

Ising Chain with Two Random Components in Zero Field

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An exact, simple, closed form, result for the free energy of a two component random Ising chain, with nearest neighbour interactions, in the two physically interesting cases of the completely quenched and completely annealing system for any concentration of the components, is presented. Systems with dilute magnetic components are particular cases of our results.

Apresenta-se um resulta exato, simples, em form fechada, para a energia livre de uma cadeia de Ising aleatória, a duas componentes, com interações entre vizinhos mais próximos. Isso é feito nos dois casos fisicamente interessantes, vale dizer, em o caso de impurezas totalmente fixas ou totalmente móveis, para qualquer concentração dos componentes. Sistemas com componentes magnéticos diluídos aparecem como casos particulares de nossos resultados.

1. INTRODUCTION

Because of the growing interest in the effects of random disorder on the properties of condensed matter, we consider once more the simple model of a linear Ising chain of two physically distinct spin 1/2 components, A and B, randomly distributed over the chain sites, which take on, according to neighbourhood, three different exchange constants, J_{AA} , J_{BB} and J_{AB} , between nearest neighbours.

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In this paper, only the case of zero magnetic field will be considered. The results of previous authors (Refs. 1-5) are simplified and generalized to arbitrary concentrations, $c_A, c_B = 1 - c_A$, to yield the free energy in the two cases:

(i) fixed (or "frozen"), temperature independent, distribution of the components, corresponding to a quenched alloy.

(ii) Completely mobile components, free to arrange themselves in the minimum free energy configurations, at any temperature, corresponding to free annealing.

In what follows, the two cases will be referred to as the "quenched" and "annealing" cases, respectively.

2. FORMULATION OF THE PROBLEM, PARTITION FUNCTION OF A GIVEN CONFIGURATION

Let us assume an open chain of N Ising spins, $a_{\mathbf{i}}$, of which m are of kind A, $n = N - m$ of kind B, so that $c_A = \frac{m}{N}$ and $c_B = \frac{n}{N}$. In this one dimensional model, the word "sequence" can and will be used to denote a given component configuration (s) , (AAA ... ABB ... BBA ...), not to be confused with the spin configurations (σ) , ($\uparrow\uparrow\uparrow \dots \downarrow\downarrow\downarrow \dots \uparrow\uparrow\uparrow \dots$), which exists independently and simultaneously with any given component configuration.

The energy, for a given sequence (s) , is

$$H_{(\sigma)}^{(s)} = - \sum_{\mathbf{i}} J_{\mathbf{i}, \mathbf{i}+1}^{(s)} \sigma_{\mathbf{i}} \sigma_{\mathbf{i}+1}, \quad (1)$$

where $a_{\mathbf{i}} = \pm 1$ and $J_{\mathbf{i}, \mathbf{i}+1}^{(s)}$ takes on the values J_{AA}, J_{BB} and J_{AB} , according to the occupation of sites \mathbf{i} and $\mathbf{i}+1$ in (s) .

The partition function for this sequence is

$$Z^{(s)} = \sum_{(\sigma)} \exp(-\beta H_{(\sigma)}^{(s)}) \quad (2)$$

which, in standard fashion, can be expressed in terms of the transfer matrix, $P_{i,i+1}$ (see Note 6), as

$$Z^{(s)} = \text{Tr} \prod_{i=1}^N P_{i,i+1} \quad (3)$$

with $\beta J_{i,i+1} = K_{i,i+1}$, so that

$$P_{i,i+1} \begin{pmatrix} \exp(K_{i,i+1}) & \exp(-K_{i,i+1}) \\ \exp(-K_{i,i+1}) & \exp(K_{i,i+1}) \end{pmatrix} = \exp K_{i,i+1} \underline{1} + \exp(-K_{i,i+1}) \sigma^x \quad (4)$$

where $\underline{1}$ is the unit matrix, and σ^x the Pauli matrix. From (4), it is evident that the three different P 's that can occur in the product in (3), P_{AA} , P_{BB} and $P_{AB} = P_{BA}$, all commute, and can therefore be simultaneously diagonalized to give the eigenvalues $\lambda_{i,i+1}^{(1)} = 2 \cosh K_{i,i+1}$ and $\lambda_{i,i+1}^{(2)} = 2 \sinh K_{i,i+1}$.

In other words, $Z^{(s)}$ does not depend on any other feature of (s) but rather on the number of times it contains neighbour pairs of type AA, AB, BA and BB, i.e., on the number $r(s)$ of AB boundaries in the sequence. This yields r factors P_{AB} , r factors P_{BA} (see Note 7), leaving $m - r$ factors P_{AA} and $n - r$ factors P_{BB} , for any such r -sequence. Of course $0 \leq r \leq \min m, n$, so that for $r = 0$ one has a single B-domain at the left of a single A-domain (...BBBB/AAA...), while for $r = n$ all B's are isolated from each other, (...AA/B/AAA.....A/B/AA.....AA/B/A.....). This independence of the details, of an r -sequence, for obtaining the partition function is the key feature of the linear chain in the field free case. With that

$$Z^{(s)} = Z(r(s)) = Z_r = \text{Tr} \left\{ P_{AA}^{m-r} P_{BB}^{n-r} P_{AB}^{2r} \right\}$$

$$= 2^N \cosh^{m-r} K_A \cosh^{n-r} K_B \cosh^{2r} K_{AB}, \quad (5)$$

(compare Note 7 to Eq. (3).)

3. QUENCHED RANDOM SYSTEM

Now, knowing the partition function of any given sequence, we treat first the quenched case. What characterizes quenched random disorder is that the free energy of the infinite system is the arithmetic mean of the free energies of all possible, distinguishable, sequences (s) of length N , $N \rightarrow \infty$. In other words, its partition function is the geometric mean of the partition functions of these sequences.

If we call $M(s)$ the number of all those different sequences, we have, therefore,

$$Z_{\text{qu}} = \left[\prod_{(s)} Z(s) \right]^{1/M(s)}. \quad (6)$$

There are as many different sequences as different permutations of the m indistinguishable A's, and the n indistinguishable B's, so that

$$M(s) = \frac{(m+n)!}{m! n!} = \binom{N}{n} = \binom{N}{m}. \quad (7)$$

According to (5), all sequences (s), with the same $r(s)$, are degenerate with respect to the partition function. Thus, all we need to evaluate (6) is the the number $N(r)$ of different sequences that contain the same number r of AB boundaries, to obtain:

$$Z_{\text{qu}} = \left[\prod_{r=0}^n (Z_r)^{N(r)} \right]^{1/M(s)} \quad (8)$$

$N(r)$ is easily found as follows. First one inserts r AB boundaries (B-inserts) between them A's; this can be done in $\binom{m}{r}$ different ways. For any such insertion, one uses r B's, the remaining $n - r$ B's can be

attached to any of the r bound B's without altering the number of AB boundaries; this, again, can be done in $\binom{n}{r}$ distinguishable ways. Therefore,

$$N(r) = \binom{m}{r} \binom{n}{r} . \quad (9)$$

Of course, as it should be,

$$\sum_{r=0}^n N(r) = \sum_{r=0}^n \binom{n}{r} \binom{N-n}{r} = \binom{N}{n} = M(s) . \quad (10)$$

Inserting (7) and (9) into (8), we obtain

$$Z_{qu} = \left[\prod_{r=0}^n Z_r \binom{m}{r} \binom{n}{r} \right] \binom{N}{n}^{-1} . \quad (11)$$

Using Stirling's formula, we find for the free energy per spin

$$= - \frac{k T}{N} \sum_{r=0}^n \left[\binom{N}{m} \right] \exp \left[-2r \log r - (m-r) \log (m-r) - (n-r) \right. \\ \left. \cdot \log (n-r) + \log \log Z(r) \right] .$$

Converting the sum into an integral, one finds the saddle point r to obey the equation

$$2 \log r_0 - \log (m-r_0) - \log (n-r_0) = 0 . \quad (12)$$

The term in $\log \log Z(r)$ contributes only $O(N^{-1})$ to the position of the saddle point, and therefore the solution r_0 does not depend on coupling constants or temperature but only on the concentrations: From (12), we find

$$r_0 = N c_A c_B ; m-r_0 = N c_A^2 ; n-r_0 = N c_B^2 \quad (13)$$

In other words, the above procedure amounts to the usual replacements of

such sums by their largest member, where upon the binomial factors cancel out and, using (5), one gets simply, up to irrelevant additive constants,

$$\begin{aligned}
 f_{\text{qu}} &= -\frac{kT}{N} \log Z(x_0) = -kT(c_A^2 \log \cosh K_A \\
 &\quad + c_B^2 \log \cosh K_B + 2c_A c_B \log \cosh K_{AB}) \\
 &= c_A^2 f_A + c_B^2 f_B + 2c_A c_B f_{AB} \quad , \quad (14)
 \end{aligned}$$

where f_A , f_B and f_{AB} are the free energies of pure Ising chains with coupling constants J_A , J_B and J_{AB} , respectively.

Of course internal energy and specific heat have similar structure as (14):

$$\begin{aligned}
 u_{\text{qu}} &= c_A^2 u_A + c_B^2 u_B + 2c_A c_B u_{AB} \quad , \\
 C_{\text{qu}} &= c_A^2 C_A + c_B^2 C_B + 2c_A c_B C_{AB} \quad , \quad (15)
 \end{aligned}$$

where

$$C_X = \frac{kK_X^2}{\cosh^2 K_X} \quad , \quad X = A, B, AB \quad .$$

4. ANNEALING RANDOM SYSTEM

In this case, all the possible distinguishable sequences are real, realizable component configurations of the system, competing thermodynamically in the energy balance of the partition function. The total partition function is, therefore, actually the sum over all component and spin configurations

$$Z_{\text{ann}} = \sum_{(s)} \sum_{(\sigma)} \exp \left[-\beta H \begin{matrix} (s) \\ (\sigma) \end{matrix} \right] = \sum_{r=1}^n N(r) Z \quad , \quad (16)$$

where, again, the degeneracy of all sequences of equal r has been used.

Inserting (5) and (9) into (16), we obtain

$$Z_{\text{ann}} = 2^N \cosh^m K_A \cosh^n K_B \sum_{r=0}^N \binom{m}{r} \binom{n}{r} x^r, \tag{17}$$

where

$$x = \frac{\cosh^2 K_{AB}}{\cosh K_A \cosh K_B}$$

Applying once more Stirling's formula, we can write

$$Z_{\text{ann}} = \text{const.} (m \cosh K_A)^m (n \cosh K_B)^n \sum_{r=0}^n \exp [r \log x - 2r \log r - (m-r) \log (m-r) - (n-r) \log (n-r)] , \tag{18}$$

where we write for the sum, as before,

$$\sum_{r=0}^n e^{g(r)} \approx \left[-g''(r_0) \right]^{-1/2} e^{g(r_0)} , \tag{19}$$

only that now the saddle point equation,

$$\log \left[\frac{r^2}{\binom{m-r}{r} \binom{n-r}{r}} \right] = \log x(T) + o(N^{-1}) , \tag{20}$$

does contain the coupling constants and temperature through $x(T)$. This is intuitively clear: when the components are free to diffuse to the minimum free energy configuration, the optimal or "typical" number r_0 of AB boundaries must depend on temperature.

Introducing the concentration of AB boundaries, $c_{AB}(T) = \frac{1}{N} r_0(T)$, one can rewrite (17) to read

$$\frac{c_{AB}^2}{(c_A - c_{AB})(c_B - c_{AB})} = x(T) = \frac{\cosh^2 K_{AB}}{\cosh K_A \cosh K_B} \quad (21)$$

whose only physical solution is

$$c_{AB} = \frac{1}{2} \frac{x}{x-1} \left[1 - (1 - 4c_A c_B \frac{x-1}{x})^{1/2} \right] \quad (22)$$

At low temperatures, when

$$|J_{AB}| < \frac{|J_A| + |J_B|}{2}, \quad x \rightarrow 0,$$

so that $c_{AB} = 0$, i.e., the A's and B's "repel" each other, tending to form two pure phases. On the other hand, for

$$|J_{AB}| > \frac{|J_A| + |J_B|}{2}, \quad x \rightarrow \infty,$$

as $T \rightarrow 0$, the mixing will be maximal, i.e., every B is inserted between two A's, the remaining A's (if any) placed anywhere, giving rise to a highly degenerate ground state. For

$$|J_{AB}| = \frac{|J_A| + |J_B|}{2},$$

in the low temperature limit, or for any $|J_{AB}|$ in the high temperature limit, $x \rightarrow 1$, so that $c_{AB} = c_A c_B$, like the distribution (13) of the quenched chain of the preceding paragraph. One can consistently define the degree of mixing in the system as c_{AB}/c_B , a kind of "component disorder parameter" that has its range between 0 and 1, according to the temperature in the different cases discussed above.

Inserting now (22) and (19) into (18), and taking the log of (18), where only the extensive terms are kept, one gets for the free energy the expression

$$f_{\text{ann}} = c_A (f_A + f_A^*) + c_B (f_B + f_B^*) \quad (23)$$

where $f_X = -kT \log \cosh K_X$, as before, and

$$f_X^* = kT \log \left(1 - \frac{c_{AB}(T)}{c_X} \right), \quad X = A, B. \quad (24)$$

In a similar form one can write the internal energy and the specific heat. For the latter, we get

$$C_{\text{ann}} = c_A(C_A + C_A^*) + c_B(C_B + C_B^*), \quad (25)$$

where

$$C_X^* = \frac{k}{T^2} \left[\frac{\left(\frac{\partial^2 c_{AB}}{\partial (1/T)^2} \right)}{(c_X - c_{AB})} + \frac{\left(\frac{\partial c_{AB}}{\partial (1/T)} \right)^2}{(c_X - c_{AB})^2} \right] \quad (26)$$

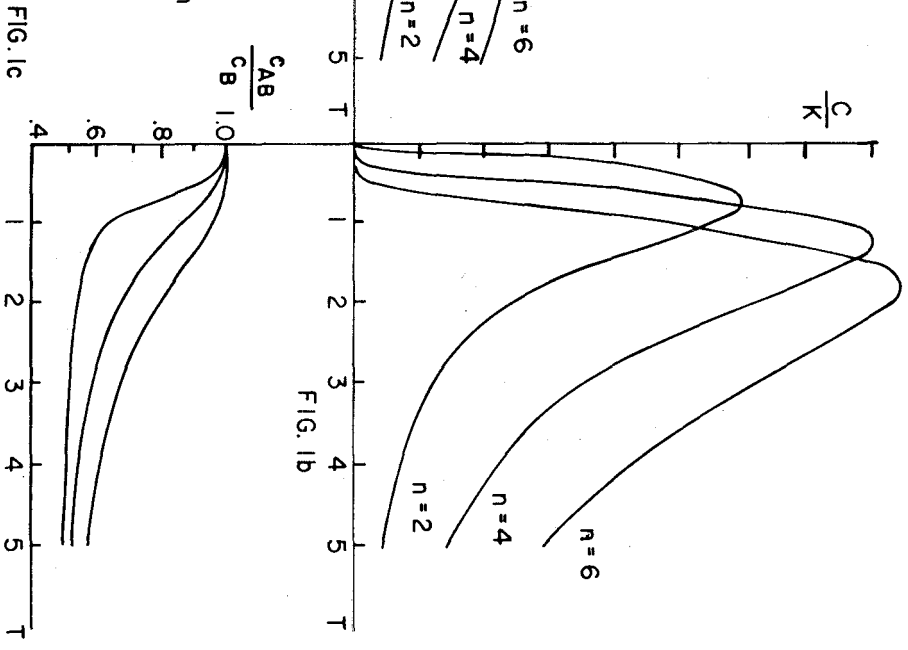
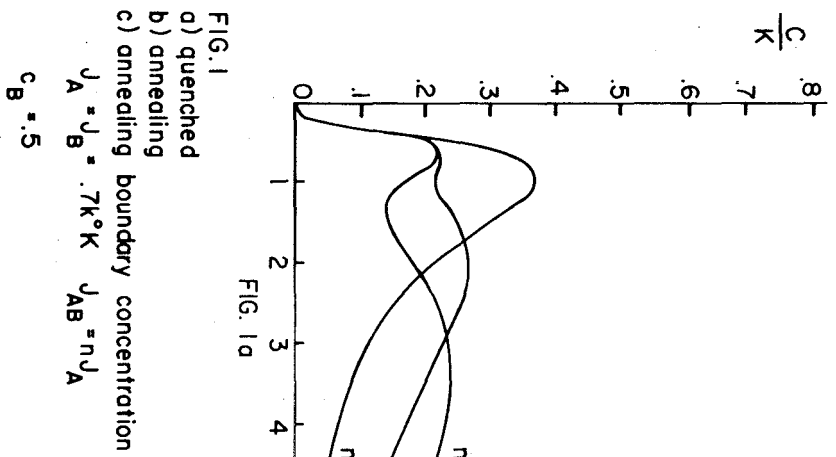
and, as before, $C_X = kK_X^2 / \cosh^2 K_X$, $X = A, B$. In (25) and (26), it is interesting to note that one has separated the pure magnetic contribution to the specific heat from the pure annealing contribution. The first of them, already present in the quenched case (15), is due to spin flips and, the latter, due to the mobility of the components, appears in the form of temperature derivatives of the AB-boundary concentration in Eq. (26).

5. RESULTS AND CONCLUSIONS

The result of the preceding paragraphs, for the concentration of AB-boundaries, was:

$$(c_{AB})_{\text{qu}} = c_A c_B; \quad (c_{AB})_{\text{ann}} = \frac{1}{2} \frac{x}{x-1} \left[1 - (1 - 4c_A c_B \frac{x-1}{x})^{1/2} \right].$$

In the quenched case, c_{AB} , is constant; the result represents the most pro-



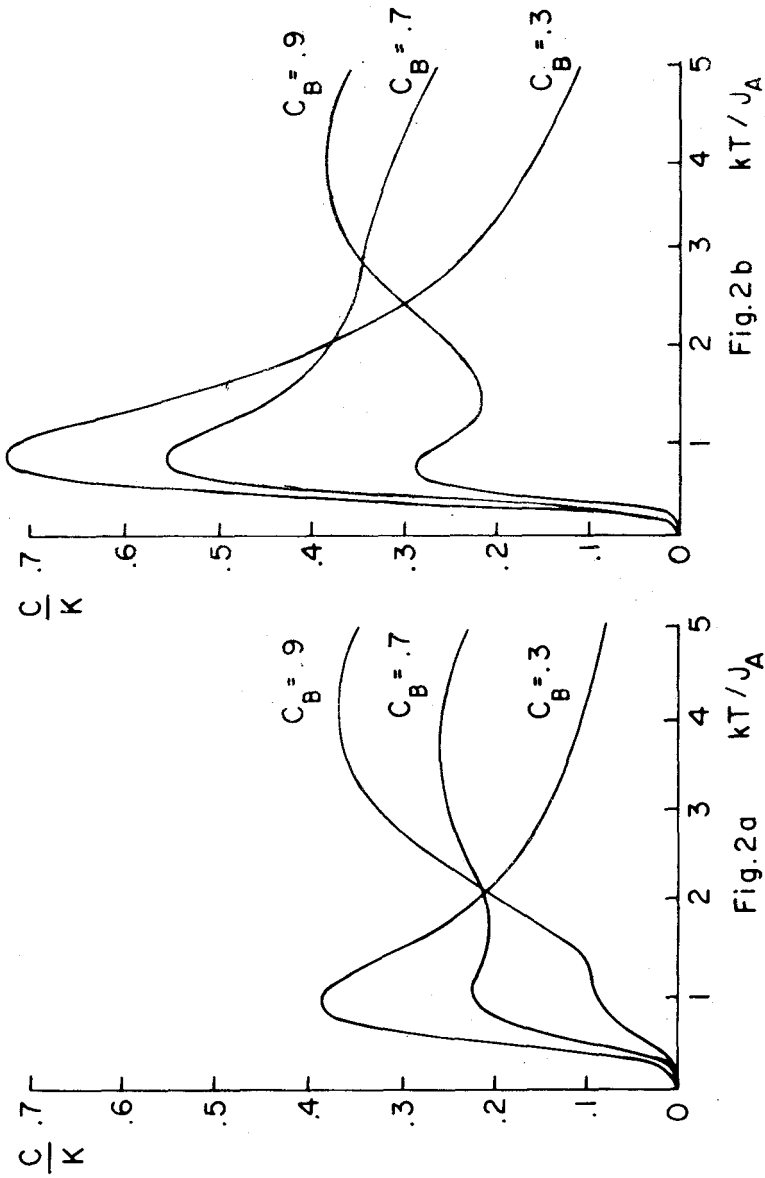


Fig. 2 a) quenched
 b) annealing

c) $J_B/J_A = 5$ $J_B/J_A = 1.25$

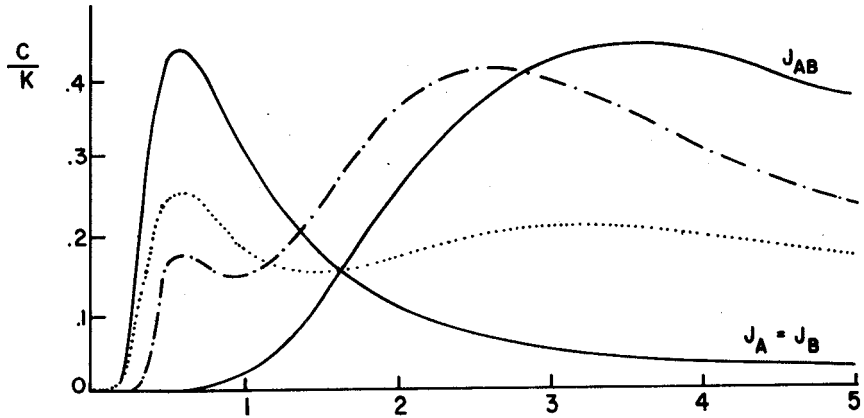


FIG.3

FIG. 3

— pure

- - - annealing $c_B = .3$

..... quenched $c_B = .3$

$$J_A = J_B = .7K^*K$$

$$J_{AB} = 6J_A$$

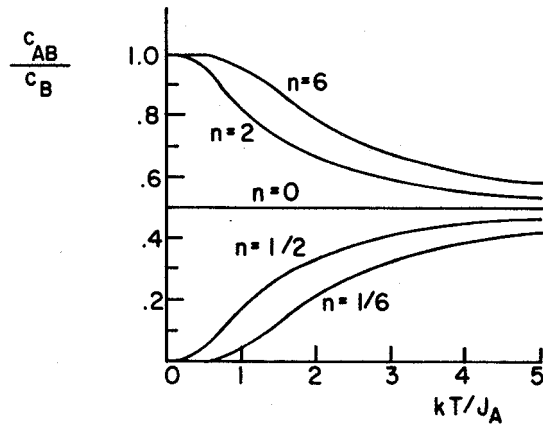


FIG.4

$$J_A = J_B$$

$$J_{AB} = nJ_A$$

$$c_B = .5$$

bable distribution of independent A's and B's on the sites. The characteristic temperature dependence of $(c_{AB})_{ann}/c_B$, on the other hand, is as illustrated in Fig. 4 and Fig. 1c: at high temperatures, i. e., when $kT \gg \max(|J|)$, it approaches $(c_{AB})_{qu}/c_B = c_A$, i.e., the statistical distribution; for $T \rightarrow 0$, we get either complete separation of the pure phases, $c_{AB} = 0$, or maximum mixing, $c_{AB} = c_B$, depending on whether $2|J_{AB}|$ is smaller or larger than $|J_A| + |J_B|$; with increasing temperature we get a gradual "melting" of the pure phase or the AB-supers-structure, respectively; this is quite as intuitively expected. The temperature, at which c_{AB} changes most rapidly with temperature, lies somewhere in the middle, between the different values of J.

Let us remark here that in this one-dimensional zero field case, all results, both for c_{AB} and for the free energy and its derivatives below, do not depend on the signs, but only on the absolute values $|J|$ of the exchange constants; this is for obvious reasons: inverting the sign of, let us say, J_A from + to -, we find, for any spin state, at $J_A \rightarrow 0$, a spin state of the same energy, at $J_A < 0$, by reverting all spins between any two successive AA-bonds along the entire chain; this one-to-one correspondence of degenerate states gives rise to unaltered thermodynamic results.

For the specific heat we had:

$$C_{qu} = c_A^2 C_A + c_B^2 C_B + 2c_A c_B C_{AB},$$

$$C_{ann} = c_A (C_A + C_A^*) + c_B (C_B + C_B^*),$$

with C^* from (26).

For the special case $J_B = J_{AB} = 0$, these results reproduce those of Ref.1 for the "dilute Ising chain".

We next consider the specific heats in some detail.

Obviously, $(C)_{qu}$ is just a superposition of the specific heats of Ising chains with coupling constants J_A , J_B and J_{AB} , whereby the broad maximum of the chain specific heat is in any case broadened, and, for largely differing J , even splits up into several maxima, as illustrated in Fig. 1a.

Fig. 2 shows how the height of the separate maxima depends on impurity concentration c_B .

Fig. 2a should be compared with the corresponding curves in Ref.5, which are quite similar, evidently due to the rapid convergence, at zero field, of the series expansion given there for the quenched case. Completely different is the behaviour of C_{ann} , as can be seen by contrasting Fig. 1a with 1b, and 2a with 2b: the dominating feature is a high and relatively narrow low temperature peak, wiping out all other structure, at least at 50% impurity concentration. This peak is more than two times higher, in all the cases of Fig.1, than those of the quenched case (or of a pure chain) with its center right between the superimposed peaks of the quenched case. Moreover, comparison of Figs. 1b and 1c shows that the annealing specific heat maxima coincide with those temperatures at which the 'melting' of the low temperature AB-superstructure goes most rapidly with temperature. All this makes it obvious that the annealing case specific heat is dominated by the entropy of compositional disorder superseding the entropy connected with spin disorder which causes the structure in the quenched case. For this reason, the area under C , i.e., $u(T=\infty) - u(T=0)$, is always larger in the annealing than in the quenched case (compare, e.g., also Fig.3, where C_{qu} and C_{ann} are plotted in one graph for another representative case, together with C for the pure AA- and the pure AB-chain).

Another way to look at the role of compositional entropy is by discussing the free energy in the annealing case, in particular the terms $c_A f_A^* + c_B f_B^*$ in (23) and (24).

In the high temperature limit, where, as discussed before, $(c_{AB})_{ann} \rightarrow c_A c_B$, these two terms go into

$$f_{\text{mixt}} = T S_{\text{mixt}} = kT(c_A \log c_A + c_B \log c_B) ,$$

which represents just the usual entropy of a mixture. Thus, the results of this paper can be stated as follows:

For zero magnetic field, the free energy and its derivatives, for a two component linear Ising chain, can be calculated exactly both for frozen and for mobile components for arbitrary concentrations and exchange constants. This is due to a degeneracy of the energy for all configurations with the same number of AB-boundaries. A magnetic field lifts this degeneracy and the degeneracy with respect to the signs of the coupling constants.

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6. Actually, Eq. (3) is the solution of the closed chain problem. For the open chain, the solution is

$$Z = \text{Tr } M \prod_{i=1}^{N-1} P_{i, i+1} ,$$

where M is the matrix $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$ which can easily be shown to project out the eigenvalues $\cosh K$, such that Eq. (5) is exact for the open chain and, in the thermodynamic limit, also true for closed chains.

7. As a matter of fact, there are $r \neq 1$ P_{BA} -factors for open chains .
 For long chains, however, $r \pm 1 \simeq r$.
8. $1-(c_{AB}/c_B)$ is the short-range order coefficient of nearest neighbours, as defined in Ref.Z.