1{\cdot}8\times10^{-11}$	$1{\cdot}5\times10^{-11}$	0·162 432 921 264
4	0·333 242 721 976 0604	$4{\cdot}7\times10^{-15}$	$5{\cdot}6\times10^{-15}$	0·162 432 921 397 391
5	0·333 242 721 976 0651		$1{\cdot}5\times10^{-18}$	0·162 432 921 397 499

In table 2 we have therefore plotted not only $\ln \kappa$ for the first five approximations, but also the differences from the last approximation, and A^6_{rem} in each case. It seems that A^6_{rem} is indeed a good measure of the error of an approximation.

We have also tabulated the density ρ, given by equation (11), for each approximation. This appears to be converging more slowly than $\ln \kappa$ to its limiting value (but still very fast). Presumably this reflects the fact that κ is derived from a variational principle, and so should be less sensitive than ρ to the error caused by truncating the matrices to finite size.

The results are clearly very encouraging for the variational method. The fourth approximation, which uses matrices no bigger than 4×4, already gives

$$\ln \kappa = 0{\cdot}333\ 242\ 721\ 976,$$

and we are confident this is correct to the twelve figures given. Unfortunately, this leads us to conclude that $\ln \kappa$ is not exactly $\frac{1}{3}$.

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