Phase boundary residual entropy and finite temperature pseudo-transition for one-dimensional models

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Abstract

Recently was observed clues of pseudo-critical temperature in one-dimensional spin models, such as the Ising-Heisenberg spin models, among others, exhibiting the pseudo-transitions. Here we report an intrinsic relationship between the zero temperature phase boundary residual entropy and pseudo-transition. Usually, the residual entropy increase at the phase boundary, which means the system becomes with more accessible states in the phase boundary compared to its adjacent states. However, this is not always the case; there are some phase boundaries where the entropy remains equal to the largest residual entropy of the adjacent states. Therefore, we propose the following statement at zero temperature. If the phase boundary residual entropy is continuous at least from the one-sided limit, then the analytic free energy exhibits a pseudo-transition at finite temperature. This condition would be essential to study more realistic models. Just by analyzing at zero temperature behavior of the residual entropy, we can know whether the system will exhibit pseudo-transition. To illustrate our argument, we use a couple of examples of Ising-Heisenberg models to show the pseudo-transitions behaviors due to the phase boundary residual entropy continuity. These are a frustrated coupled double tetrahedral chain and an unfrustrated diamond chain.

Keywords: Residual entropy; Quasi-phases; Pseudo-transitions; Ising-Heisenberg

1. Introduction

In 1950 van Hove[1], verified the absence of phase transition with a short-range order for the uniform one-dimensional system. Writing the partition function by using the transfer matrix technique and reducing the problem to the largest eigenvalue, which implies that the free energy is an analytic function. Thus established a theorem to prove that one-dimensional models with short-range coupling do not exhibit any phase transitions. Recently, Cuesta and Sanchez[2] argued that van Hove’s theorem should satisfy the following conditions: (i) Homogeneity, excluding automatically inhomogeneous system, i.e., disordered or periodic. (ii) The Hamiltonian does not include particles position terms, e.g., external fields. (iii) Hard-core particles, this means the theorem cannot be applied to point-like or soft particles. Hence, Cuesta and Sanchez[2] proposed a more general non-existence theorem for phase transition at finite temperature. Mainly they included an external field and considered point-like particles. Which broadens the non-existence theorem, but it is not yet a fully general theorem, e.g., were not included mixed particle chains and more general external fields.

Unlike, there are some one-dimensional models with a short-range coupling that exhibit a first-order phase transition at finite temperature. The Kittel model (also known as a zipper model)[3], is a typical simple model with a finite transfer matrix. Whose constraint on zipper corresponds to an infinite potential, and this condition leads to the non-analytic free energy. Consequently, the system exhibits a first-order phase transition. Another model is that considered by Chui-Weeks model[4], with a typical set of models called solid-on-solid for surface growth. Whose transfer matrix dimension is infinite, but can be solved exactly. Imposing the impenetrable condition to subtract, the model shows
the existence of phase-transition. Dauxois-Peyrard model\textsuperscript{[5]}, is another model with infinite transfer matrix dimension, which can only be solved numerically. Recently Sarkanych et al.\textsuperscript{[6]} proposed a one-dimensional Potts model with invisible states and short-range coupling. The term invisible essentially refers to an additional energy degeneracy, which contributes to the entropy, but not the interaction energy. These invisible states are the responsible for generating a first order phase transition. This one is similar to the infinite energy potential in Kittel model\textsuperscript{[3]}. In a nutshell, all these models break the Perron-Frobenius Theorem, because free energy becomes non-analytical at the phase transition temperature, or equivalently some elements of the transfer matrix become null (corresponding to infinite energy).

On the other hand, the term "pseudo-transition" was introduced by Timonin\textsuperscript{[7]} in 2011 when studied the spin ice in a field, to refer to a sudden change in first derivative of the free energy, while a strong vigorous peak appears in the second derivative of free energy, although there are no discontinuity or divergence, respectively. Later this definition was adopted for our group\textsuperscript{[8, 9, 10]} because we found the same kind of property. The pseudo-transition does not violate the Perron-Frobenius theorem, because the free energy is always analytic. Equivalently, some elements (Boltzmann factor) of the transfer matrix become only a tiny amount compared to other elements, or the corresponding energy becomes large but finite compared to ground state energy. So, we can ignore the small Boltzmann factor without changing its exact result significantly. To illustrate better this behavior, let us consider a decorated model that can be mapped into a simple spin-1/2 Ising-like model with Hamiltonian

$$H = - \sum_{i=1}^{N} \left[ K_{0} + K s_{i} s_{i+1} + \frac{1}{2} B (s_{i} + s_{i+1}) \right],$$

(1)

where $K_{0}$, $K$ and $B$ are effective parameters which in general could depend on temperature, and with $N$ unit cells. Therefore, the transfer matrix can be expressed as $V = \begin{bmatrix} w_{1} & w_{0} \\ w_{0} & w_{-1} \end{bmatrix}$, like discussed in reference \textsuperscript{[10]}. Each elements of transfer matrix $w_{n}$ or Boltzmann factors with $n = \{-1, 0, 1\}$, (we will call as sectors), can be written as

$$w_{n} = \sum_{k=0} g_{n, k} e^{-\beta \varepsilon_{n, k}}.$$  

(2)

Here $\varepsilon_{n, k}$ represent the energy levels $k = \{0, 1, \ldots\}$ and $g_{n, k}$ denotes the degeneracy for each energy level and assuming $g_{n, k} = \{1, 2, 3, \ldots\}$. With $\beta = 1/k_{B} T$, $k_{B}$ Boltzmann constant and $T$ is the absolute temperature.

With the corresponding transfer matrix eigenvalues provided by

$$\lambda_{\pm} = \frac{1}{2} \left( w_{1} + w_{-1} \pm \sqrt{(w_{1} - w_{-1})^2 + 4 w_{0}^2} \right).$$

(3)

Assuming the chain with a periodic boundary condition, the partition function becomes $Z_{N} = \lambda_{+}^{N} + \lambda_{-}^{N}$. Consequently, the free energy can be obtained in the thermodynamic limit ($N \to \infty$) as

$$f = -\frac{1}{\beta} \ln \left[ \frac{1}{2} \left( w_{1} + w_{-1} + \sqrt{(w_{1} - w_{-1})^2 + 4 w_{0}^2} \right) \right].$$

(4)

As discussed in the previous literature\textsuperscript{[10]}, if we consider $\tilde{w}_{0} \equiv \frac{w_{0}}{|w_{1} - w_{-1}|} \to 0$, or in terms of $\min(\varepsilon_{0,0} - \varepsilon_{1,0}, \varepsilon_{0,0} - \varepsilon_{-1,0}) \to +\infty$. Ignoring the higher order terms correction $O(\tilde{w}_{0}^2)$, the free energy reduces to

$$f = -\frac{1}{\beta} \ln \left[ \max (w_{1}, w_{-1}) \right].$$

(5)

This result could mean, the presence of a genuine phase transition at finite temperature, because \textsuperscript{[5]} becomes a non-analytic function when $w_{1} = w_{-1}$. Of course, this cannot happen, unless the lowest energy in sector $n = 0$ satisfies.
From now on, we will focus on the thermodynamic properties when $w_1$ and $w_{-1}$ are competing term or equivalently means around the “quasi-phase” transition between sectors $n = 1$ and $n = -1$.

Recent investigations revealed a number of decorated one-dimensional models, particularly the Ising and Heisenberg models with a variety of structures. Such as the Ising-Heisenberg in the diamond chain[11, 12]. One-dimensional double-tetrahedral model, where the nodal site is assembled by localized Ising spin, and alternating with a pair of mobile electrons delocalized within a triangular plaquette[13]. Ladder model with alternating Ising-Heisenberg coupling[14]. As well as the triangular tube model with Ising-Heisenberg coupling[15]. In all these models pseudo-transition clues were observed. The first derivative of the free energy, such as entropy, internal energy or magnetization show an abrupt jump as varying the temperature. Which is similar to the first order phase transition, but the function is continuous. While a second order derivative of free energy, like the specific heat and magnetic susceptibility, resembles a typical behavior of second-order phase transition at finite temperature. Therefore, this peculiar behavior drew attention to a more careful study, as considered in reference[10]. Lately, in reference[8] has been made an additional discussion on this property and detailed study of the correlation function for arbitrarily distant spins around the pseudo-transition.

The rest of the article is organized as follows: In sec.2 we present the phase boundary residual entropy and its connection to the pseudo transitions. In Sec.3 the frustrated Ising-Heisenberg tetrahedral chain was investigated, and the pseudo-transition using the conditions proposed in Sec.2 is taken into account. Analogously, in Sec. 4 is considered an unfrustrated Ising-Heisenberg diamond chain, and we investigate phase boundary residual entropy according to Sec.2. Finally, in sec.5 our conclusions and perspectives are provided.

2. Phase boundary residual entropy

Now we analyze the residual entropy in the phase boundary of states in sectors $n = 1$ and $n = -1$. For this purpose, we will use the free energy given in (4) when $T \rightarrow 0$. Hence, we can get the residual entropy at zero temperature. Let us assume that the energies $\varepsilon_{1,0}$ and $\varepsilon_{-1,0}$ depend on some arbitrary parameter $x$ (as illustrated in fig.1), e.g., magnetic field. Changing the parameter $x$, we can tune for a particular $x_c$, where adjacent states coexist, with the energy $\varepsilon_c$ of the phase boundary and corresponding degeneracy $G_c$.

Thus the energies $\varepsilon_{1,0}(x)$ and $\varepsilon_{-1,0}(x)$, in the phase boundary becomes $\varepsilon_{1,0}(x_c) = \varepsilon_{-1,0}(x_c) = \varepsilon_c$ with its corresponding degeneracies at phase boundary $g_{1,0}^c$ and $g_{-1,0}^c$. The degeneracy in phase boundary could become greater than in adjacent states degeneracies, i.e. $g_{1,0}^c \geq g_{1,0}$ and $g_{-1,0}^c \geq g_{-1,0}$ (see fig.1b). The lowest energy, in sector $n = 0$ satisfy $\varepsilon_{0,0}(x_c) > \varepsilon_c$, then we have $\bar{w}_0 \rightarrow 0$. Thus, the free energy around the boundary state becomes

$$f = -\frac{1}{\beta} \ln \left[ \frac{1}{2} \left( g_{1,0}^c + g_{-1,0}^c + |g_{1,0}^c - g_{-1,0}^c| \right) e^{-\beta \varepsilon_c} \right] = \varepsilon_c - \frac{1}{\beta} \ln \left[ \max \left( g_{1,0}^c, g_{-1,0}^c \right) \right]. \quad (6)$$

![Figure 1: Ground state-energy phase transition, the phase boundary occurs at $x_c$. Blue lines correspond to sector $n = -1$ energy levels, red lines correspond to sector $n = 1$ energy levels, and black line denoting the sector $n = 0$ energy levels. Tick lines correspond to lowest energies in each sector, and thin lines mean excited energies. In (a) boundary energy is composed only by lowest energies of sectors $n = 1$ and $n = -1$. In (b) Some excited energies could contribute in the phase boundary.](image)
Afterward, we can obtain the corresponding phase boundary residual entropy,

\[ S_c = \ln \left[ \max \left( g_{1,0}, g_{-1,0} \right) \right], \]

(7)

through the article we will consider the entropy in units of \( k_B \). The phase boundary degeneracy per unit cell, results in \( G_c = \max \left( g_{1,0}, g_{-1,0} \right) \).

It is worth mentioning, according to the third law of thermodynamics or often referred to as Nernst’s postulate. At zero temperature, the entropy leads to a constant and must be independent of any parameter (such as \( x \)), so the residual entropy is determined only by its degeneracy of the ground state energy.

\[ \lim_{x \to x^-} S(x) = S(x_c) = S_c \quad \text{and} \quad \lim_{x \to x^+} S(x) = S(x_c) = S_c, \]

(9)

and both limits are identical, then we say the entropy is continuous at \( x_c \).

In principle, this would mean the absence of phase transition. But there are types of phase with identical entropy, which satisfy this condition. We will see later this case when we apply to a specific unfrustrated model.

When \( g_{1,0} \neq g_{-1,0} \), the residual entropy is illustrated schematically in fig[2b]. Assuming the phase adjacent residual entropies satisfy \( S_1 < S_{-1} \), then the left and right limit of entropy at \( x_c \) becomes,

\[ \lim_{x \to x^-} S(x) < S(x_c) = S_c \quad \text{and} \quad \lim_{x \to x^+} S(x) = S(x_c) = S_c. \]

(10)

In this case, the entropy is continuous from the right-sided limit but discontinuous from the left-sided limit. Therefore we can say the entropy is continuous from the one-sided limit at \( x_c \).
• Second, when \( g_{1,0} > g_{1,0} \) and/or \( g_{-1,0} > g_{-1,0} \), the energy levels are illustrated in fig[1]. In this case, the phase boundary residual entropy satisfy \( G_c > g_{1,0} \) and \( G_c > g_{-1,0} \). The entropy is discontinuous at \( x_c \), and we have two possibilities: The case when \( g_{1,0} \neq g_{-1,0} \), is reported in fig[2]:

\[
\lim_{x \to x_c^-} S(x) \neq \lim_{x \to x_c^+} S(x) < S(x_c) = S_c. \tag{11}
\]

So the entropy in \( x_c \) has non-sided limit, with a jump-point discontinuity at \( x_c \).

Similarly, for the case \( g_{1,0} = g_{-1,0} \), as depicted in fig[2],

\[
\lim_{x \to x_c^-} S(x) = \lim_{x \to x_c^+} S(x) < S(x_c) = S_c, \tag{12}
\]

the entropy is discontinuous at \( x_c \). Because there is no left or right sided limit, so it has a point discontinuity at \( x_c \).

Further phase boundary residual entropies for other combinations among sectors are given in Appendix A. Where we show a number of combinations among other sectors, and always the phase boundary degeneracy is strictly larger than their adjacent phase degeneracies.

An alternative way to obtain phase boundary residual entropy could be by using the combinatorial technique. Similar to that discussed in the reference[16, 17] to find residual entropy.

In summary, if the residual entropy is continuous at least from the one-sided limit, then the analytic free energy exhibits a pseudo-transition at finite temperature. For our case, the entropy provided by (8) automatically satisfies the condition of continuity in at least from the one-sided limit.

2.1. Low temperature free energy and pseudo transition

Using the relation (5), we can write the free energy explicitly as a function of temperature and parameter \( x \),

\[
f(x, T) = -T \ln \left[ \max \left( w_1(x, T), w_{-1}(x, T) \right) \right]. \tag{13}
\]

First, let us consider the Boltzmann factor in the low-temperature region, which we express with good approximation just including ground state and lowest excited state energy in each sector. Thus we have

\[
w_1(x, T) = g_{1,0} e^{-\beta \varepsilon_{1,0}(x)} + g_{1,1} e^{-\beta \varepsilon_{1,1}} = e^{-\beta \bar{\varepsilon}(x)} g_{1,0} e^{-\beta \bar{\varepsilon}(x)/2} \left[ 1 + \frac{g_{1,1}}{g_{1,0}} e^{-\beta \delta_1(x)} \right], \tag{14}
\]

\[
w_{-1}(x, T) = g_{-1,0} e^{-\beta \varepsilon_{-1,0}} + g_{-1,1} e^{-\beta \varepsilon_{-1,1}} = e^{-\beta \bar{\varepsilon}(x)} g_{-1,0} e^{-\beta \bar{\varepsilon}(x)/2} \left[ 1 + \frac{g_{-1,1}}{g_{-1,0}} e^{-\beta \delta_{-1}(x)} \right], \tag{15}
\]

where \( \bar{\varepsilon}(x) = \frac{(\varepsilon_{1,0}(x) + \varepsilon_{-1,0}(x))}{2} \) is the average energy, \( \varepsilon(x) = \varepsilon_{1,0}(x) - \varepsilon_{-1,0}(x) \) is energy gap between sectors, and \( \delta_1(x) = \varepsilon_{1,1}(x) - \varepsilon_{1,0}(x) \) and \( \delta_{-1}(x) = \varepsilon_{-1,1}(x) - \varepsilon_{-1,0}(x) \) are energy gap within each sectors.

Next, the free energy becomes

\[
f(x, T) = \bar{\varepsilon}(x) - T \ln \left\{ \max \left[ g_{1,0} e^{-\beta \bar{\varepsilon}(x)/2} \left( 1 + \frac{g_{1,1}}{g_{1,0}} e^{-\beta \delta_1(x)} \right), g_{-1,0} e^{-\beta \bar{\varepsilon}(x)/2} \left( 1 + \frac{g_{-1,1}}{g_{-1,0}} e^{-\beta \delta_{-1}(x)} \right) \right] \right\}. \tag{16}
\]

For the particular case when \( x \to x_c \), and assuming the energy gap temperature leads to \( \beta \delta_1(x_c) \to +\infty \) and \( \beta \delta_{-1}(x_c) \to +\infty \), which implies \( \varepsilon(x_c) \to 0 \) and \( \bar{\varepsilon}(x) \to \varepsilon_c \). So the free energy can be expressed as

\[
f(x_c, T) = \varepsilon_c - T \ln \left[ \max \left( g_{1,0}, g_{-1,0} \right) \right], \tag{17}
\]

recovering the previous result in (7).
2.2. Pseudo-critical temperature

As already discussed above, a condition to emerge the pseudo-critical temperature is because we can write the phase boundary residual entropy as \( S_c = \ln \max (g_{1,0}, g_{-1,0}) \). Thus the pseudo-critical temperature can be found using the following relation

\[
 w_1(x_p, T_p) = w_{-1}(x_p, T_p).
\]  

where \( x_p \) and \( T_p \) correspond the parameters where occurs the pseudo-transition.

![Quasi-phase diagram](image)

Figure 3: Quasi-phase diagram \( x \) against \( T \). Only in zero temperature there is real phase transition at \( (x_c, 0) \). For finite temperature arises a pseudo transition at \( (x_p, T_p) \) for \( T > 0 \).

As a first approximation, we can consider just the ground state energy of the Boltzmann factor. For each of the sectors we have \( w_1 = g_{1,0} e^{-\beta \varepsilon_{1,0}} \) and \( w_{-1} = g_{-1,0} e^{-\beta \varepsilon_{-1,0}} \).

Assuming \( \varepsilon_p = \varepsilon_{1,0}(x_p) - \varepsilon_{-1,0}(x_p) \) in (19), we find the following relation,

\[
e^{-\beta \varepsilon_p} = \frac{g_{-1,0}}{g_{1,0}}, \quad \Rightarrow \quad T_p = \frac{\varepsilon_p - \varepsilon_{1,0}(x_p) + \varepsilon_{-1,0}(x_p)}{\ln \left( \frac{g_{1,0}}{g_{-1,0}} \right)}, \tag{20}
\]

The result (20) was already found in reference [13] [14] [15], and in this limiting case, we can obtain an analytical expression for pseudo-critical temperature. It is also worth mentioning that the critical temperature for the Kittel model [13] [14] [15] has a quite similar expression.

However, eq. (20) cannot be useful, for the case \( g_{1,0} = g_{-1,0} \). Then it is necessary to include the lowest excited energies in at least one sector. Hence, we assume the ground state energy and the lowest excited energy levels in each of the sectors as \( w_1 = g_{1,0} e^{-\beta \varepsilon_{1,0}} + g_{1,1} e^{-\beta \varepsilon_{1,1}} \) and \( w_{-1} = g_{-1,0} e^{-\beta \varepsilon_{-1,0}} + g_{-1,1} e^{-\beta \varepsilon_{-1,1}} \). Therein we can write a transcendental equation as

\[
e^{-\beta \varepsilon_p} = \frac{g_{-1,0} + g_{1,1} e^{-\beta \delta_{1,1,p}}}{g_{1,0} + g_{1,1} e^{-\beta \delta_{1,0,p}}} = \left( \frac{g_{-1,0}}{g_{1,0}} \right) \frac{1 + \frac{g_{1,1}}{g_{1,0}} e^{-\beta \delta_{1,1,p}}}{1 + \frac{g_{1,1}}{g_{1,0}} e^{-\beta \delta_{1,0,p}}}, \tag{21}
\]

where \( \varepsilon_p = \varepsilon_{1,0}(x_p) - \varepsilon_{-1,0}(x_p) \) is the energy gap between sectors at \( x_p \), \( \delta_{1,0,p} = \varepsilon_{1,1}(x_p) - \varepsilon_{1,0}(x_p) \) and \( \delta_{1,1,p} = \varepsilon_{-1,1}(x_p) - \varepsilon_{-1,0}(x_p) \) are the energy gap for each of the sectors. As schematically reported in fig[1].

Usually, when ground state degeneracy is unequal, it is enough to use (20). Nevertheless, when the ground state degeneracy is identical, we need to use eq. (21). If higher energies demand to find pseudo-critical temperature, is better to consider the full expression (19).

In fig[3] we illustrate schematically a typical pseudo-transition curve given by (20) and (21). Here we remark that only at zero temperature occurs a real transition at \( x_c \).

In ref [13] a similar approach was considered, when analyzing the maximum of the peak for the specific heat, and to relate the height of the peak with the degeneracy of the ground state.
3. Coupled tetrahedral Ising-Heisenberg chain

![Schematic representation of coupled tetrahedral Ising-Heisenberg chain. Small balls (σ_i) corresponds to Ising spins, and large balls (S_{a(b),i}) correspond to Heisenberg spins.](image)

Previously, in reference [19, 20] the Heisenberg version of the coupled tetrahedral Heisenberg chain was considered. Whereas, Galisova and Strecka [13, 21] considered the Ising and delocalized electrons in the tetrahedral chain. Later, in the reference [22, 23] the Ising-Heisenberg version of the model was introduced (see eq. 4). Although this model has already been discussed in reference [22, 23], here we focus on the pseudo-transition property that has not yet been explored. Thus, we present the Hamiltonian of the model as

\[
H = -\sum_{i=1}^{N} \left\{ J_{a,i} S_{a,i} S_{b,i} + J_{b,i} S_{b,i} S_{c,i} + J_{c,i} S_{c,i} S_{a,i} + \frac{h}{2} (\sigma_{i} + \sigma_{i+1}) \right\} + \left( S_{a,i}^z + S_{b,i}^z + S_{c,i}^z \right) \left[ h_z + J_0 (\sigma_{i} + \sigma_{i+1}) \right],
\]

(22)

where \( J(S_{a,i}, S_{b,i}) = J S_{a,i}^x S_{b,i}^x + J S_{a,i}^y S_{b,i}^y + J S_{a,i}^z S_{b,i}^z \), with \( S_{a,i}^x \), denoting the Heisenberg spin-1/2, and \( \alpha = \{x, y, z\} \), while \( \sigma_{i} \) denotes the Ising spin \( (\sigma_{i} = \pm \frac{1}{2}) \). In a similar way are defined for sites \( b \) and \( c \) in [22].

The triangle structure with Heisenberg coupling is an operator of dimension \( 8 \times 8 \). Thus we can express as block matrices, one quadruplet and two doublet states, which can be diagonalized readily. Below we present the triplet eigenvalues and eigenstates

\[
e_{\pm \frac{1}{2}} = -\frac{3J_z}{4},
\]

with corresponding eigenvectors

\[
\left| \frac{3}{2}, \frac{3}{2} \right> = \left| +\right>, \text{ and } \left| \frac{3}{2}, -\frac{3}{2} \right> = \left| -\right>.
\]

(23)

The other eigenvalue is

\[
e_{\pm \frac{1}{2}} = -J + \frac{J_z}{4},
\]

whose eigenvectors are given by

\[
\left| \frac{3}{2}, \frac{1}{2} \right> = \frac{1}{\sqrt{2}} \left( \left| +\right> + \left| -\right> \right), \text{ and } \left| \frac{3}{2}, -\frac{1}{2} \right> = \frac{1}{\sqrt{2}} \left( \left| +\right> - \left| -\right> \right).
\]

(24)

While the two doublet states are degenerate. Whose eigenvalue is

\[
e_{\pm \frac{1}{2}} = \frac{J_z}{2} + \frac{J_z}{4},
\]

and the corresponding four-fold eigenstates are

\[
\left| \frac{3}{2}, \frac{1}{2} \right> = \frac{1}{\sqrt{6}} \left( 2 \left| +\right> - \left| -\right> \right), \text{ and } \left| \frac{3}{2}, -\frac{1}{2} \right> = \frac{1}{\sqrt{2}} \left( \left| +\right> - \left| -\right> \right).
\]

(25)

\[
\left| \frac{1}{2}, +\frac{1}{2} \right> = \frac{1}{\sqrt{6}} \left( 2 \left| +\right> - \left| -\right> \right), \text{ and } \left| \frac{1}{2}, -\frac{1}{2} \right> = \frac{1}{\sqrt{2}} \left( \left| +\right> - \left| -\right> \right).
\]

(26)
3.1. Zero temperature phase diagram

Now using the eigenvalues found above. We can express the energy levels and corresponding
degeneracy for \( n = \{-1, 0, 1\} \),

\[
\varepsilon_{n,0} = \frac{1}{2} (J_0 - h) n - J + \frac{J_z}{4} + \frac{h_z}{2}, \quad g_{n,0} = 1, \tag{27}
\]

\[
\varepsilon_{n,1} = \frac{1}{2} (3J_0 - h) n - \frac{3J_z}{4} + \frac{3h_z}{2}, \quad g_{n,1} = 1, \tag{28}
\]

\[
\varepsilon_{n,2} = \frac{1}{2} (J_0 - h) n + \frac{J_z}{2} + \frac{J_z}{4} + \frac{h_z}{2}, \quad g_{n,2} = 2, \tag{29}
\]

\[
\varepsilon_{n,3} = -\frac{1}{2} (J_0 + h) n + \frac{J_z}{2} + \frac{J_z}{4} - \frac{h_z}{2}, \quad g_{n,3} = 2, \tag{30}
\]

\[
\varepsilon_{n,4} = -\frac{1}{2} (3J_0 + h) n - \frac{3J_z}{4} - \frac{3h_z}{2}, \quad g_{n,4} = 1, \tag{31}
\]

\[
\varepsilon_{n,5} = -\frac{1}{2} (J_0 + h) n - J + \frac{J_z}{2} - \frac{h_z}{2}, \quad g_{n,5} = 1. \tag{32}
\]

To analyze the phase diagram at zero temperature, we express some relevant states below.

![Figure 5: (a) Zero temperature phase diagram in the plane of \( J_z - h \), assuming fixed parameters \( J = -10 \), \( J_0 = -10 \) and \( h_z = h \). (b) Entropy density plot for temperature \( T = 0.6 \), assuming the same set of parameters considered in (a). Here the prefix letter "q" is to assign the quasi-phases.](image-url)

Therefore, first, we report the ground state energy of the saturated phase (SA) which read as,

\[
E_{SA} = \varepsilon_{1,4} = -\frac{1}{2} (3J_0 + h) - \frac{3J_z}{4} - \frac{3h_z}{2}.
\]

Whose ground states, Ising spin magnetization, Heisenberg spin magnetization, and total magnetization, respectively are

\[
|SA\rangle = \prod_{i=1}^{N} \left| \frac{3}{2}, \frac{3}{2} \rightangle_i \left| + \rightangle_i, \quad \text{with} \quad m_I = \frac{1}{2}, \quad m_H = \frac{1}{2}, \quad \text{and} \quad m_t = 2. \tag{33}
\]

Similarly, the ground state energy for ferrimagnetic (FI) phase can be expressed as

\[
E_{FI} = \varepsilon_{-1,4} = \frac{1}{2} (3J_0 + h) - \frac{3J_z}{4} - \frac{3h_z}{2};
\]

and its ground state and magnetizations become,

\[
|FI\rangle = \prod_{i=1}^{N} \left| \frac{3}{2}, \frac{-1}{2} \rightangle_i \left| - \rightangle_i, \quad \text{with} \quad m_I = -\frac{1}{2}, \quad m_H = \frac{1}{2}, \quad \text{and} \quad m_t = 1. \tag{34}
\]
The next phase we consider is a frustrated phase, given by

$$E_{FR_1} = \varepsilon_{1,2} = \frac{1}{2} (J_0 - h) + \frac{J}{2} + \frac{J_z}{4} + \frac{h_z}{2},$$

with corresponding ground state and magnetizations, are written as

$$|FR_1\rangle = \prod_{i=1}^{N} |\frac{1}{2}, -\frac{1}{2}\rangle_i + |\frac{1}{2}, \frac{1}{2}\rangle_i, \text{ with } m_l = \frac{1}{2}, \ m_H = -\frac{1}{6}, \text{ and } m_t = 0. \tag{35}$$

The other frustrated ground state energy is

$$E_{FR_2} = \varepsilon_{1,3} = -\frac{1}{2} (J_0 + h) + \frac{J}{2} + \frac{J_z}{4} - \frac{h_z}{2},$$

and its respective ground state and magnetizations read as

$$|FR_2\rangle = \prod_{i=1}^{N} |\frac{1}{2}, +\frac{1}{2}\rangle_i + |\frac{1}{2}, -\frac{1}{2}\rangle_i, \text{ with } m_l = \frac{1}{2}, \ m_H = \frac{1}{6}, \text{ and } m_t = 1. \tag{36}$$

In fig.1b, the phase diagram is shown at zero temperature, where the ground states are given for each region. The phase boundary between $FR_1$ and $FR_2$ is given by $h = 10$, the phase boundary degeneracy is composed by $g_{1,0} = 2$, $g_{1,1} = 2$, $g_{-1,0} = 2$ and $g_{0,0} = 2$, then the residual entropy can be obtained using the eq.(A.6), which becomes $S = \ln(3 + \sqrt{3})$. The straight line $h = J_z$ describes the interface between $FR_1$ and $FI$. Hence, the phase boundary residual entropy can be get using the eq.(A.2), thus we have $S = \ln(3)$, because $g_{1,0} = 2$ and $g_{-1,1} = 1$. In the same way, the boundary between $FI$ and $SA$ is given by $h = 30$. So we can obtain the residual entropy using the eq.(A.6), which becomes $S = \ln(2)$ since $g_{1,0} = 1$ and $g_{-1,0} = 1$. Another case is the boundary between $SA$ and $FR_2$ given by $h = J_z$. The phase boundary entropy at zero temperature can obtained using the eq.(A.4), where the residual entropy becomes $S = \ln(3)$, because $g_{1,0} = 2$ and $g_{1,1} = 1$. All the above phase boundaries are entirely discontinuous, indicating the absence of the pseudo-transition. At last, we obtain the phase boundary in the interface of $FI$ and $FR_2$ described by $J_z = -15$ (red dashed line). The residual entropy is given by eq.(A.6) with degeneracies $g_{1,0} = 2$ and $g_{-1,0} = 1$. Hence, the phase boundary residual entropy becomes $S = \ln(2)$. It is worth to remark the phase boundary residual entropy is equal to the largest adjacent residual entropy. Therefore, we can affirm this boundary should lead to a pseudo-transition, as we must confirm further below.

3.2. Thermodynamics

Now we can obtain the free energy eq.(4) as a function of the Boltzmann factors. For the present model, the Boltzmann factor is taken using the energy levels given by eq.(37).

$$w_n = \sum_{k=0}^{5} g_{n,k} e^{-\beta \varepsilon_{n,k}}. \tag{37}$$

Hence, the Boltzmann factor can be expressed as follows,

$$w_n = 2e^{\beta (\frac{h}{2} - \frac{J}{2})} \left\{ \left( e^{\beta J} + 2e^{-\beta J/2} \right) \cosh \left( \frac{h + J_z}{2} \right) + e^{\beta J_z} \cosh \left( \frac{3}{2} (J_0 + h_z) \right) \right\}, \tag{38}$$

where $n = \{-1, 0, 1\}$. Using the free energy eq.(4), we can find the entropy of the system at finite temperature. In fig.5a, we illustrate the density plot of the entropy as a function of $J_z$ and $h$, for fixed $T = 0.6$, and using the same scale of fig.5b. Here we can observe that the entropy follows the vestige of zero temperature phase diagram. Definitely, the thermal excitation influences the phase boundaries. All except one, display an increase of the entropy around the phase boundaries. The entropy in the boundary $qFI$ and
The first column corresponds to density plot, in the plane $J_z - T$ (top) for a fixed $J = -10$, $J_0 = -10$ and $h = 20$, and in the plane $h - T$ (bottom) for $J = -10$, $J_0 = -10$ and $J_z = -14.6$. Middle column reports the density plot of Ising spin magnetization. The last column illustrates the density plot of Heisenberg spin magnetization.

$qFR_2$ (the prefix "q" is to assign the quasi-phases defined by Timonin[7]) does not increase. Because in zero temperature the entropy is continuous from the one-sided limit at the phase boundary.

In fig.6(left column) reports density plot of entropy in the plane $T - J_z$ (top) and $T - h$ (bottom), for the parameters considered in the caption. The phase boundary between quasi-phases $qFR_2$ and $qFI$ are easily identified. In fig.6(middle column) illustrates the Ising spin magnetization $m_I$ in the plane $T - J_z$ (b), and in the plane $T - h$ (e). While the right column reports for Heisenberg spin magnetization ($3m_H$) in the plane $T - J_z$ (c), and in the plane $T - h$ (f).

In fig.7a is depicted the entropy as a function of $J_z$ in the low-temperature region. We can observe the track of frustrated ($FR_2$) phase which is a state macroscopically degenerate, with residual entropy $S = \ln(2)$. The peak corresponds to the phase boundary between $FR_2$ and $SA$ with corresponding...
phase boundary residual entropy $S = \ln(3)$. Here we can see how a discontinuous residual entropy spreads due to thermal excitation. In fig.7b is illustrated the entropy as a dependence of $J_z$, where we can observe the phase boundary between $FR_2$ with $S = \ln(2)$ and $FI$ with $S = 0$. Whose phase boundary entropy is shown and clearly remains at $S = \ln(2)$ for $T \lesssim 1$. This is because the entropy is continuous from the one-sided limit at phase boundary. In fig.7b is reported the entropy as a function of temperature, in the interface between $qFR_1$ ($S = \ln(2)$ ) and $qFR_2$ ($S = \ln(2)$ ), whose phase boundary residual entropy is $S = \ln(3 + \sqrt{5})$ for $J_z \lesssim -20$. Whereas for $J_z = -15$, the phase boundary joins three phases $qFR_1$, $qFR_2$ and $qFI$, at first glance this is similar to fig.7b. But the phase boundary residual entropy is larger than its adjacent phases, which can be obtained using the eq.(A.6). Where the degeneracy for each sector are $g_{1,0} = 4$, $g_{-1,0} = 3$ and $g_{0,0} = 2$, under these circumstances the entropy becomes $S = \ln(\frac{7+\sqrt{17}}{2})$. We can observe better this point in a magnified plot in the inner part of the fig.7c. Due to this small peak, the right side curve spreads destroying any evidence of pseudo-transition. In fig.7d is plotted the entropy as a function of magnetic field $h$. And we observe a residual entropy between phase boundaries, which are in agreement with previous plots.

In fig.8 is depicted the entropy as a function of temperature assuming fixed parameters $J = -10$, $J_0 = -10$, $h = 20$ and $J_z = \{-13, -14.1, -14.3, -14.5, -14.6\}$. A strong change in the entropy curvature at the pseudo-critical temperature is evident. So, when the temperature increases, the strong jump becomes smoother and then gradually vanishing. In fig.8b is illustrated the correlation length $\xi$ as dependence of temperature. Hence, it is shown a sharp and robust peak at pseudo-critical temperature. In fig.8c is reported the specific heat $C$ against temperature. Whereas in fig.8d is plotted the magnetic susceptibility $\chi$ as a function of temperature. The magnetic susceptibility exhibits small sharp peaks, because the magnetization at zero temperature is identical for $Fr_2$ and $FI$ phases, according to (34) and (36) respectively. But thermal excitation in Ising and Heisenberg spins provokes different responses showing small sharp peaks around pseudo-critical temperature.

4. Ising-XYZ diamond chain

![Diagram of Ising-Heisenberg diamond chain]

Figure 9: Schematic representation of Ising-Heisenberg diamond chain. Small balls ($\sigma_i$) correspond to Ising spins and large balls ($S_{a(b),i}$) correspond to Heisenberg spins.
Another model we consider here is, the Ising-XYZ diamond chain structure as illustrated in fig.[9] which was previously discussed in reference [11][12]. Where $\sigma_i$ (small balls) represents the Ising spin-1/2, and $S_{\alpha(b),i}$ (large balls) denotes the Heisenberg spin-1/2, with $\alpha = \{x, y, z\}$. However, we will direct our attention to the non-frustrated property. Thus, here we just give a revisiting of the spin-1/2, and $S_{\alpha(b),i}$. Where $\alpha = \{x, y, z\}$ and the corresponding ground states is expressed as

$$H = -\sum_{i=1}^{N} \left[ J(1+\gamma)S_{a,i}^x S_{b,i}^x + J(1-\gamma)S_{a,i}^y S_{b,i}^y + J_z S_{a,i}^z S_{b,i}^z + J_0(S_{a,i}^z + S_{b,i}^z)(\sigma_i + \sigma_{i+1}) \right.
\left. + h_z(S_{a,i}^z + S_{b,i}^z) + \frac{1}{2}(\sigma_i + \sigma_{i+1}) \right],$$

(39)

here $J$ corresponds to $xy$-axes exchanges and $\gamma$ being the XY-anisotropy, $J_z$ corresponds to $z$-axis of Heisenberg spins exchange. While $J_0$ denotes Ising-Heisenberg spins exchange, and $h_z(h)$ corresponds to the external magnetic field acting in Heisenberg spins (Ising spins) respectively, along the $z$-axis.

Some of the relevant ground state energy found in reference [11][12] are summarized below, assuming $n = \sigma_i + \sigma_{i+1}$ :

(i) For sector $n = 1 (\uparrow\uparrow)$ the first ground state energy is

$$\varepsilon_{1,0} = E_{MF_2} = -\frac{J_4}{4} - \frac{h_2}{2} - \sqrt{(h_z + J_0)^2 + \frac{1}{4}J^2\gamma^2},$$

(40)

Named as modulated ferromagnetic Heisenberg spin ($MF_2$) phase. With corresponding ground state

$$|MF_2\rangle = \prod_{i=1}^{N} \left( \cos \theta_1 |\uparrow\rangle_i + \sin \theta_1 |\downarrow\rangle_i \right) \otimes |\uparrow\rangle_i,$$

(41)

where $\theta_n = \frac{1}{2} \tan^{-1} \frac{2h_z}{2h_z \pm J_0}$ defined in $0 < \theta_n < \pi$.

Whereas the ferrimagnetic (FI) phase, is given by

$$\varepsilon_{1,1} = E_{FI} = -\frac{J_4}{4} + \frac{J_4}{4},$$

(42)

and the corresponding ground states is expressed as

$$|FI\rangle = \prod_{i=1}^{N} \frac{1}{\sqrt{2}} \left( |\uparrow\rangle_i + |\downarrow\rangle_i \right) \otimes |\uparrow\rangle_i,$$

(43)

(ii) For sector $n = -1 (\downarrow\downarrow)$, the ground state energy, becomes

$$\varepsilon_{-1,0} = E_{MF_0} = -\frac{J_4}{4} + \frac{h_2}{2} - \sqrt{(h_z - J_0)^2 + \frac{1}{4}J^2\gamma^2},$$

(44)

with respective modulated ferromagnetic ($MF_0$) state, given by

$$|MF_0\rangle = \prod_{i=1}^{N} \left( \cos \theta_{-1} |\uparrow\rangle_i + \sin \theta_{-1} |\downarrow\rangle_i \right) \otimes |\downarrow\rangle_i,$$

(45)

The free energy for this model was obtained in reference [11][12]. So from (4) we express using the Boltzmann factor for Ising-XYZ diamond chain

$$w_n = 2e^{\frac{\beta nh}{2}} \left[ e^{-\frac{\beta J_z}{2}} \text{ch} \left( \frac{\beta J_z}{2} \right) + e^{\frac{\beta h_z}{2}} \text{ch} \left( \beta \Delta_n \right) \right],$$

(46)

where $\Delta_n = \sqrt{(h_z + J_0n)^2 + \frac{1}{4}J^2\gamma^2}$.
Performing the derivative of (4) one can find the Heisenberg spin magnetization $m_H = -\frac{\partial f}{\partial h}$ and Ising spin magnetization $m_I = -\frac{\partial f}{\partial h}$.

At zero temperature, the interface between $MF_0$ and $MF_2$ (see fig.10) assuming $h = h_c$, occurs at a critical magnetic field

$$h_c = \frac{(\gamma^2 - 1) + 2J_zJ + 4J_0^2 - J_z^2}{4J + 8J_0 - 4J_z}.$$  \hspace{1cm} (47)

For $h < h_c$ the system is in $MF_0$ state, and for $h > h_c$ the system becomes in another state $MF_2$.  

Figure 10: Density plot for fixed parameters $J = 100$, $\gamma = 0.8$, $J_z = 24$ and $J_0 = -24$. (a) Entropy (b) Heisenberg spin magnetization. (c) Ising spin Magnetization.

In fig.10, we illustrate the density plot entropy as a function of temperature for fixed parameters $J = 100$, $\gamma = 0.8$, $J_z = 24$ and $J_0 = -24$. The boundary between quasi-phases $qMF_0$ and $qMF_2$ is indistinguishable. Because, in zero temperature both phases $MF_0$ and $MF_2$ are non-degenerate with entropy $S = 0$. Thus, the phase boundary residual entropy also becomes null according to relation (8), which is easily observed in the density plot entropy. However, in fig.10b is displayed the density plot of Heisenberg spin magnetization $(m_H)$, the boundary between quasi-phase $qMF_2$ and quasi-phase $qFM_0$ is undoubtedly distinguishable. At $T = 0$ and $h < h_c = 13.063045$, the Heisenberg spins are parallel ordered with greater probability pointing up. The maximum magnetization per spin is $m_{M_1} \sim 0.3$, which is pictorially denoted as effective canting spin (yellow region). Similarly, for $h > h_c = 13.063045$ the Heisenberg spin magnetization becomes negative $m_H \sim -0.1$, pictorially illustrated by effective canting spin down (cyan region). For more detailed information concerning Heisenberg spin magnetization, we refer the reader to ref. [8]. In fig.10c is displayed the density plot of Ising spin magnetization, for $h < h_c$ the magnetization is nearly $m_I = -0.5$ what means most of the Ising spins are aligned with spin down, whereas for $h > h_c$ most of the spins are pointing up aligning with the external magnetic field. Consequently, this behavior could be easily misinterpreted as a real phase transition. Nevertheless, we do not expect a true phase transition at finite temperature, because all derivative of the free energy is analytic. At finite temperature, there is no critical magnetic field, but only a pseudo-critical magnetic field $h_p \lesssim h_c$, which vanishes roughly at $T \sim 1.0$, for temperature $T \gtrsim 1.0$ the system becomes a standard disordered system predominantly.

Fig.11 illustrates the entropy as a function of $h$, for a range of temperature $T = \{0.3, 0.5, 1.0, 1.5, 2.0\}$. There is a sudden change for $T \lesssim 1.0$, this corresponds to the pseudo-transition at $h = 13.063945$. Therefore, for any region or phase, the entropy vanishes when $T \to 0$. Similarly, in fig.11a is plotted entropy as a dependence of $h$. We observe a sudden change for $h = 12.8$, again as soon as temperature decreases the entropy vanishes. However, around $h \approx 39$ corresponds to the phase boundary between $FI$ and $MF_2$ [10,11,12] with a residual entropy $S = \ln(2)$, and obviously in this boundary there is no pseudo-transition. In fig.11b-d is plotted the entropy against $\gamma$, for $h = 18$ and $h = 12$. For temperature $T \lesssim 1$ arises a sudden change showing the pseudo-transition. Here, also the entropy vanishes when $T \to 0$ according to the phase boundary residual entropy. In reference [8,10,11,12], we can find other detailed discussions concerning this model.
Figure 11: Entropy for fixed parameters $J = 100, J_z = 24, J_0 = -24$ and temperature $T = \{0.3, 0.5, 1.0, 1.5, 2.0\}$. (a) Entropy as a function of $h$ considering $\gamma = 0.8$. (b) Entropy as a function of $h$ considering $\gamma = 0.7$. (c) Entropy as a function of $\gamma$ considering $h = 18$. (d) Entropy as a function of $\gamma$ considering $h = 12$.

5. Conclusions.

Although few one-dimensional models exhibit the phase transition, recently were investigated a pseudo-critical temperature in one-dimensional spin models\[8, 10\]. There is a number of models exhibiting pseudo-transition, like the Ising-Heisenberg spin models with a variety of structures\[11, 12, 13, 14, 15\]. Here we report an intrinsic relation between zero temperature phase boundary residual entropy and pseudo-transition. In general, the residual entropy increases in the interface where occurs the phase transition. What means the system increased its accessible states in the interface compared to adjacent states. However, there exist some cases where the phase boundary entropy remains equal to the largest residual entropy of neighboring states, and the entropy is given by $S = \ln \left[ \max \left( g_{1,0}, g_{-1,0} \right) \right]$. Our main result dwells in a simple condition to recognize pseudo-transition. If the phase boundary residual entropy is continuous at least from the one-sided limit, then analytical free energy exhibits a pseudo-transition. To show this property, we have considered two Ising-Heisenberg spins models, one frustrated model in a coupled double tetrahedral chain and another unfrustrated diamond chain. Finding pseudo-transition in more realistic systems would be a fascinating investigation. However, this would be a tough numerical task, even seeing vestiges of pseudo-transition, one could confuse with a true phase transition. In this sense, the condition of the phase boundary entropy is essential. Because we can apply this condition at zero temperature, and searching for the continuity of entropy would be a more easy task, compared to the study full thermodynamic quantities. Once found the entropy is continuous in at least from the one-sided limit. Thus, for analytic free energy we can observe a pseudo-transitions at a finite temperature around a specific region using numerical techniques.

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Appendix A. Other phase boundaries

Appendix A.1. Phase boundary between states of sector $n = 0$ and $n = \pm 1$

First let us consider the sector $n = 1$ and $n = 0$. Assuming the ground state energies are given by $\varepsilon_{1,0}(x)$ and $\varepsilon_{0,0}(x)$, the boundary state occurs when $\varepsilon_{1,0}(x_c) = \varepsilon_{0,0}(x_c) = \varepsilon_c$ with corresponding degeneracy $g_{1,0}^c \geq g_{1,0}$ and $g_{0,0}^c \geq g_{0,0}$. The lowest energy $\varepsilon_{-1,0}(x)$ in sector $n = -1$, will be strictly higher than $\varepsilon_c$ ($\varepsilon_{-1,0} > \varepsilon_c$), what means $w_{-1}/w_0 \rightarrow 0$ and $w_{-1}/w_1 \rightarrow 0$ when $T \rightarrow 0$. So the free energy in (4) at sufficiently low temperature reduces to

$$f = -\frac{1}{\beta} \ln \left[ \frac{1}{2} \left( g_{1,0} + \sqrt{(g_{1,0})^2 + 4(g_{0,0}^c)^2} \right) e^{-\beta \varepsilon_c} \right].$$ (A.1)
Consequently, the phase boundary residual entropy is

\[
S_c = \ln \left[ \frac{1}{2} (g_{c,0}^1 + \sqrt{(g_{c,0}^1)^2 + 4(g_{0,0}^c)^2}) \right], \quad (A.2)
\]

where the degeneracy in phase boundary is given by

\[
\epsilon_c \text{ and } \epsilon_0 \text{ residual entropies, because the case with an energy gap, the system still has entropy discontinuity (non-sided limit at } x = 0). \quad \text{Because the phase boundary residual entropy is strictly larger than its adjacent states.}
\]

In Appendix A.3, Appendix A.2, the phase boundary lies in three sectors and respective degeneracies are

\[
\epsilon_0 > \epsilon_{1,0} > \epsilon_{-1,0} \text{, can coexist for particular } x_c. \quad \text{In this case, the free energy becomes}
\]

\[
f = -\frac{1}{\beta} \ln \left( \frac{1}{2} (g_{1,0}^c + g_{-1,0}^c + \sqrt{(g_{1,0}^c)^2 + 4(g_{0,0}^c)^2}) e^{-\beta \epsilon_c} \right) = -\frac{1}{\beta} \ln \left( (g_{1,0}^c + g_{-1,0}^c) e^{-\beta \epsilon_c} \right). \quad (A.3)
\]

Whereas, the corresponding boundary residual entropy, reduce to

\[
S_c = \ln (g_{1,0}^c + g_{-1,0}^c). \quad (A.4)
\]

For sector \( n = -1 \) and \( n = 0 \), the result of free energy will be equivalent to the previous case. We can obtain by merely exchanging \( \epsilon_{1,0}^c(x_c) \rightarrow \epsilon_{-1,0}^c(x_c) \), in expression (A.2).

Appendix A.2. Phase boundary lies in a single sector

Considering \( \epsilon_{1,0}^c(x) \) and \( \epsilon_{1,1}^c(x) \) are ground states energies describing each adjacent states. Thus assuming that occurs a phase transition between these states, then the boundary energy is given by

\[
\epsilon_{1,0}^c(x_c) = \epsilon_{1,1}^c(x_c) = \epsilon_c \text{ at } T = 0. \quad \text{In general, it is possible that some additional states can coincide in the phase boundary, then the degeneracies can be expressed as } g_{1,0}^c \geq g_{1,1}^c \text{ and } g_{1,1}^c \geq g_{1,1}^c. \quad \text{Therefore,}
\]

\[
\text{all other energy levels must be higher than } \epsilon_c, \text{ so when } T \rightarrow 0 \text{ the spectral energy in other sectors can be neglected (} w_0/w_1 \rightarrow 0 \text{ and } w_{-1}/w_1 \rightarrow 0). \quad \text{Hence, the free energy in the low-temperature limit is expressed as}
\]

\[
f = -\frac{1}{\beta} \ln (g_{1,0}^c + g_{1,1}^c) \text{, (A.3)}
\]

\[
S_c = \ln (g_{1,0}^c + g_{1,1}^c). \quad (A.4)
\]

Thereby, the degeneracy in phase boundary is given by \( G_c = (g_{1,0}^c + g_{1,1}^c) \).

Once again, the phase boundary residual entropy is strictly higher than any residual entropy of adjacent states, because \( G_c > g_{1,0}^c \text{ and } G_c > g_{1,1}^c \).

A schematic representation of the phase boundary residual entropy is illustrated in fig 2.

Appendix A.3. Phase boundary lies in three sectors

The three sectors can constitute phase boundary, this means the states with energies \( \epsilon_{1,0}^c(x), \epsilon_{0,0}^c(x) \) and \( \epsilon_{-1,0}^c(x) \), can coexist for particular \( x_c \). So we assume \( \epsilon_{1,0}^c(x_c) = \epsilon_{0,0}^c(x_c) = \epsilon_{-1,0}^c(x_c) = \epsilon_c \), and the respective degeneracies are \( g_{1,0}^c, g_{0,0}^c \text{ and } g_{-1,0}^c \). In this case, the free energy becomes

\[
f = -\frac{1}{\beta} \ln \left[ \frac{1}{2} (g_{1,0}^c + g_{-1,0}^c + \sqrt{(g_{1,0}^c - g_{-1,0}^c)^2 + 4(g_{0,0}^c)^2}) e^{-\beta \epsilon_c} \right]. \quad (A.5)
\]

Finally, the phase boundary residual entropy reads

\[
S_c = \ln \left[ \frac{1}{2} (g_{1,0}^c + g_{-1,0}^c + \sqrt{(g_{1,0}^c - g_{-1,0}^c)^2 + 4(g_{0,0}^c)^2}) \right]. \quad (A.6)
\]

Then the energy boundary degeneracy is \( G_c = \frac{1}{2} (g_{1,0}^c + g_{-1,0}^c + \sqrt{(g_{1,0}^c - g_{-1,0}^c)^2 + 4(g_{0,0}^c)^2}). \)

Similar to the previous cases, the phase boundary residual entropy is strictly larger than its adjacent states residual entropies, because \( G_c > g_{1,0}^c, G_c > g_{0,0}^c \text{ and } G_c > g_{-1,0}^c \).

In all cases, the entropy inevitably exhibits a jump-point discontinuity or a point discontinuity at \( x_c \). Because the phase boundary residual entropy is strictly larger than its adjacent states. Even for the case with an energy gap, the system still has entropy discontinuity (non-sided limit at \( x_c \)).
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