Surface Tension and Phase Coexistence

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Using inequalities, we give a simple proof that the surface tension τ of an Ising model with interaction $\beta J = K$ on a d-dimensional lattice, $\sigma_i = \pm 1$, satisfies the inequality $d\tau(K)/dK \geq 2[m^*(K)]^2$, where $m^*(K)$ is the spontaneous magnetization. When combined with our previous results that $\tau = 0$ for temperatures above $T_{c,s}$, the critical temperature for spontaneous magnetization, this proves that (i) $\tau = 0$, for $T > T_c$, and $\tau > 0$, for $T < T_c$, the critical temperature for the full d-dimensional system; and (ii) $T_{c,s} = T_c$. (Both results were known only for $d = 2$.)

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In a previous paper[1] we proved a number of inequalities for the surface tension τ of an Ising spin system with energy $-\beta H = K\sum_{nn}\sigma_i\sigma_j$, $\sigma_i = \pm 1$, $i \in Z^d$, a simple-cubic (sc) lattice in d dimensions. In this note we extend these results. All our results hold when the σ_i are distributed according to an even probability $\nu(d\sigma_i)$, e.g., distributed uniformly in $[-1,1]$.

To define τ we start with our system confined in a parallelepiped $\Lambda \subset Z^d$ of sides $L_{d'}$, $d' = 1, \ldots, d$, centered on the origin; in particular, $L_1 = 2M$, $-M \leq i_1 \leq M-1$. We shall write $\Lambda = (M, \underline{L})$, $\underline{L}$ being the infinite cylinder obtained by letting $M \to \infty$. Let μ_Λ^γ be the Gibbs measure (canonical ensemble) on the spins in Λ with boundary conditions (b.c.) γ, with $\gamma = +, -,$ or $\pm$. The + (−) b.c. corresponds to $\sigma_1 = +1$ (-1) for all i outside Λ; for the $\pm$ b.c., $\sigma_1 = 1 (i_1 \geq 0)$ or $\sigma_i = -1 (i_1 < 0)$ for $i \in \Lambda$.

For $A \subset \Lambda$ we call $\langle\sigma_A\rangle_{\gamma,\Lambda}$ the average of $\sigma_A = \prod_{i\in A}\sigma_i$ in Λ; $\langle\sigma_A\rangle_{\gamma,\underline{L}}$ and $\langle\sigma_A\rangle_\gamma$ the averages, respectively, in the cylinder $\underline{L}$ (infinite in the 1 direction) and in the infinite-volume limit $L_{d'} \to \infty$, $d' = 1, \ldots, d$. This limit is known to exist and the approach has some monotonicity properties.[2] We shall sometimes write $i = (i_1, x)$, $x \in Z^{d-1}$.

Let $Z_\Lambda^\gamma(K)$ be the partition function in Λ,

$$Z_\Lambda^\gamma(K) = \sum_{\sigma_i = \pm 1} \exp(K \sum_{nn} \sigma_j \sigma_k),$$

where the sum in the exponent is over all nearest-neighbor pairs, such that $j \in \Lambda$; if $k \in \Lambda$, then σ_A is determined by γ.

Define

$$\tau_\Lambda(K) = |\underline{L}|^{-1} \ln[Z^+(K)/Z^\pm(K)], \tag{1}$$

where $|\underline{L}| = L_2 \cdot L_3 \cdots L_d$ is the cross-sectional area,

$$\tau_{\underline{L}}(K) = |\underline{L}|^{-1} \lim_{M\to\infty} \tau_\Lambda(K); \tag{2}$$

then the surface tension (times β) is given by Abraham, Gallavotti, and Martin,[3]

$$\tau(K) = \lim_{\underline{L}\nearrow Z^d} \tau_{\underline{L}}(K). \tag{3}$$

The limits (2) and (3) exist and $\tau(K) \equiv \tau(K;d)$ is monotonically increasing in K and (consequently) also in d.[1]

For $d = 1$, $\tau(K) = 0$, while for $d = 2$ Onsager[4] derived the formula $\tau(K;2) = 2K + \ln(\tanh K)$ for $K \geq K_c$ and $\tau(K;2) = 0$ for $K \leq K_c$, where $K_c = J/T_c$ and T_c is the $d = 2$ critical temperature. For $d > 2$, one still expects that $\tau(K) = 0$ for $K < K_c$ and $\tau(K) > 0$ for $K > K_c$, K_c being defined by the nonvanishing of the spontaneous magnetization for $K > K_c$. A proof that $\tau = 0$ for K sufficiently small and $\tau > 0$ for K sufficiently large was given by Fontaine and Gruber.[5] In Ref. 1 we gave proof that $\tau(K) = 0$ for $K < K_c$ by deriving the following inequalities:

$$\tau(K) \leq 2K[m^*(K)]^2, \tag{4}$$

$$\tau(K) \leq 2K\langle\sigma_0\rangle_{+,\text{s.i.}}, \tag{5}$$

where $\langle\sigma_i\rangle_{+,\text{s.i.}}$ is the expectation value of the spin at the origin in the semi-infinite system with + b.c., i.e., imagine all bounds between the surface $i_1 = 0$ and $i_1 = -1$ to be cut. It is known that generally $\langle\sigma_0\rangle_{+,\text{s.i.}} \leq m^*(K)$ and that for $d = 2$, $\langle\sigma_0\rangle_{+,\text{s.i.}} > 0$ for $T > T_c$ [near T_c, for $d = 2$, $\langle\sigma_0\rangle_{+,\text{s.i.}} \sim (T_c - T)^{1/2}$].[6] It was not known before, however, whether $\langle\sigma_0\rangle_{+,\text{s.i.}} > 0$ for all $T > T_c(d)$ in $d \geq 3$ dimensions. It is a consequence of our result that this is the case.

We now state the main result of this note:

$$d\tau_{\underline{L}}(K)/dK \geq 2|\underline{L}|^{-1}\sum_x [\langle\sigma_{i_1,x}\rangle_{+,\underline{L}}(K)]^2. \tag{6}$$

Note that $\langle\sigma_{i_1,x}\rangle_{+,\underline{L}} = \langle\sigma_{0,x}\rangle_{+,\underline{L}}$, independent of i_1, since the system in $\underline{L}$ with + b.c. is translation invariant in the 1 (vertical) direction. The inequality carries through in an obvious way in the limit $\underline{L}\to\infty$ to yield

$$d\tau(K)/dK \geq 2\langle\sigma_0\rangle_+^2(K) = 2[m^*(K)]^2. \tag{7}$$

Proof.—It follows from the definition that

$$d\tau_{M,\underline{L}}^{(K)}/dK = |\underline{L}|^{-1}\sum_{j=-M,\,x}^{M}\sum{}'(\langle\sigma_{j,x}\sigma_{j',x'}\rangle_{+,\Lambda} - \langle\sigma_{j,x}\sigma_{j',x'}\rangle_{\pm,\Lambda}), \tag{8}$$

where $\sum'$ is the sum over all neighbors of the site $i=(j,x)$. By known inequalities,[7] each term in the sum is nonnegative. We now take the limit $M\to\infty$. Using the fact that $\underline{L}$ is "one dimensional" so that the terms in the sum go to zero exponentially fast as $|j|\to\infty$, we obtain

$$d\tau_{\underline{L}}/dK = |\underline{L}|^{-1}\sum_{j=-\infty}^{\infty}(\langle\sigma_{j,x}\sigma_{j+1,x}\rangle_{+,\underline{L}} - \langle\sigma_{j,x}\sigma_{j+1,x}\rangle_{\pm,\underline{L}}) + R, \tag{9}$$

where R is the sum over horizontal neighbors of the site (j,x) which is nonnegative.

The next step is to use another simple inequality,[7]

$$\langle\sigma_A\sigma_B\rangle_{+,\underline{L}} - \langle\sigma_A\sigma_B\rangle_{\pm,\underline{L}} \geq |\langle\sigma_A\rangle_{+,\underline{L}}\langle\sigma_B\rangle_{\pm,\underline{L}} - \langle\sigma_A\rangle_{\pm,\underline{L}}\langle\sigma_B\rangle_{+,\underline{L}}|. \tag{10}$$

This yields, for (9),

$$d\tau_{\underline{L}}/dK \geq |\underline{L}|^{-1}\langle\sigma_{0,x}\rangle_{+,L}\sum_j(\langle\sigma_{j+1,x}\rangle_{\pm,\underline{L}} - \langle\sigma_{j,x}\rangle_{\pm,L}), \tag{11}$$

where we have used the translation invariance of $\langle\sigma_{j,x}\rangle_{+,\underline{L}}$ in the 1 direction. Using now again the fact that

$$\langle\sigma_{j,x}\rangle_{\pm,\underline{L}} = \begin{cases}\langle\sigma_{0,x}\rangle_{+,\underline{L}}, & j\to\infty\\ \langle\sigma_{0,x}\rangle_{-,\underline{L}} = -\langle\sigma_{0,x}\rangle_{+,L}, & j\to-\infty,\end{cases} \tag{12}$$

the sum in (11) telescopes to yield the desired result, Eq. (6) (the derivative existing almost everywhere).

It follows now from (4) and (7) that if near T_c, $m^*\sim(T-T_c)^\beta$ and $\tau\sim(T-T_c)^\mu$, then

$$2\beta\leq\mu\leq2\beta+1. \tag{13}$$

In mean field (presumably correct for $d\geq5$) $\beta=\frac{1}{2}$ so that μ must lie between 1 and 2 (cf. discussion by Oliveira, Furman, and Griffiths[8]).

We make the following extensions and remarks:

(1) It should be pointed out (cf. Ref. 1) that $\tau(K)$ in three dimensions is equal to $\alpha(K^*)$, the coefficient of the area decay of the Wilson loop in the dual gauge model with interactions K^*. It follows then from (7) that $\alpha(K^*)>0$ for $K^*<K_c^*$, the dual critical point. Thus the fact that extrapolation of low-temperature series indicates a vanishing of $\alpha(K^*)$ at some $K_R^*<K_c^*$ may indeed be an indication[9] of a breakdown of analyticity of $\tau(K)$ at the "roughening temperature" $T_R<T_c$. At low temperatures $\tau-2K$ is analytic in $\exp(-K)$.[1]

(2) It is clear from the derivation of (7) that $d\tau/d\beta\geq2m^*$ holds for general even ferromagnetic interactions between the spins. It also holds when $\sigma_1=\pm1$ is replaced by a more general one-component spin system with an even *a priori* measure.[7] We do not, however, know how to prove results about the surface tension when the different pure phases are not related by symmetry.

(3) Equation (7) remains valid for a two-component rotator with an anisotropic interaction $\beta J = K$. This follows from (10), which holds when σ_A is replaced by $\cos\varphi_i$ and σ_B by $\cos\varphi_j$. The b.c. now refer to the values taken by $\cos\varphi_j$ for $j\notin\underline{L}$.

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New Models for Metal-Induced Reconstructions on Si(111)

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Angle-resolved photoelectron spectroscopy and surface–core-level chemical shifts have been used to study electronic structure and derive structural models of the Al, Ag, and Ni metal-induced reconstructions on Si(111). We show, for the first time, the connection between the Ni-stabilized $\sqrt{19}\times\sqrt{19}$ and clean 7×7 surfaces, and report a new Si(111)-($\sqrt{7}\times\sqrt{7}$)Al structure at < 0.5 monolayer coverage of Al.

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The origin of the surface reconstructions on the Si(111) surface have been of active interest for some time.[1,2] The interaction between silicon and initial metal overlayers has also been the subject of many studies with low-energy electron-diffraction (LEED), electron energy-loss, Auger, and photoelectron spectroscopies,[3,4] but a full understanding of the reconstructions and surface electronic states has not been obtained.[5]

New results are presented in this paper which provide insight into metal-silicon surface structures from angle-resolved valence-band photoemission and surface–core-level chemical-shift measurements carried out on ordered metal-silicon systems where the number of metal atoms ranges from < 0.1 monolayer Ni to 0.5 monolayer Al to 1.0 monolayer Ag. We show the similarity of the electronic states for the ($\sqrt{19}\times\sqrt{19}$)Ni and 7×7 reconstructions and present for the first time a model which relates the two. By using the angular dependence of the emission as well as the energy dispersion of the metal-silicon bands we derive structural models for the ($\sqrt{3}\times\sqrt{3}$)Al and ($\sqrt{3}\times\sqrt{3}$)Ag and the new ($\sqrt{7}\times\sqrt{7}$)Al surface structures on Si(111).

The metal-silicon structures have been prepared by evaporating controlled amounts of metal onto clean room-temperature Si(111) 7×7 surfaces. This generally results in a metal-covered surface that shows a 7×7 reconstruction, but does not necessarily correspond to an ordered metal overlayer. To obtain the ordered metal-silicon reconstructions, the surfaces have to be annealed. Typically the change to an ordered phase is accompanied by a change in surface chemical shifts. For example, for the Al $2p$ at submonolayer coverages on Si(111), a binding energy 0.15 eV higher than the metallic core line is obtained. When the surface reconstructs to either the $\sqrt{3}\times\sqrt{3}$ or the $\sqrt{7}\times\sqrt{7}$, the shift to higher binding energy further increases to 0.35 eV. The line shape broadens by 15% with respect to the metallic core line because of the Si-Al bond. We have also studied the characteristic surface–core-level line shapes and shifts of the Si(111) $2p$ for the 2×1 and 7×7 surfaces[6,7] in the course of this work and this will be reported elsewhere.

We discuss first the Si(111) $\sqrt{19}\times\sqrt{19}$, which is often obtained as an unintentional impurity-stabilized surface[8] after long annealings at quite high temperatures (1000–1200 °C). The Auger spectra always show some amount of impurity Ni. We also have found that, under some circumstances, such high-temperature annealing can produce cop-

