Pramāṇa, Vol. 3, No. 3, 1974, pp 133–142. © Printed in India.

Phase transition in a class of Hamiltonians*

G ANANTHAKRISHNA** and J EDUARDO SUGER+
Molecular Physics Group, The University of Texas at Austin, Austin, Texas 78712 USA

MS received 20 May 1974; after revision 28 August 1974

Abstract. We consider a class of Hamiltonians for a system of one localized spin-$\frac{1}{2}$ particle per lattice site with the total spin as a good quantum number. We introduce a set of conditions in the form of a hypothesis relating the subpartition function, which is the partition function defined by the subset of energies with a specific value of spin. If the equality in the hypothesis is satisfied, then the system undergoes a phase transition as a consequence of Yang-Lee theorem. As an application, we estimate the bounds on the spectrum of the Heisenberg Hamiltonian.

Keywords. Phase transition; Yang-Lee theorem; partition function; Heisenberg Hamiltonian; critical temperature.

1. Introduction

It is well known that only few model Hamiltonians which undergo a phase transition can be solved exactly. Many attempts have been made to construct approximation procedures which provide at least a qualitative understanding concerning the critical region. In either case most of the insight obtained about the mechanism leading to a phase transition is obtained from model oriented analysis, with a notable exception, namely, the analysis of Yang and Lee (1952) (although, the analysis refers to the liquid-gas system). Their analysis tells us the " mathematical mechanism " leading to a phase transition. Briefly, the singularities that appear in the thermodynamic quantities are attributed as arising due to the existence of a finite density of zeros of grand partition function in an arbitrarily small neighbourhood of the positive real fugacity axis. If a line of roots cuts the positive real fugacity axis, then the limiting function $\bar{X} = \lim (1/V) \log \Xi$ has two distinct analytic pieces and $\bar{X}$ is continuous at the point, but the derivative in general has a discontinuity. The corresponding results also hold in the case of canonical partition function (*see* for example Fisher 1965 and Jones 1966). As we will see later, the hypothesis that we use in this paper is motivated from these considerations. We will restrict our considerations to ferromagnetic phase transitions.

The main purpose of the paper is to be able to use the Yang–Lee theorem in some way. This is achieved by introducing a hypothesis which is again motivated

* Supported by the National Science Foundation, Washington D.C. and the Robert A. Welch Foundation, Houston, Texas and partly supported by the United States Atomic Energy Commission, Contract Grant AT (40–1) 3992.

** Present address: Department of Physics, Indian Institute of Science, Bangalore 560012.
+ Permanent address: The Universidad de San Carlos de Guatemala, Central America.

by the Yang–Lee analysis. Assuming that the hypothesis (for $T = T_c$) holds and by going over to the complex magnetic field plane, we show that there is a line of zeros of partition function closing on to the positive real activity axis in the thermodynamic limit. The form of the Hamiltonian is quite general (except that it represents a ferromagnetic system) and is so chosen that the partition function can be written as a symmetric function in the activity variable with coefficients which depend exclusively on the spectrum at zero magnetic field. The hypothesis relates these coefficients among themselves. The entire analysis is done in section 2. As an application, we estimate bounds on the spectrum assuming that the three-dimensional Heisenberg Hamiltonian undergoes a phase transition. Finally, section 4 contains concluding remarks.

2. Conditions for critical behaviour

Consider a lattice system with one spin–1/2 particle localized on each site. We wish to consider a general Hamiltonian which has a symmetry that enables us to express the partition function as a symmetric function in the activity variable. The Hamiltonian characterizing the interaction may be spin or spin-free (Matsen *et al* 1971) or both. The symmetry property that we require for the Hamiltonian is that it commutes with the total spin of the system, *i.e.*,

$$[H_0, S^2_{tot}] = 0 \tag{2.1}$$

where

$$S^2_{tot} = \Big(\sum_i s_i\Big)^2 \tag{2.2}$$

with s_i representing the spin at the site i. The application of a uniform magnetic field h in the z-direction gives rise to the total Hamiltonian

$$H_T = H_0 + H_1 \quad \text{and} \quad [H_T, S^2_{tot}] = 0 \tag{2.3}$$

with

$$H_1 = g\mu h \sum_{j=i}^{N} s_j^z \tag{2.4}$$

where μ is the Bohr magneton and g the gyromagnetic ratio. Then the partition function for such system is

$$Z = \sum_{S}^{N/2} \sum_{M=-S}^{S} \sum_{F=1}^{f^S} \exp\{-\beta E(F, S) - \beta g\mu h M\} \tag{2.5}$$

where $\beta = 1/kT$, F distinguishes among the f^S states with the same S, and M is the eigenvalue of S^z_{tot} in this subspace. Let

$$\gamma_S = \sum_{F=1}^{f^S} \exp\{-E(F, S)/kT\} \tag{2.6}$$

We call γ_S, the sub-partition function. Defining the activity variable

$$z = \exp(\alpha/2) \tag{2.7}$$

with $\alpha = \beta g\mu h$, the partition function (2.5) takes the form

$$Z(z) = \sum_{S}^{n=N/2} \gamma_S [z^{2S} + z^{2S-2} + \ldots + z^{-2S}] \tag{2.8}$$

This can be written in the form:

$$Z(z) = \sum_{S}^{n=N/2} \gamma_S \frac{\sinh (S + 1/2)\, a}{\sinh a/2} \tag{2.9}$$

Thus Z is a symmetric function in the activity variable z with the coefficients γ_S which depend exclusively on the spectrum of the system at zero magnetic field. Since the $\gamma_S > 0$ by definition (2.6) [and since $z > 0$ by definition (2.7)], we see that $Z(z)$ has no real positive zeros, and thus Z is analytic in β and z for all finite N. However, in the limit as $N \to \infty$ these complex roots may coalesce into a 'line' of finite density that pinches the real positive z-axis for some value of temperature. If this happens, then by the Yang-Lee theorem this indicates the existence of a phase transition.

We want to consider the behaviour of the system at zero magnetic field ($z = 1$) and we notice that for $z = 1$, Z reduces to $\Sigma \gamma_S (2S + 1)$. So we allow the magnetic field to take on complex values and then let $\mathrm{Re}(h) \to 0^+$. Thus we introduce a variable y by $= z^{iy}$. Since the Re h is zero, $y \in [0, 2\pi]$. With this variable the partition function can be written as

$$Z(y) = \frac{1}{\sin y} \sum_{S}^{n} \gamma_S \sin (2S + 1)\, y \tag{2.10}$$

Let

$$\hat{Z}(y) = \Sigma\, \gamma_S \sin (2S + 1)\, y \tag{2.11}$$

Let us assume that the system undergoes a phase transition at some temperature T_c and that Yang-Lee's criterion is also a necessary condition. (This may not be so, since it has not been shown that if the system undergoes a phase transition then there is a finite density of roots in an arbitrarily small neighbourhood of the real activity axis). Then we know that the free energy per spin is non-analytic at that value $z = z_c$ where the line of zeros cuts the real activity axis and that there are two distinct analytic pieces for real positive values of interest, one to the left of z_c and the other to the right of z_c. Below this temperature any region R containing the real activity axis is free of zeros and therefore the free energy per spin is completely analytic. This is again true for $T > T_c$. But the functional form of the free energy per spin in general is different from the functional form below $T = T_c$. However, the limiting value of the free energy per spin as $T \to T_c^+$ and $T \to T_c^-$ with Re h fixed at Re $h_c + \epsilon$ (where ϵ is arbitrarily small and real), can be expected to be the same. Since the free energy per spin is a function of γ_s and since we expect the functional form of the free energy per spin to be different below and above T_c, we should expect the relation between γ_s and $\gamma_{s'}$ to change across $T = T_c$. Further, at $T = T_c$ we expect that all the γ_s to be the same up to a multiplicative factor which is positive and independent of S and which will be determined later on (*see* Appendix A). (Since we expect the values of free energy per spin for $T > T_c$ and $T < T_c$ to coincide at $T = T_c$).

Thus we are led to consider the following hypotheses.

$$\frac{1}{N} \log \frac{\gamma_S}{\gamma_{S-1}} > \frac{1}{N} \log A_n \qquad \forall\, S \tag{2.12 a}$$

with $\quad A_n > 0 \quad \text{for} \quad T < T_c'$

$$\frac{1}{N}\log\frac{\gamma_S}{\gamma_{S-1}} < \frac{1}{N}\log A_n \quad \text{for} \quad T > T_c' \tag{2.12 b}$$

and

$$\frac{1}{N}\log\frac{\gamma_S}{\gamma_{S-1}} = \frac{1}{N}\log A_n \quad \text{for} \quad T = T_c' \tag{2.12 c}$$

these relations should hold for all S in the sense for finitely many S, these relations may be violated. Certainly, these are not the most general kind of inequalities one can think off, but they have been taken for their simplicity. In Appendix A we show that the allowed form of A_n is $A_n = 1 + B/(2n+1)$; $B > 0$ and finite. The existence of the quantities $(1/N)\log\gamma_S$ in the limit of $N\to\infty$ is easy to see and a sketchy 'proof' is given in Appendix (C).

For most part we will be considering the equality in the hypothesis. By using this we will show that the partition function has a line of roots closing on to the real activity axis and therefore the equality in hypothesis corresponds to the temperature $T_c' = T_c$. In the sequel we will assume N to be even. For convenience we will use the following form of y.

$$y_1 = \frac{r\pi}{2\ (2n+1)}, \qquad r = 1 \text{ to } 4\,(2n+1) \tag{2.13}$$

By using the hypothesis and the form of y_1 it can be shown that

$$\hat{Z} < \gamma_0 \sum_{S=0}^{n} A_n^S \sin(2S+1)\,y_1 = \bar{Z} \qquad \text{for } T < T_c' \tag{2.14 a}$$

$$\hat{Z} > \gamma_0 \sum_{S=0}^{n} A_n^S \sin(2S+1)\,y_1 = \bar{Z} \qquad \text{for } T > T_c' \tag{2.14 b}$$

and

$$\hat{Z} = \gamma_0 \sum_{S=0}^{n} A_n^S \sin(2S+1)\,y_1 = \bar{Z} \qquad \text{for } T = T_c' \tag{2.14 c}$$

Equations (2.14) has been shown to follow from (2.12) and (2.13) in Appendix A. We shall now focuss our attention on $\bar{Z}$ at $T = T_c'$ given by (2.14 c). In Appendix B we have shown that for successive values of $r/2$ the function $\hat{Z} = \bar{Z}$ changes sign. Thus, there is at least one zero between any two successive values of $r/2$. In fact, these are the only roots as can be seen. Since the number of zeros of $\bar{Z}$ increases linearly with N, these roots which are at approximate intervals of $\pi/(N+1)$ coalesce into a 'line' of uniform density of roots in the limit $N\to\infty$. It is also clear that all these points defined by $y_1 = r\pi/2\,(2n+1)$; r ranging, closes on to real z-axis. The corresponding complex conjugate roots also close on to the real z-axis. Thus, given an arbitrarily small neighbourhood about $y = 0$, the number zeros of $\bar{Z}$ (and therefore that of Z at $T = T_c'$) indefinitely increases in the limit as $N\to\infty$. Thus from the Yang-Lee theorem the free energy per spin is non-analytic at that point and the system undergoes a phase transition. Therefore, the temperature T_c' corresponds to the critical temperature T_c. It can be observed that the function $\bar{Z}$ which is an upper bound function for $T > T_c$ goes over into the lower bound function for $T < T_c$. (Although, we have used the specific form of y_1 to obtain these two bounds, they can be easily seen to hold for any general value of y with the restriction that the total number of changes in sign is even).

Thus if the spectrum of H_0 is such that the equality in the hypothesis is satisfied then the system undergoes a phase transition at a temperature T_c determined by (2.12 *c*). Although, these conditions have been obtained, for a Hamiltonian which has properties defined by (2.3), they may or may not be satisfied by any such Hamiltonian. Thus we have only a sufficient condition and not a necessary condition. The hypothesis may be satisfied at more than one temperature in which case we have more than one phase transition.

3. Upper and lower bounds of the spectrum

In conclusion, we illustrate how the energy bounds can be obtained as a function of critical temperature. Consider the Heisenberg Hamiltonian with $J > 0$.

$$\mathcal{H} = -2J \sum_{\langle i,j \rangle} s_i s_j \tag{3.1}$$

What we wish to obtain is an estimate of the difference between the antiferromagnetic ground state and the ferromagnetic ground state energies, granting that the spectrum of the Heisenberg Hamiltonian satisfies the critical conditions. (Although, there is no rigorous proof that the three-dimensional nearest neighbour Heisenberg Hamiltonian undergoes a phase transition, there is a strong evidence from the high temperature extrapolation procedures (*see* for example Baker *et al* 1967).

Since $f^n = 1$, we have

$$\gamma_n = \exp\left\{-\frac{E_F}{kT}\right\} \tag{3.2}$$

where E_F is the ferromagnetic ground state energy. For $S = 0$,

$$f^0 = \frac{N\,!}{(N/2)\,!\;(\tfrac{1}{2}N+1)\,!} \tag{3.3}$$

and

$$\gamma_0 = \sum_{F=1}^{f^0} \exp\left\{-\frac{E_A}{kT}\right\} \tag{3.4}$$

Replacing every energy eigenvalue $E(F, 0)$ by the highest one, which is the antiferromagnetic ground state energy E_A, we have

$$\bar{\gamma}_0 = f^0 \exp\left\{-\frac{E_A}{kT}\right\} < \gamma_0 \tag{3.5}$$

Hence

$$\frac{\gamma_n}{\gamma_0} < \frac{\gamma_n}{\bar{\gamma}_0} = \left[\exp\left\{\frac{-(E_F - E_A)}{kT}\right\}\right] \Big/ f_0 \tag{3.6}$$

Using Stirling's approximation we get, in the limit of large n

$$f^0 \sim \frac{2^{2n}}{n^{3/2}\,(2\pi)^{1/2}} \tag{3.7}$$

and

$$\frac{\gamma_n}{\bar{\gamma}_0} = \frac{[(\exp\{-(E_F - E_A)/kT_c\}]\, n^{3/2}\,(2\pi)^{1/2}}{2^{2n}} > \exp C$$

where we have used $T = T_c$ and $A_n = 1 + C/n$. Thus, we have

$$-\lim_{n\to\infty} \frac{(E_F - E_A)}{2nkT_c} > -\frac{3}{4}\log n - \frac{1}{4n}\log 2\pi + \log 2$$

or

$$E_F - E_A > -\frac{JN\log 2}{\theta_c} \tag{3.8}$$

Of course $\theta_c = J/kT_c$ differs from crystal to crystal, depending on the lattice structure and dimensionality of the lattice. Thus, by using the critical conditions we are able to obtain an expression for the bounds of the spectrum. For the case of one dimension this result is not meaningful since we know that there is no phase transition. However, if we take the values of θ_c for the F.C.C. the B.C.C. and the S.C. that are estimated from the high temperature expansion, namely, $\theta_c \sim 0{\cdot}24$, $0{\cdot}4$ and $0{\cdot}6$, respectively, we obtain:

$$\frac{E_A - E_F}{N} > \begin{cases} 4J\log 2 & \text{for the F.C.C.} \\ 2{\cdot}5J\log 2 & \ldots \text{B.C.C.} \\ 1{\cdot}666\log 2 & \ldots \text{S.C.} \end{cases} \tag{3.9}$$

4. Summary and discussion

To summarize, we have considered a class of Hamiltonians with S_{tot} as a good quantum number. The partition function for such a system under a uniform applied magnetic field can be written as a symmetric function in z. Since we were interested in the zero magnetic field situation, we let the magnetic field take on complex values and the real part approach zero. By introducing a hypothesis relating the subpartition functions with different values of S we were able to show that when the equality holds, given an arbitrary small neighbourhood about $z = 1$, the number of zeros indefinitely increases in the limit as $N \to \infty$, thus indicating that the system undergoes a phase transition. We then obtained an estimate of the bounds on the spectrum of the Heisenberg Hamiltonian. Unfortunately we are unable to find a model which satisfies our hypothesis.

Thus we have succeeded in using the Yang-Lee's theorem on the mechanism of phase transition. It may be argued that the quantities obtained, namely, γ_s are quite complicated so that not much reduction has been obtained. For this we remark that the main purpose of the analysis is not very much to obtain any reduction of the difficulties involved in the computation of Z (which is altogether a different problem), but to be able to use Yang-Lee theorem to obtain some information about the system. The analysis of the problem may be well appreciated if it is recalled that the Yang-Lee theorem has not been used since its publication (to the best of our knowledge). Further, the analysis of the present problem does indicate how it may be possible to use a similar approach for other problems of the same nature. In addition, if one considers a sequence of groups which commute among themselves and with the Hamiltonian, then depending on the number of Casimir invariants the reduction of Z into quantities similar to γ_s would be greatly enhanced. (A possible example would be a Hamiltonian which is invariant under unitary group in N-dimensions.)

If one wants to consider proving the necessity for the hypothesis one meets with the following formidable problem. Since there are several orders of phase transition, these, in the spirit of the present problem, will have to be related to the density of zeros at the point where they close onto the real activity axis. This problem is quite open and so the problem of obtaining both necessary and sufficient conditions appears to be quite hard.

Acknowledgements

We wish to thank Professors E C G Sudarshan, F A Matsen and N Kumar for useful discussions. One of us (G A) wishes to thank CSIR, New Delhi, for the award of a pool officership.

Appendix A

By using the hypothesis and the form of y_1, we will prove that $\bar{Z}$ in an upper bound function of $\hat{Z}$. It is obvious that the sum in (2.11) changes sign as the argument of the sine function increases from zero to k, where k is some integer. Accordingly we split the sum (2.11) into two sets of sums, one of which is positive and the other is negative. Due to the form of y_1 we use, the sine function changes sign at approximate intervels of S characterized by the integer value of $m = (2n+1)/r$, which we denote by m_1. Let the number of such m_1's be l. [For simplicity we will assume l to be even. Slight modification is necessary when l is odd and for that case $\hat{Z} > \gamma_0 \ \Sigma \ A_n{}^S \sin(2S+1)\, y_1$.] Rewriting (2.11) we have

$$\begin{aligned}\hat{Z}(y_1) = &\sum_{S=0}^{m_1=(1)} \gamma_S \sin(2S+1)\, y_1 + \sum_{(1)+1}^{m_1+m_2=(2)} \gamma_S \sin(2S+1)\, y_1 \\ &+ \ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots \\ &+ \sum_{S=(k-1)+1}^{(k)} \gamma_S \sin(2S+1)\, y_1 + \sum_{(k)+1}^{(k+1)} \gamma_S \sin(2S+1)\, y_1 \\ &+ \ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots \\ &+ \sum_{S=(l-2)+1}^{(l-1)} \gamma_S \sin(2S+1)\, y_1 + \sum_{(l-1)+1}^{(l)=n} \gamma_S \sin(2S+1)\, y_1 \end{aligned} \tag{A.1}$$

where $(k) = \sum_{i=1}^{k} m_i$. The odd terms are positive and even terms are negative. Using the hypothesis (2.12 *a*) we replace each term by its upper bound. Thus we have

$$\begin{aligned}\hat{Z}(y_1) < &\frac{\gamma_{(1)}}{A_n{}^{(1)}} \sum_{S=0}^{(1)} A_n{}^S \sin(2S+1)\, y_1 + \frac{\gamma_{(1)}}{A_n{}^{(1)}} \sum_{(1)+1}^{(2)} A_n{}^S \sin(2S+1)\, y_1 \\ &+ \ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots \\ &+ \frac{\gamma_{(k)}}{A_n{}^{(k)}} \sum_{(k-1)+1}^{(k)} A_n{}^S \sin(2S+1)\, y_1 + \frac{\gamma_{(k)}}{A_n{}^{(k)}} \sum_{(k)+1}^{(k+1)} A_n{}^S \sin(2S+1)\, y_1 \\ &+ \ldots\ldots\ldots\ldots + \ldots\ldots\ldots\ldots \\ &+ \frac{\gamma_{(l-1)}}{A_n{}^{(l-1)}} \sum_{(l-2)+1}^{(l-1)} A_n{}^S \sin(2S+1)\, y_1 + \frac{\gamma_{(l-1)}}{A_n{}^{(l-1)}} \sum_{(l-1)+1}^{n} A_n{}^S \sin(2s+1)\, y_1 \end{aligned} \tag{A.2}$$

It is easy to show that

$$\sum_{S=0}^{m} A_n^S \sin(2S+1)y$$
$$= \frac{A_n^{m+2}\sin(2m+1)y - A^{m+1}\sin(2m+3)y + (1+A_n)\sin y}{A_n^2 - 2A_n\cos 2y + 1} \quad (A.3)$$

The denominator of (A.3) is positive for any $y \in (0, 2\pi)$ and finite N because

$$A_n^2 - 2A_n \cos 2y + 1 = (A_n - 1)^2 + 4A_n \sin^2 y > 0$$

(Note that $A_n > 0$). The m_i's can at the most differ by unity. Thus $m_1 + m_2 = 2m$ or $2m+1$. Consider

$$\sum_{S=0}^{2m} A_n^S \sin(2S+1)y_1.$$

Using (A.3), the form of y_1 and $m = (2n+1)/r$, [apart from a denominator which is exactly the same as in (A.3)], we have

$$A_n^{2m+2}\sin\left(2\pi + \frac{r\pi}{2(2n+1)}\right) - A_n^{2m+1}\sin\left(2\pi + \frac{3r\pi}{2(2n+1)}\right)$$
$$+ (1+A_n)\sin y_1$$

(For convenience we have used $m = (2n+1)/r$ instead of its integer value. The result that follows from this is equally true even when the integer value of m is used). When n is large and $r \ll n$, we can use $\sin y = y$, Using this we have

$$\frac{r\pi}{2(2n+1)}[A_n^{2m+1}(A_n - 3) + 1 + A_n].$$

This quantity is less than or equal to zero for $1 \leqslant A_n < 3$. In particular the form of A_n we use is $A_n = 1 + B/(2n+1)$. This choice follows from the discussion given in Appendix B. The equality holds at $A_n = 1$. [These results hold even if we drop the restriction that $r \ll n$ for $A_n = 1 + B/(2n+1)$ and $y \in (0, \pi/2)$.]

Thus we have

$$\sum_{S=0}^{2m} A_n^S \sin(2S+1)y_1 < 0.$$

Similarly, we can show that

$$\sum_{S=(k)+1}^{(k)+2m+1} A_n^S \sin(2S+1)y_1 < 0. \quad (A.4)$$

[Although eq. (A.4) was shown to hold when $(k+2)-(k) = 2m$, it holds even when $(k+2)-(k) = 2m+1$]. Using (A.4) and $\gamma_0 < \gamma_{(k)}/A_n^{(k)}$ for $k > 0$ we obtain

$$\hat{Z} < \gamma_0 \sum_{S=0}^{n} A_n^S \sin(2S+1)y_1 = \bar{Z}$$

Then $\bar{Z}$ has the form given in (A.3) with $m = n$ except for the multiplicative factor γ_0. Thus we have obtained $\bar{Z}$ to be the upper bound of the function Z.

Similarly, using (2.12b) it can be shown that (2.14b) follows. Although, these relations have been proved for a specific choice of y_1, clearly they hold for any choice of y which satisfies the conditions that the total number of changes in sign is even.

Appendix B

Consider the function $\bar{Z}$ given in (2.14 *c*). Since γ_0 is positive (for $0 > \beta > \infty$) it is sufficient to show that $\sum_{S=0}^{n} A_n^S \sin(2S+1)\,y_1$ alternates in sign for successive values of $r/2$. From (A.3) it is clear that it is sufficient to show that the numerator of (A.3) alternates in sign (with $n = m$) for successive values of $r/2$. Rewriting the numerator of (A.3) with $m = n$ and $y_1 = r\pi/2\,(2n+1)$, we get

$$f(A_n, y_1) = A_n^{n+2} \sin\frac{r\pi}{2} - A_n^{n+1} \sin\frac{r\pi}{2} \cos\frac{r\pi}{2n+1}$$

$$- A_n^{n+1} \cos\frac{r\pi}{2} \sin\frac{r\pi}{2n+1} + (A_n + 1) \sin\frac{r\pi}{2\,(2n+1)} \qquad \text{(B.1)}$$

Case 1: r and $r/2$ are even

$$f_1(A_n, y_1) = -A_n^{n+1} \sin\frac{r\pi}{2n+1} + (A_n + 1)\sin\frac{r\pi}{2\,(2n+1)}$$

The choice of A_n we use is $A_n = 1 + B/(2n+1)$. For all those values of r for which $r\pi/(2n+1)$ is within the first quadrant, $\sin r\pi/(2n+1) > \sin r\pi/2\,(2n+1)$. (Note that it is sufficient to consider small angles in the first quadrant, since in the limit as $n \to \infty$ there are infinitely many such values.) Thus, $f_1(A_n, y_1)$ is negative for all finite n. In the limit $n \to \infty$, $A_n^n \to e^{B/2}$ and $\sin r\pi/(2n+1) \sim r\pi/(2n+1)$. Using these limits, we have

$$f_1(A_n, y_1) \to (-e^{B/2}\, 2A_n + A_n + 1)\frac{r\pi}{2\,(2n+1)} \qquad \text{(B.2)}$$

Thus $f_1(A_n, y_1)$ approaches zero from the negative side.

Case 2: r is even and $r/2$ is odd.

In this case, we have

$$f_2(A_n, y_1) = A_n^{n+1} \sin\frac{r\pi}{2n+1} + (A_n + 1)\sin\frac{r\pi}{2\,(2n+1)}\,.$$

For such values of r, and $\frac{r\pi}{2n+1} \in (0, \pi/2)$, $f_2(A_n, y_1)$ is always positive for all finite n. Thus in the limit of large n, we have

$$f_2(A_n, y_1) \to (2A_n e^{B/2} + A_n + 1)\frac{r\pi}{2\,(2n+1)} \qquad \text{(B.3)}$$

This approaches zero from the positive side. (Note that these results hold even when the restriction that $r \ll n$ is dropped for $A_n = 1 + B/(2n+1)$ and $y \in (0, \pi/2)$)

Thus, given an arbitrarily small neighbourhood about $y = 0$, the number of zeros of $f(A_n, y_1)$ indefinitely increases in the limit as $n \to \infty$.

Some remarks on the choice of A_n are in order. The constant A_n which is a function of N only relates γ_S to γ_{S-1}. These relations imply that γ_S is an increasing function of S. Since only the constant relates γ_S to γ_{S-1} one must expect to eliminate the constant in the calculation (as was seen in the example considered). At the first sight, it appears that there is a considerable amount of arbitrariness in the choice of A_n. However this is only in the choice of B $A_n = 1 + B/(2n+1)$. All those choice of A_n that alternate the sign of (B.1) for successive values of $y_1 = r\pi/2\,(2n+1)$ are permitted. From equation (B.1) [or (B.2) and (B.3)] it is clear that A_n infinitesimally close to unity is the best choice. If A_n is very much larger than unity and less than 3, then $A_n^{n+1} \to \infty$. Though this choice alternates the sign, the function is not well behaved in the limit as $N \to \infty$. Thus there is not much arbitrariness in the choice of A_n.

Appendix C

We argue in the following that $(1/N) \log \gamma_s$ is intensive. In the limit of large N the free energy per particle, $(1/N) \log Z$, is an intensive quantity (*see* Griffiths 1964). Then it can easily be seen that $(1/N) \log \gamma_s$ cannot have any dependence on N, N^2, etc. By choosing a proper scale, the following relation holds $\infty > Z > \gamma_S > 1$. Thus

$$\frac{1}{N} \log Z > \frac{1}{N} \log \gamma_S > 0$$

$\log \gamma_s$ can be expanded in powers of N.

$$A'N + B'N^2 + C'N^3 + \dots$$

Then it is clear that all constants except A' should be zero, otherwise, the inequality breaks down (The choice of A' is also restricted to $A' < (1/N) \log Z$). Thus we see that $(1/N) \log \gamma_S$ is intensive. Thus it is clear that the quantities $(1/N) \log \gamma_s$ and $(1/N) \log \gamma_s$ differ from their limiting values by terms of order of $(1/N)$ and higher.

References

Baker Jr G A, Gilbert H E, Eve J and Rushbrooke G S 1967 *Phys. Rev.* **164** 800 and the references contained therein

Fisher M E 1965 *Lectures in theoretical physics* (University of Colorado Press, Boulder) pp. 1–159

Griffiths B R 1964 *J. Math. Phys.* **5** 1215 and relevant references therein

Jones L G 1966 *J. Math. Phys.* **1** 2000

Matsen F A, Klein D T and Foyt D C 1971 *J. Phys. Chem.* **75** 1866

Yang C N and Lee T D 1952 *Phys. Rev.* **87** 404