More Inequalities for Ising Ferromagnets

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We consider an Ising spin system with ferromagnetic pair interactions. Combining the old Griffiths inequalities with the recent Fortuin-Kasteleyn-Ginibre inequalities we obtain some new bounds on the correlations and thermodynamic functions. These bounds appear to be of interest in the neighborhood of the two-phase region of these systems, \( \beta \geq \bar{\beta}_c \), \( h \rightarrow 0 \) (\( \bar{\beta}_c \) is the reciprocal of the critical temperature, and \( h \) is the external magnetic field), where they yield relations between singularities in the spontaneous magnetization \( m^*(\beta) \) and the susceptibility \( \chi(h, h) \): e.g., \( m^*(\beta) \) is upper semicontinuous, and a discontinuity in \( m^*(\beta) \) at \( \beta \) implies that the susceptibility cannot be bounded near \( h=0 \) by an integrable function of \( h \) as \( \beta \rightarrow \bar{\beta}_c \) from the left. We also find some inequalities among the critical indices.

I. INTRODUCTION

We consider an Ising spin system, or lattice gas, on a \( d \)-dimensional lattice \( Z^n \), enclosed in a finite box \( \Lambda \); i.e., at each point \( i \) of the lattice there is a spin variable \( \sigma_i = \pm 1 \) and a corresponding occupation number \( \rho_i = \frac{1}{2} (\sigma_i + 1) = (0, 1) \). For a given boundary condition, which corresponds to a specification of the \( \sigma_i \) (and thus the \( \rho_i \)) for \( i \) outside \( \Lambda \), the spin and lattice-gas Hamiltonians are given, respectively, by

\[
H_S(\Lambda) = \frac{1}{2} \sum_{i \in \Lambda} \sum_{j \in \Lambda \setminus \Lambda} J(i-j) \sigma_i \sigma_j - \sum_{i \in \Lambda} \sigma_i \left( h + \sum_{j \in \Lambda} J(i-j) \sigma_j \right) + \text{const.,}
\]

and

\[
H_L(\Lambda) = -2 \sum_{i \in \Lambda} \left( \sum_{j \in \Lambda} J(i-j) \rho_i \rho_j - \sum_{i \in \Lambda} \rho_i \left( \mu + 4 \sum_{j \in \Lambda} J(i-j) \rho_j \right) \right) + \text{const.,}
\]

where \( J(i-j) = J(j-i) \geq 0 \) is a translationally invariant stable potential and

\[
\mu = 2(h - \alpha), \quad 0 \leq \alpha = \sum_{j \in \Lambda} J(i-j) < \infty.
\]

\( h \) is a uniform external magnetic field, \( \mu \) is the corresponding chemical potential, and the constant in (1.2) does not depend on the configuration inside \( \Lambda \).

Let \( A \), \( B \), denote subsets of \( \Lambda \) and let

\[
\sigma_A = \prod_{i \in A} \sigma_i, \quad \rho_A = \prod_{i \in A} \rho_i.
\]

The spin-correlation functions are given by

\[
\langle \sigma_A \rangle = \sum_{\sigma_A^{\text{neq}+1}} \prod_{i \in A} \sigma_i \exp -\beta \Lambda g(\Lambda) / \sum_{\sigma_A^{\text{neq}+1}} \exp -\beta \Lambda g(\Lambda)
\]

\[
= M_A(A; \{J\}; \bar{h}) = m^*_A(A; \beta, \bar{h}),
\]

where

\[
\bar{h} = \beta h = \frac{1}{2} \bar{\mu} + \bar{\alpha}, \quad \bar{\mu} = \beta \mu, \quad \bar{\alpha} = \beta \alpha
\]

and we write \( M(A; \beta, \bar{h}) \) when we wish to consider a fixed pair potential. Taking the thermodynamic limit, \( A \rightarrow \infty \) with the external field \( h \rightarrow 0 \),

\[
\lim_{A \rightarrow \infty} \langle \sigma_A \rangle = \langle \sigma_A \rangle = \langle \sigma_A \rangle \text{ exists and is independent of the boundary condition, translationally invariant, analytic in } \bar{h} \text{ for } \Re \bar{h} \neq 0, \text{ real analytic in } \beta \geq 0, \text{ and has "good" clustering properties.} \]

\[
\langle \sigma_A \rangle \text{ satisfy the obvious symmetry relations}
\]

\[
M(A; \{J\}; \bar{h}) = (-1)^{|A|} M(A; \{J\}; \bar{h}),
\]

where \( |A| \) denotes the number of sites in \( A \).

We shall make use of the following results:

(i) \( M(A; \{J\}; \bar{h}) \) is a nondecreasing function of \( \beta \).

(ii) If \( f(\sigma_{i_1}, \sigma_{i_2}, \ldots, \sigma_{i_n}) \) is a nondecreasing function of \( \sigma_{i_j} \) for \( 1 \leq \sigma_{i_j} \leq 1, j = 1, \ldots, n \), e.g., \( f(\sigma_{i_1}, \sigma_{i_2}, \ldots, \sigma_{i_n}) = \exp \left( \sum_{i \in A} \sigma_i - \beta \sum_{j \in A} J(i-j) \rho_j \right) \)

then \( \langle f(\sigma_{i_1}, \sigma_{i_2}, \ldots, \sigma_{i_n}) \rangle \) considered as a function of \( \{J\} \) and of \( \mu \) is a nondecreasing function of the \( \{J\} \) and of \( \mu \), for \( \beta \) arbitrary [Fortuin, Kasteleyn, and Ginibre (FKG) inequalities].

We now define

\[
M^*(A; \{J\}) = \lim_{\bar{h} \rightarrow 0^+} M(A; \{J\}; \bar{h}) = m^*(A; \beta)
\]

for fixed \( \{J\} \),

where the existence of the limit is guaranteed by GKS. When \( A \) consists of a single site \( i \), \( M(i; \{J\}; \bar{h}) = M_i(\{J\}) = M(\{J\}) \), independent of \( i \), for \( \bar{h} \neq 0 \), because of translational invariance. \( M(\{J\}; \bar{h}) \) is the magnetization per site and its limit as \( h \rightarrow 0^+ \), \( m^*(\{J\}) = m^*(\beta) \), is the spontaneous magnetization. The reciprocal of the critical temperature \( \beta_c \) is defined for a given \( \{J\} \) by the inequalities

\[
m^*(\beta) = 0 \quad \text{for } \beta < \beta_c,
\]

\[
m^*(\beta) > 0 \quad \text{for } \beta > \beta_c.
\]

This definition of \( \beta_c \) is unique since by GKS \( m^*(\beta) \) is monotone in \( \beta \). Indeed, it can be shown that when \( m^*(\beta) = 0 \), i.e., \( m(\beta, \bar{h}) \) is continuous at \( \bar{h} = 0 \),

\[
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\]

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then \( m(A; \beta, \tilde{h}) \) is also continuous at \( \tilde{h} = 0 \) for all \( A \), and \( m(A; \beta, 0) = m^*(A; \beta) \) exists and is independent of the boundary conditions.

II. INEQUALITIES FOR MAGNETIZATION

We now make the following observation, which is central, to what follows: If we change the pair interaction \( \{J(i - j)\} \) with \( \{J(i - j)\} \) (translationally invariant) and at the same time change \( h \) in such a way as to leave \( \mu \) unchanged, i.e., \( \delta h = \delta \tilde{h} = \sum_j (J(i - j)/\beta J(i - j)) \) then, according to FKG, the expectation values \( M(\{J(i - j)\}; \sigma) \), described in Sec. I, will be monotone in \( \{J(i - j)\} \) independent of the sign of \( \tilde{h} \). Now, if \( \tilde{h} < 0 \), an increase in the strength of the interaction \( \{J(i - j)\} \), keeping \( \tilde{h} \) fixed, will lead to a decrease in \( \{\sigma\} \), while an increase in \( \tilde{h} \) for fixed \( \{J(i - j)\} \) will lead to an increase in \( \{\sigma\} \) for \( |A| \) even. (The opposite happens for \(|A| \) odd.) Hence by combining a \( \{J(i - j)\} \) with a \( \delta \tilde{h} \) and using FKG appropriately, one can obtain new inequalities between the changes in \( \{\sigma\} \) produced by a change in the pair interactions (or the temperature) and those produced by a change in the external magnetic field.

Applying these ideas to \( M_{\{J(i - j)\}; \tilde{h}} \) leads to the following lemma.

**Lemma 1.** For an Ising spin system with ferromagnetic pair interactions \( J(i - j) \)
\[
M(\{J(i - j)\}; \tilde{h}) \leq M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h}),
\]
(2.1)
\[
0 \leq M(\{J(i - j)\}; \tilde{h}) - M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h}) \leq M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h}),
\]
(2.2)

whenever
\[
\delta J(i - j) \geq 0, \quad \beta J(i - j) - \beta J(i - j) \geq 0, \quad \tilde{h} > 0.
\]
(2.3)

**Proof.** According to FKG
\[
M(\{J(i - j)\}; \tilde{h}) \geq M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h})
\]
for \( \delta J(i - j) \geq 0 \). Letting \( \tilde{h} - \delta \tilde{h} = - \tilde{h} \) gives
\[
M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h}) \geq M(\{J(i - j)\}; \tilde{h} + \delta \tilde{h} - \delta \tilde{h}) \).

Using (2.1) (with \( |A| = 1 \)) yields the second inequality in (2.1). We now set \( \{J(i - j)\} = \{J(i - j)\} \) in this inequality and obtain
\[
M^*(\{J(i - j)\}; \tilde{h}) \leq M^*(\{J(i - j)\}; \tilde{h} + \delta \tilde{h}),
\]
which is just the second inequality in (2.2). These inequalities are thus valid for all \( \tilde{h} \). The first inequalities in (2.1) and (2.2) follow from GKS when \( \tilde{h} > 0 \).

Letting \( \tilde{h} = 0 + \) in (2.1) and (2.2) yields
\[
0 \leq M^*(\{J(i - j)\}) \leq M^*(\{J(i - j)\}) \leq M(\{J(i - j)\}; \delta \tilde{h}),
\]
(2.4)

where \( \chi(\beta, \eta) = \lim_{\eta \to 0^+} m(\beta, \eta) \) is the susceptibility.

Now let \( \delta \tilde{h} \to 0 \) in (2.4) in such a way that \( \tilde{h} \to 0 \); then we see immediately that \( M^*(\{J(i - j)\}) \) is the upper semicontinuous. Similar results hold for all correlation functions \( M^*(\{J(i - j)\}) \). (This result can also be obtained, by different methods, without making use of FKG. [5])

We can state this more precisely in the following way:

**Definition.** A sequence of translationally invariant ferromagnetic pair potentials \( \{J(i - j)\} \), \( \gamma \) real, will be called monotone (increasing) in \( \gamma \) if
\[
\beta J(i - j) \geq \beta J(i - j), \quad \tilde{h} \geq 0 \text{ for } \tilde{h} \geq \gamma).
\]

We write
\[
\{J(i - j)\}_{\gamma_0} \leq \{J(i - j)\}_{\gamma_0}
\]
whenever \( \gamma \geq \gamma_0 \).

**Lemma 2.** Given a monotone sequence of potentials \( \{J(i - j)\}_{\gamma_0} \), then we have
\[
\lim_{\gamma \to \gamma_0} M^*(\{J(i - j)\}_{\gamma_0}) = M^*(\{J(i - j)\}_{\gamma_0})
\]

**Corollary.** For a fixed interaction \( J(i - j) \) the correlation functions \( m^*(A; \beta) \) are upper semicontinuous in \( \beta \). In particular, for spontaneous magnetization \( m^*(\beta) \), we have \( m^*(\beta) = \lim_{\beta \to 0} m^*(\beta) \).

The results of Lemma 2 and its corollary may be applied to Dyson’s hierarchical model. [6] Dyson showed that for this model (the reader is referred to Dyson for details) there exists a sequence of pair potentials \( \{J(\beta)\} \) such that for \( \gamma \geq \gamma_0 \) there exists a phase transition at some finite \( \beta \), while for \( \gamma < \gamma_0 \), \( m^*(\beta) = 0 \) for all \( \beta < \beta_c \). For \( \gamma < \gamma_0 \), the long-range order parameter (thermal average of spin-spin correlations at infinite distance in zero magnetic field) jumps discontinuously at \( \beta = \beta_c \), where \( \beta_c \) is the critical temperature for \( \{J(\beta)\} \). Thus \( m^*(\beta) \geq 0 \) for \( \beta > \beta_c \). According to our results, then \( m^*(\beta) \geq m^*(\beta) \) and \( m^*(\beta) = \lim_{\beta \to \beta_c} m^*(\beta) \).

Using (2.4) for fixed \( \{J(i - j)\} \) and \( \delta \tilde{h} = \delta \), we see that the magnetization satisfies the inequality
\[
0 \leq \frac{\delta m^*(\beta) - \delta m^*(\beta)}{\delta \beta} \leq \alpha \chi^*(\beta)
\]
(2.6)

Letting \( \delta \to 0 \) in (2.6) we see that
\[
\frac{\delta m^*(\beta)}{\delta \beta} \leq \alpha \chi^*(\beta),
\]
where
\[
\chi^*(\beta) = \lim_{\eta \to 0^+} m(\beta, \eta).
\]
(2.7)
Hence if the right derivative of \( m^* (\beta) \) is infinite as \( \beta = \beta_\alpha \), then the susceptibility \( \chi^* (\beta) \) must also become infinite as \( \beta = \beta_\alpha \).

It is usually assumed\(^2\) that for Ising systems in two and higher dimensions, \( m^* (\beta) \) and \( \chi^* (\beta) \) behave for \( \beta > \beta_\alpha \) as powers of \( (\beta - \beta_\alpha) \) and \( m (\beta_\alpha, \bar{h}) \) as a power of \( \bar{h} ; m^* (\beta) = (\beta - \beta_\alpha)^{\beta'} \), \( \chi^* (\beta - \beta_\alpha)^{\gamma'} \), \( m (\beta_\alpha, \bar{h}) = \bar{h}^{\delta'} \), for \( \beta > \beta_\alpha \), where \( \gamma' \), \( \beta' \), and \( \delta' \) are "critical exponents" (\( \beta' \) and \( \delta' \) are usually called \( \beta \) and \( \delta \)). Equation (2.7) implies that\(^6\)

\[
\beta' + \gamma' \geq 1. \tag{2.8}
\]

In addition, by (2.4) we have

\[
m (\beta_\alpha, \bar{h}) \geq m^* (\beta_\alpha + \bar{h} / \alpha) \tag{2.9}
\]

and thus (as pointed out by Griffiths\(^5\))

\[
\delta' \geq 1 / \beta. \tag{2.10}
\]

We now consider the limit \( \delta (\beta) = 0 \) in (2.5). It is then clear immediately that a discontinuity in \( M^* (\beta J) \) implies that \( \chi (\beta J - \beta J, \eta) \) cannot be uniformly bounded, for \( \eta > 0 \), by an integrable function \( \Psi (\eta) \). We state this more precisely in the following form.

Lemma 3. Given a monotonous sequence of potentials \( \{ \beta J_i \} \rightarrow \{ \beta J \} \eta \) and \( \chi (\beta J, \eta) \leq \Psi (\eta) \), for \( \eta > 0 \), as \( \gamma \rightarrow \gamma_0 \) with \( \Psi (\eta) \) integrable at \( \eta = 0 \), then

\[
\lim_{\gamma \rightarrow \gamma_0} M (\beta J, \eta) = M (\beta J, \eta_0), \tag{3.1}
\]

so that \( M (\beta J, \eta) \) is "continuous" at \( \gamma_0 \).

Keeping \( \{ J \} \) fixed we see that a discontinuity in \( m^* (\beta) \) at \( \beta_\alpha \) implies that \( \chi (\beta - \beta_\alpha, \eta) \) is not bounded by any integrable function \( \Psi (\eta) \) as \( \delta = 0 \). Furthermore, since \( \chi (\beta, \eta) \) is, for systems with ferromagnetic pair potentials, monotone decreasing\(^8\) in \( \eta \), a discontinuity in \( m^* (\beta) \) at \( \beta_\alpha \) implies that

\[
\lim_{\alpha \rightarrow 0} [\delta (\beta - \beta_0 \eta)] > 0 \quad \text{so that} \quad \chi (\beta_0 - \beta_\alpha, \eta) \quad \text{diverges at least as} \quad \delta^{-1} \quad \text{as} \quad \delta = 0. \]

These results are applicable to Dyson's hierarchic model discussed earlier.

III. INEQUALITIES FOR \( \langle \alpha, \alpha \rangle \)

While the spin-pair-correlation functions \( \langle \sigma_j \sigma_j \rangle \) do not themselves satisfy the FKG inequalities, the averages \( \{ \langle \sigma_j \rangle + \langle \sigma_j \rangle \pm \langle \sigma_j \sigma_j \rangle \} \) do. Applying the methods and notation of Sec. II to these averages we readily find upon changing \( \beta \) to \( \beta + \delta \) and \( \bar{h} \) to \( \bar{h} + \alpha \delta \) that, for fixed \( \{ J \} \), \( m^* (i, j; \beta) \) is upper semi-continuous and that

\[
m (i, j; \beta, \bar{h} + \alpha \delta) \geq m (i, j; \beta - \delta, \bar{h}) \tag{3.1}
\]

Various inequalities can be derived from (3.1); we shall only mention one here. Letting \( \bar{h} \rightarrow 0^+ \) and using GKS for \( m^* (i, j; \beta) \), we find

\[
0 \leq m^* (i, j; \beta) \leq m^* (i, j; \beta - \delta) \leq 2 [m^* (\alpha \delta) - m^* (\beta - \alpha \delta)] \tag{3.2}
\]

where the second term on the right side of (3.2) is identically zero for \( \beta < \beta_\alpha \). The internal energy per site, \( u^* (\beta) \), of the spin system at \( h = 0 \) is given by

\[
u = \frac{1}{\beta} \sum_i [m^* (i, j; \beta) \chi (\beta - \beta_\alpha, \eta)] \tag{3.3}
\]

It follows from (3.2) and (3.3) that if \( C^* (\beta) \) diverges at some value of \( \beta \), say \( \beta = \beta_\alpha \) (as Onsager found in his solution of the two-dimensional Ising system with nearest-neighbor interactions), then either \( m^* (\beta) \) has a singularity at \( \beta_\alpha \) and thus \( \beta_\alpha > \beta_\alpha \), or \( \chi^* (\beta) \) diverges at \( \beta_\alpha \) or both.

This lends further credence to the universal belief that for Ising ferromagnets with translationally invariant pair potentials all correlation functions are real analytic in \( h \) and \( \beta \) for \( 0 \leq \beta \leq \beta_\alpha \).

In terms of the critical indices,\(^5\)

\[
\chi^* (\beta) \sim (\alpha \delta) \chi^* (\beta) \sim (\beta - \beta_\alpha)^{\gamma} \tag{3.4}
\]

implies that \( \alpha \leq \gamma \). \( \alpha \) is here a critical index and should not be confused with the \( \alpha \) of Eq. (1.3).]

Choosing \( \beta = \beta_\alpha \) in (3.2), and assuming that \( m^* (\beta_\alpha) = 0 \), (3.2) yields an inequality between the divergence \( C^* (\beta) \) as \( \beta \rightarrow \beta_\alpha \) and the divergence \( \chi^* (\beta_\alpha, \eta) \) as \( \eta \rightarrow 0^+ \), the divergence of the latter being the "stronger."

IV. REMARK ON ANTIFERROMAGNETS

The FKG inequalities remain valid also when the external magnetic field is not uniform. Indeed, the direction of the field at different sites need not be the same. Results derived from these inequalities can therefore be applied in a straightforward way to antiferromagnets, since it is only necessary to fix the spin on one of the sublattices to transform the antiferromagnetic interactions to ferromagnetic ones.\(^4\)\(^10\) The reader is referred to Refs. 4 and 10 for details.

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\(^2\) R. Griffiths, J. Math. Phys. 8, 478 (1967); 9, 484 (1967); D. G. Kelly and S. Sherman, ibid. 9, 466 (1968).


Structural Aspects of the Metal-Insulator Transitions in Cr-Doped VO$_2$

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The temperature-composition phase diagram of $V_{1-x}$Cr$_x$O$_2$ with $0 \leq x \leq 0.025$ is found to contain four phases: rutile (R), normal monoclinic VO$_2$ ($M_1$), and two monoclinic phases ($M_2$ and $M_3$). For each $M_2$ with $x = 0.024$ at 298 K, $2\alpha R = \alpha M = 9.0664$, $2\alpha R = \beta R = 5.7970$, $\alpha R = c_M = 4.5255 \text{ Å}$, and $\beta = 91.8^\circ$. The $M_2$ and $M_3$ regions are separated by a volume discontinuity. There are two types of V atoms in these structures. The first type form pairs and the second type form zig-zag chains along the $b_y$ axis. This contrasts with VO$_2$ where all the vanadium atoms are paired. The structures $R$, $M_2$, and $M_3$ with $x = 0.024$ have been refined from single-crystal $x$-ray data. High-pressure resistivity and $x$-ray measurements vs temperature give $dT/dP = -0.9 \pm 0.1 \text{ K/kbar}$ and $V_R - V_{M_2} = -0.11 \text{ cm$^2$/mole VO}_2$. At higher pressures $dT/dP = 0 \pm 0.2 \text{ K/kbar}$. These results cannot be simply interpreted in terms of the homopolar bond model proposed for the $M_1$ phase of VO$_2$.

I. INTRODUCTION

Many of the vanadium oxides exhibit temperature-induced metal-insulator transitions. Those in $V_2$O$_5$ and the Magnéli phases $V_n$O$_{2n}$ ($4 \leq n < 8$) are distinguished from the transition in VO$_2$ as only in the latter is there no antiferromagnetic phase. Recent studies of $V_2$O$_5$ doped with Cr and Ti have led to a generalized phase diagram for the sesquioxides and this diagram has been interpreted in terms of a Mott transition from itinerant-to-localized-electron states. The experiments reported in the literature on doped VO$_2$ indicate that this transition is quite different. The addition of Ti, Cr, Al, or Fe leads to phases at room temperature which have different structures from the normal monoclinic phase of pure VO$_2$. It is not clear if these different phases are related as they have been reported as having orthorhombic, monoclinic, or triclinic symmetry by x-ray-diffraction methods.

Recently, Villeneuve et al. reported a phase diagram for the system $V_{1-x}$Cr$_x$O$_2$ which is based on magnetic susceptibility, electrical resistivity, and powder-x-ray-diffraction measurements. They find on adding Cr a sequence of phases with increasing temperature of monoclinic to orthorhombic to tetragonal (rutile) with the insulator-to-metal transition being associated with the latter crystallographic transition. The metallic phase is more dense than the insulating phase, in contrast to pure VO$_2$ where the insulator is slightly more dense. This implies that the transition temperature of Cr-doped VO$_2$ will decrease with increasing pressure. As crystals of VO$_2$ doped with 2.4-at. % Cr were available from the earlier studies of Mac-chesney and Guggenheim, a complete determination of the crystal structure of the intermediate phase was undertaken and measurements of the pressure dependence of the transition temperature were made. In the course of this work it became necessary to study the low-Cr-concentration region in more detail and this was done using ceramic samples.

This paper is divided into four parts. The temperature-composition phase diagram is given in Sec. II and the temperature-pressure diagram for crystals of VO$_2$ + 2.4-at. % Cr in Sec. III. The crystal structure is given in Sec. IV for three different temperatures corresponding to three different phases. Finally in Sec. V this work is related to current theories for the metal-insulator transitions in VO$_2$.

II. TEMPERATURE-COMPOSITION PHASE DIAGRAM

The phase diagram was determined using both the single-crystal sample of $V_{0.975}$Cr$_{0.025}$O$_2$ and ceramic samples made in different ways. The sequence of