An Introduction to Basic Statistical Mechanics for Mathematicians I: Background

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(work in progress!)

Contents

1 Preface

Part 1 is a version of some talks given to the Leeds Stat Mech Discussion Group. The brief was to introduce basic statistical mechanics, so as to explain the common setting in which the various different interactions with Mathematics sit.

1.1 What/Why Statistical Mechanics?

We are going to have to assume some basic Physics, and hopefully move on from there. ...So where does Statistical Mechanics fit in to Physics?

> *"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."* **Paul Dirac**

In this quote Dirac points out that the problems of Physics do not end, by any means, with the determination of fundamental principles. They include such fundamental problems; and also problems of computation.

(Indeed for the subject we are going to describe here, its original historical development was assumed to be on the fundamental side. Only a better understanding of its setting later showed otherwise.)

An example of the laws that Dirac is refering to would be Newton's laws, which do a good job of determining the classical dynamics of a single particle moving through a given force-field. Two-body systems are also manageable but after that, even though it may well still be Newtonian (or some other well-understood) laws that apply in principle, exact dynamics will simply not be computationally accessible.

Do we really need to know about many-body dynamics? Yes. At least some understanding of the modelling of many-body systems is needed in order to work with a number of important materials (magnets, magnetic recording materials, LCDs, non-perturbative QFT etc). In each such case, the key dynamical components of the system are numerous, and interact with each other. Thus the force fields affecting the movement of one, are caused by the others; and when it moves, its own field changes, moving the others.

The solution:

The equilibrium Statistical Mechanical approach to such problems is to try to model only certain special types of observation that could be made on the system. One then models these observations by weighted averages over all possible instantaneous states of the system. In other words dynamics is not modelled directly (questions about dynamics are not asked directly). As far as is appropriate, dynamics is encoded in the weightings – the probabilities asigned to states.

The first problem is to describe these states, and determine appropriate probabilities.

It is most convenient to pass to an example. We shall have in mind a bar magnet. [1] We shall assume that the metal crystal lattice is essentially fixed (the formation of the lattice is itself a significant problem, but we will have enough on our plate). The set of states of the system that we shall allow are the possible orientations of the atomic magnetic dipoles (not their positions, which shall be fixed on the lattice sites).

What next?

2 Towards the partition function

2.1 Classical reminders

A good rule of thumb when analysing a physical system is: "follow the energy". (This begs many questions, all of which we ignore.)

The kinetic energy of a system of N point particles with masses m_i and velocities v_i is

$$E_{kin} = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2$$

What can affect a particle's subsequent velocity, and hence change its kinetic energy? That is, what causes $\frac{dv}{dt}$ to be non-zero? A force can do this:

$$F = m \frac{dv}{dt}$$

Thus we also need to understand the forces acting on the particles.

For example: If they are really pointlike then they interact pairwise via the Coulomb force

$$F_1 = \frac{q_1 q_2}{4\pi\epsilon_0} \frac{r_{12}}{r_{12}^3} = -F_2$$

Here q_1, q_2 are the charges (perhaps in coulombs); ϵ_0 is a constant (depending on that unit choice); and $\underline{r}_{12} = \underline{r}_1 - \underline{r}_2$.

For a moment we can think of this as a force field created by the second particle, acting on any charged first particle. This is a conservative force field; meaning that there is a function $\phi(\underline{r})$ such that

$$F = -\nabla \phi$$

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[1] This provides a number of simplifications of the general problem, without trivialising the key features.

The function $\phi(\underline{r})$ is part of the potential energy of the first particle. In other words its 'total energy' is of the form

$$E = \frac{1}{2}mv^2 + \phi$$

In practice, since ϕ is only defined up to an additive constant, E itself is not so significant as *changes* in E.

2.2   Stats/Gibbs canonical distribution

Notice that system energy E depends on the velocities and positions of all the atoms in the system. There are 10^{23} or so atoms in a handful of Earthbound matter, so we are not going to be able to keep track of them all (nor do we really want to). We would rather know about the bulk, averaged behaviour of the matter.

Let us call the inaccessible complete microscopic specification of all positions and velocities in the system a 'microstate'. Then for each microstate σ we know, in principle, the total energy $E(\sigma)$. We could ask: What is the probability P of finding the system, at any given instant, in a specific microstate?

Then we could compute an expected value for some bulk observation $\mathcal{O}$ by a weighted average over the microstates:

$$\langle \mathcal{O} \rangle = \sum_{\sigma} \mathcal{O}(\sigma) P(\sigma) \tag{1}$$

In principle the probability P could depend on every aspect of σ. This would make computation very hard. At the other extreme, P could be independent of σ. But this turns out to be a problematic assumption for a number of Mathematical and Physical reasons. Another working assumption would be that two microstates are equally likely if they have the same energy; i.e. that P depends on σ just through E. That is, that P depends only on the total energy of the system. Let us try this.

The next question is: How does P depend on E? What is the function $P(E)$?

If we have a large system, then we could consider describing it in two parts (left and right side, say), separated by some notional boundary, with the total microstate σ being made up of σ_L and σ_R. These halves are in contact, of course, along the boundary. But if the system is also in contact

with other systems (so that energy is not required to be locally conserved), then it is plausible to assume that the states of the two halves are independent variables. In this case

$$P(\sigma) = P(\sigma_L)P(\sigma_R)$$

as for such probabilities in general. Similarly, the total energy

$$E = E_L + E_R + E_{int}$$

(where E_{int} is the interaction energy between the halves) is reasonably approximated by

$$E \sim E_L + E_R$$

(Why is this reasonable?!... Clearly the kinetic energy is localised in each of the two halves. The potential energy is made up of contributions from all pairs, including pairs with one in each half. But we assume that the pair potential is greater for pairs that are closer together; and that the boundary is a structure of lower dimension that the system overall. In this sense E_{int} is localised in the boundary (pairs that are close together but in separate halves are necessarily close to the boundary); while being part of the overall potential energy, which is spread with essentially constant density over the whole system. Thus E_{int} is a vanishing proportion of the whole energy for a large system. (We shall return to these core Physical assumptions of Statistical Mechanics later. They imply an intrinsic restriction in Statistical Mechanics to treating interactions that are, in a suitable sense, short-range. Fortunately this seems Physically justifiable.))

The L and R subsystems will each have their own 'energy-only' probability function. Thus we have something like

$$P(E_L + E_R) = P_L(E_L)P_R(E_R) \tag{2}$$

In this expression E_L and E_R are independent variables, so

$$\frac{\partial P(E_L + E_R)}{\partial E_L} = \frac{\partial P(E_L + E_R)}{\partial E_R}$$

so $P'_L(E_L)P_R(E_R) = P_L(E_L)P'_R(E_R)$, so

$$\frac{P'_L(E_L)}{P_L(E_L)} = \frac{P'_R(E_R)}{P_R(E_R)}$$

This separates. We write $-\beta$ for the constant of separation. We have $P'_L(E_L) = -\beta P_L(E_L)$ (and similarly for R). This is solved by a function of form

$$P(E) = C \exp(-\beta E)$$

where C is any constant. In our case C is determined by

$$\sum_\sigma P(E(\sigma)) = 1$$

The separation constant β is interesting, since it is the only thing (other than the form of the function itself) that connects the subsystems. We will see later that this connection corresponds (inversely) to a notion of *temperature*.

2.3 Partition Function

The normalisation function for our system

$$Z(\beta) = \sum_\sigma \exp(-\beta E(\sigma))$$

(Z for *zustatensummen*, or some such name due to Boltzmann) is called the partition function. That is, for given β,

$$P(E) = \frac{\exp(-\beta E)}{Z}$$

Recall that, by our derivation, β represents the effect of thermal (energetic) contact with the universe of other systems. Our usual notion of the bulk contribution of neighbouring systems on the energetics of a given system, at least where long-time-stable (equilibrium) properties are concerned, is the notion of temperature. Thus β encodes temperature. How specifically does it do this? See later.

First we want to consider the pay-off for the analysis we have made so far. The idea was that we would be able to compute time-averaged bulk properties of the system.

Z is 'just' a normalising factor. But

$$\frac{d \ln Z}{d\beta} = -\frac{1}{Z} \sum_\sigma E(\sigma) \exp(-\beta E(\sigma))$$

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the *internal energy* (or compute $\frac{1}{N}$ of this for the energy *density*), so its analysis contains Physics!

Suppose

$$E : S \to \pm \mathbb{N}$$

(i.e. the energy is quantised).[2] Then Z is polynomial in $\exp(\mp\beta)$. Its only analytic structure is *zeros*. However, we will see how these zeros are indeed physically significant.

Figure 1 gives a quick glimpse of the distribution of zeros in the complex $x = \exp(\beta)$ plane for a three-dimensional Ising model (what this is will be explained later).

Question: What does this tell us?

The *specific heat* tells us the rate of change of internal energy with temperature (or, in practice, the other way round — we measure the amount of energy we have to put into a fixed mass of material to change its temperature by 1 degree):

$$\mathcal{S} = \frac{\partial^2 \frac{1}{N} \ln Z}{\partial \beta^2}$$

Consider the formulation

$$Z = \prod_j (x - z_j)$$

In terms of the complex zeros $\{z_j = x_j + iy_j\}$ we have:

$$\frac{\partial \frac{1}{N} \ln Z}{\partial \beta} = \frac{x}{N} \sum_j \frac{1}{x - z_j}$$

$$\mathcal{S} = \frac{\partial^2 \frac{1}{N} \ln Z}{\partial \beta^2} = \frac{x}{N} \left(\sum_j \frac{1}{x - z_j} - x \sum_j \frac{1}{(x - z_j)^2} \right)$$

Note that the complex zeros appear in conjugate pairs. Performing the sum within each conjugate pair this becomes

$$\mathcal{S} = \frac{2x}{N} \left({\sum_j}' \frac{x - x_j}{(x - x_j)^2 + y_j^2} - x {\sum_j}' \frac{(x - x_j)^2 - y_j^2}{((x - x_j)^2 - y_j^2)^2 + 4(x - x_j)^2 y_j^2} \right)$$

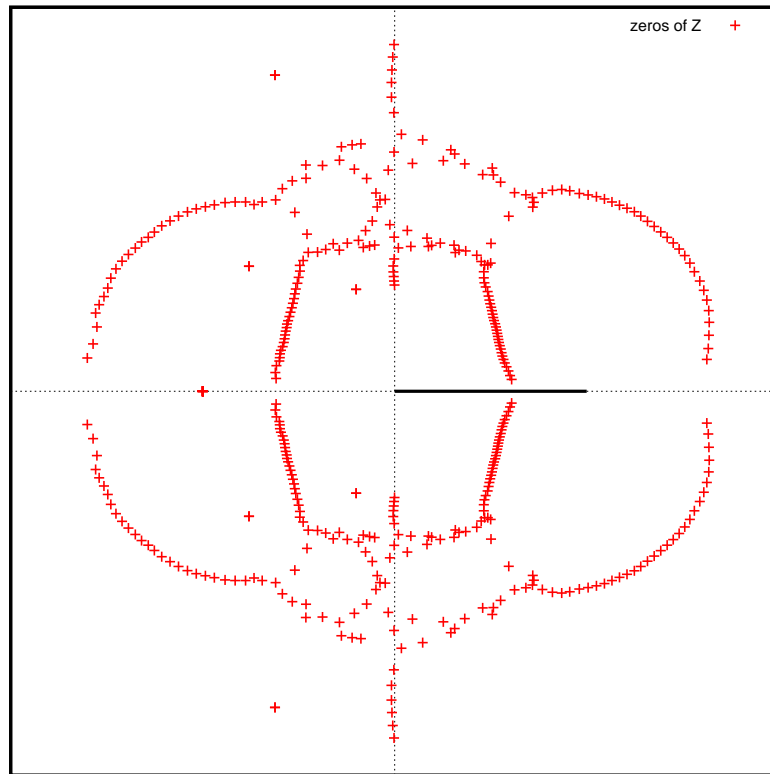[2]This is far from always true, but it is not unrealistic.

Figure 1: Complex zeros of the partition function for a cubical lattice Ising model of about $N = 150$ sites [8, 9].

Consider the contribution of the j-th term (i.e. from a pair of zeros) to $\mathcal{S}$, at some point on the real x axis. Note that if y_j is large, or if $x - x_j$ is large, then this contribution is small. Meanwhile the contribution is large if the zeros are close to the axis, and x is close to these zeros. In particular the contribution is large if $x = x_j$, whereupon

$$\mathcal{S}_j \sim \frac{2x^2}{Ny_j^2}$$

Simply put, this says that, moving along the real line (real temperature), $\mathcal{S}$ and U go crazy when there are complex zeros close by (as there are at a particular point in Figure 1, for example).

Accordingly we shall call a region of the complex plane that is close to the real axis and contains zeros of Z a *critical neighbourhood* of Z.

Let us (very crudely) compare with physical observation.

When we boil a kettle we put roughly equal amount of energy into the water in each unit of time. At first the temperature rises, and the rate of rise does not change very much as the temperature goes up. That is, the specific heat changes slowly and smoothly with temperature. Close to and at the boiling point, however, the temperature rise essentially stops, i.e. the amount of energy required to further change the temperature becomes very large. In the practical experiment there are a number of reasons for this, but one of them is that the specific heat becomes very large. Thus we associate divergent specific heat with a phase transition (in this case the liquid-gas transition at the boiling point).

Another quick picture, of a different model, is shown in Figure 2. Once again you are invited to study the distribution of zeros close to the 'physical' region: the real interval $[0, 1]$.

In practice we are never even going to know N accurately for a real physical system. Nor is such an accurate knowledge important to us, since realistic observations do not depend on it. Indeed for intensive quantities we expect them to be stable under even large changes in N, so long as N is large enough. Thus intensive observations in our model also need to be large N stable. [3]

Our pictures give a clue as to the sense in which this can happen: Different polynomials (different N; different but suitably 'similar' physical

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[3]Note that we do not require a large N *limit* per se for Physics. But stability and the existence of such a limit amount to the same thing computationally.
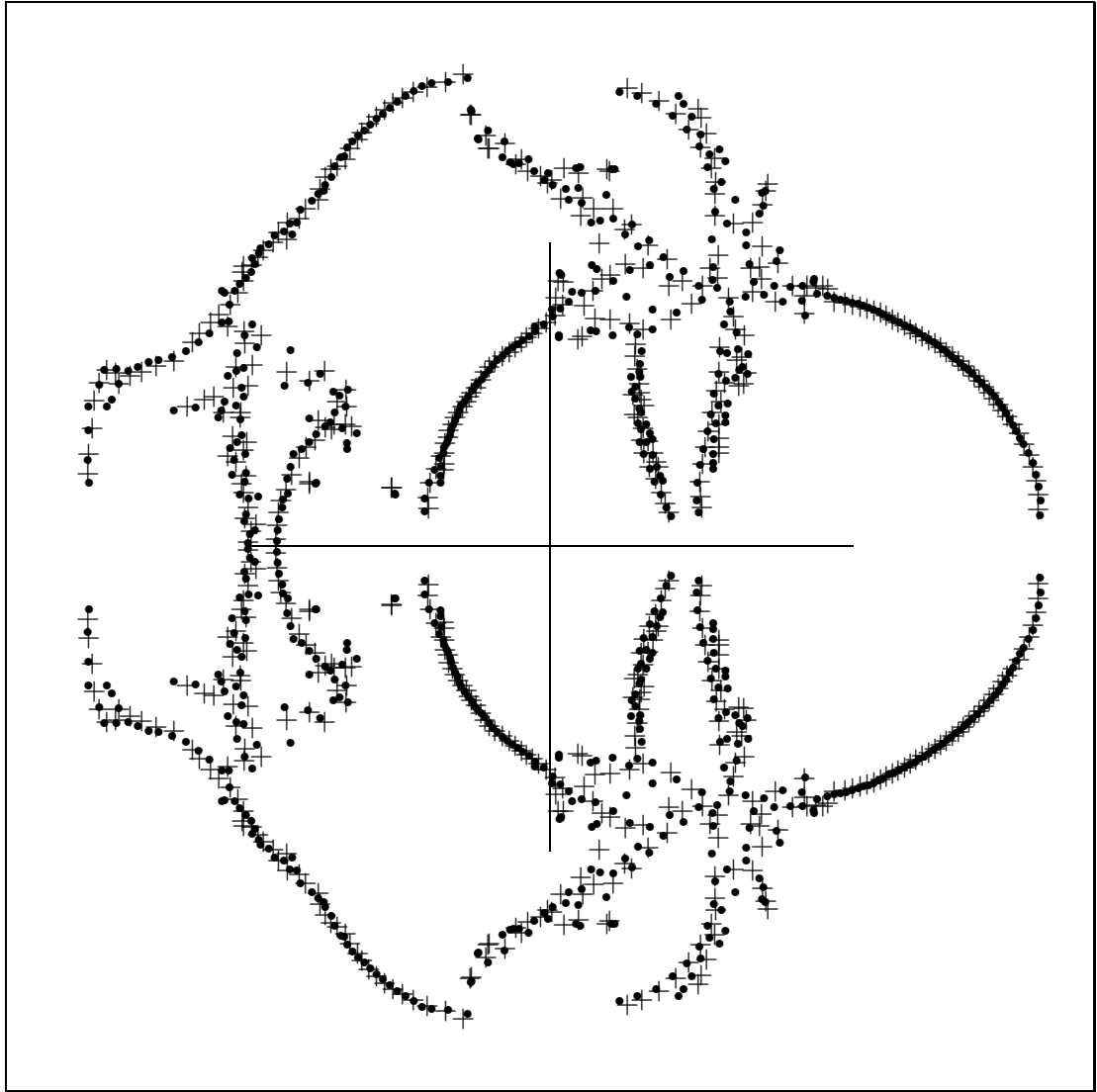
Figure 2: Complex zeros of the partition function for a two-dimensional clock model at two different lattice sizes [7].

systems) could have similar distributions, real accumulation points, etc.; and hence manifest behaviour on the physical line in similar ways.

Can we at least have a model for *this*?

3   Models

We now briefly introduce a simple choice for E (the microstate energy function), called the Potts model, from a Physics perpective. [4]

As noted, to introduce a choice for E for physical modelling, we must actually introduce one for each of a whole collection of 'similar' systems, then check the stability of observables across this collection. Mathematically, it is convenient to introduce one for each of a rather large collection of (nominally but not necessarily adequately similar) systems, then refine this collection by physical considerations post hoc. (We will make all this very precise later.)

Some statistical mechanics nomenclature: While kinetic-energy-only (non-interating) models are rather simple, models in which only the potential energy is accounted for in the microstate energy are much richer (partly because aspects of the kinetic energy of the system are encoded in β anyway). Excluding kinetic energy from E means that we are essentially treating our particles as fixed (that is, not translating). Instead system dynamics is manifested in other ways. For example we can consider non pointlike particles, hence with the possibility of magnetic dipole moments. System dynamics in this case can be manifested in magnetic dipole orientation. In such a setting, particles are called *spins*. Also, the microstate energy function is called the *Hamiltonian* (and typically written H not E).

Let Γ be the set of graphs, and for $G \in \Gamma$ let V_G be the vertex set. Adopt the notation

$$\underline{n} = \{1, 2, ..., n\}$$

and for any set S (such as a set of graph vertices) write

$$Q^S = Hom(S, \underline{Q})$$

for the set of maps from S to Q — each map f asigns state q to vertex s by $f(s) = q$.

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[4]REMARK: In SMDG the first lecture (given by Jeanne Scott) gave a formal introduction to Potts models treated as combinatorial entities.

A Q-state graph Hamiltonian is a map asigning to each graph G a map in $Hom(Q^{V_G}, \mathbb{Z})$. We say that this map gives the 'energy' of state $\sigma \in Q^{V_G}$.

The idea of a model like this is that each graph represents a given physical system, with the degrees of freedom residing on the vertices, and the geometrical relationship of the vertices encoded (somehow) in the edges.

Fixing Q (e.g. $Q = 2$)

$$...FIXME!$$

Lots of stuff missing from here.

4 Computation

4.1 Partition vector

4.2 Transfer matrix

4.3 Analysis

We have seen quite generally that in the physical temperature region the limit free energy density is $\ln \lambda_0$ where λ_0 is the largest magnitude eigenvalue of the transfer matrix. What becomes of this when we look in the complex $x = \exp(\beta)$ plane, and in particular in our 'critical' neighbourhood of the physical region? (As defined in Section 2.3.)

To get a bit more out of the 1d Ising model here consider other boundary conditions. For example, for the A_N graph but with end spin states fixed

$$Z'(A_N) = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}(\lambda_1^N + \lambda_2^N)$$

while

$$Z(\hat{A}_N) = \mathrm{Tr} \begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix}^N = \lambda_1^N + \lambda_2^N = (x+1)^N + (x-1)^N$$

There are a number of ways that we can recast this simple expression to help think about what might happen in general for large N.

Firstly, we can rewrite

$$(x+1)^N + (x-1)^N = (x-1)^N((\frac{x+1}{x-1})^N + 1)$$

Ignoring the first factor we have

$$Z \sim Y^N + 1 = Y^{N/2}(Y^{N/2} + Y^{-N/2})$$

(where $Y = \frac{x+1}{x-1}$), that is, the remaining zeros are distributed evenly around a circle. It is the same circle for any N, but the line density increases with N. Setting $Y = \exp(\beta')$

$$f = \frac{1}{N}\ln Z = \frac{1}{N}(\ln(2) + \frac{N}{2}\ln Y + \ln(\cosh(\frac{N}{2}\beta')))$$

so

$$U = -\frac{\partial \frac{1}{N}\ln Z}{\partial \beta'} = -1 - \tanh(\frac{N}{2}\beta')$$

That is, the internal energy changes fast (at $\beta' = 0$) for large N.

As we have already seen, the physics is dominated by the zeros close to the real line, so we can approximate

$$\lim_{N\to\infty} f \sim \beta'/2 + \frac{1}{2\pi}\int_{-\infty}^{\infty} a(y)\ln(\beta' + iy)dy$$

where $a(y) = 1$ (in our case) is the line density of zeros. Thus

$$U \sim \frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{a(y)dy}{y - i\beta'}$$

The integrand has a simple pole at $y = i\beta$, so the integral changes by $2\pi a(0)$ as β' changes sign. In other words, if the limit line density $a(0) \neq 0$ the internal energy changes discontinuously at this point — a *first order phase transition*.

In practice, in more complicated systems, we can get

$$a(y) \sim |y|^{1-p} \qquad (0 \leq p \leq 1)$$

but we will return to this shortly.

Notice in our 2×2 transfer matrix example that the distribution of zeros corresponds to the locus of points where the largest eigenvalue is actually degenerate (with the other eigenvalue, regarded as an analytic function of β). In fact a large class of models have a transfer matrix reducible to a 2×2 polynomial matrix T'. As before

$$\lim_{N\to\infty}\frac{\ln Z}{N} = \lim_{N\to\infty}\ln(\lambda_+^N + \lambda_-^N) \stackrel{*}{=} \ln\lambda_+$$

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where * means on the real axis. What happens to the zeros this time?

Consider the general identity

$$C^N + D^N = \prod_{n=-\frac{N-1}{2}}^{\frac{N-1}{2}} (C + \exp(\frac{2\pi i n}{N})D) = \prod_{n=1/2}^{\frac{N-1}{2}} (C^2 + D^2 + 2\cos(2\pi n/N)CD)$$

(the explicit limits are for the case N even — the reader will easily compute the odd case). Using this we can rewrite

$$\lim_{N\to\infty} \frac{\ln Z}{N} = \lim_{N\to\infty} \ln(\lambda_+^N + \lambda_-^N) = \frac{1}{2\pi} \int_0^\pi \ln(2(A^2 + B) + 2\cos y(A^2 - B))dy$$

where $A^2 - B = CD = \lambda_+\lambda_-$ and $2(A^2 + B) = C^2 + D^2 = \lambda_+^2 + \lambda_-^2$, that is

$$\lambda_\pm = A \pm \sqrt{B}$$

Since T' is polynomial, so are A and B, and hence the limit is (the log of) an infinite product of polynomials. One readily confirms that the zeros of this infinite product are the loci

$$|\lambda_+| = |\lambda_-|$$

and the endpoints of these loci (if any) are the points where $\lambda_+ = \lambda_-$, i.e. at roots of the polynomial B (if B nonvanishing).

(**4.1**) REMARKS: This analysis is essentially taken from [6, Ch.11].

Acknowledgements

A   What is Physics?

Statistical Mechanics is part of Physics. *Physics* might be characterised, in the large, as the scientific exercise (as opposed to involuntary reflex) of modelling of the observable physical world. That is, the representation of part of the physical world by something 'simpler', which nonetheless captures some of the physical world's humanistically essential features.

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There are various phases to this exercise, such as:

(i) deciding which toy is the model;

(ii) working out what the model itself does; and

(iii) interpreting this behaviour as a prediction for the physical world.

The simple toys at our disposal include *real* toys (scale models of bridges and so on), and systems of equations in mathematics. [5] In particular Scientists have had notable success summarizing large amounts of observational data from the physical world with certain relatively simple mathematical models. A very successful such model is, reasonably, regarded as close to nature itself; and hence fundamental. Key to this is the expectation that such a model, pushed into an as yet unobserved (but suitably nearby) regime, will correctly predict the result of observations subsequently made there. There has been notable success too in this predictive aspect of Physics, and great technological benefits have accrued.

Bibliography

Some relevant texts are, for Statistical Mechanics: Baxter[2], Domb and Green[3], Levy[5], Martin[6], and Wannier[10];

for generalities: Abramowitz and Stegun[1], Feynman[4].

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[3] C Domb and M S Green (eds.), *Phase transitions and critical phenomena I*, Academic Press, London, New York, 1972.

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[5]Note that these toys either exist themselves in the physical world, or are abstractions formulated by creatures living in the physical world (and whose thought processes are tied to making sense of this experience). This is of course unavoidable, but singular. Other problems in representation theory are not constrained to have all representations built inside the thing being represented.

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