Theory and feasibility of using low-energy electron diffraction to study specific-heat anomalies at surface phase transitions

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We expound the idea that as a probe of short-range order, low-energy electron diffraction can be used to study the energy singularity associated with surface phase transitions. We demonstrate its feasibility by performing Monte Carlo simulations on two triangular lattice gases with second-order transitions in universality classes distinguished by the critical exponent α: The first has a $(\sqrt{3} \times \sqrt{3})R\,30°$ ordered state; the second has a $p(2 \times 2)$ ordered state. As multiple scattering is short ranged, it is no hindrance to this technique.

I. INTRODUCTION

Systems of atoms adsorbed on single-crystal metal surfaces undergo a great variety of phase transitions. The most natural way of examining these phase transitions, and the way in which these transitions are usually first detected, is by using low-energy electron diffraction (LEED). Real scattering experiments are limited to measuring correlations over a finite range. In LEED (and neutron scattering) this problem is particularly severe—the instrumental resolution in LEED is typically an order of magnitude smaller than in x-ray diffraction experiments. This fact has hindered the widespread use of LEED as a probe of critical phenomena. The purpose of this paper is to point out that the nonanalyticities inherent in phase transitions are still manifest in LEED measurements. In fact, as emphasized here, finite resolution LEED experiments provide a natural way of studying the specific-heat exponent α in second-order transitions. The basic idea is that as finite-resolution LEED is sensitive only to short-range correlations, LEED measurements show the same singularity as the energy.

Our discussion will be in terms of the lattice-gas model of adsorption. This model assumes that the energy of the adsorbate can be determined uniquely by specifying a configuration of adsorbed atoms on a discrete set of binding sites. That is,

$$E(\{n(\mathbf{r})\}) = \sum_{\mathbf{r}} E^{(1)}(\mathbf{r})n(\mathbf{r})$$
$$+ \sum_{\mathbf{r},\mathbf{r}'} E^{(2)}(\mathbf{r},\mathbf{r}')n(\mathbf{r})n(\mathbf{r}+\mathbf{r}')$$
$$+ \sum_{\mathbf{r},\mathbf{r}',\mathbf{r}''} E^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')n(\mathbf{r})n(\mathbf{r}+\mathbf{r}')n(\mathbf{r}+\mathbf{r}'') \,,$$

(1.1)

where $n(\mathbf{r})$ represents the occupancy (0 or 1) of the site at $\mathbf{r}$. This model, for example, assumes the energy of the adsorbate is independent of the internal degrees of freedom

of the substrate. While it is convenient to frame our discussion in terms of this model, our conclusions are independent of it.

A common objection to the use of LEED to probe phase transitions is that, due to the large electron-atom scattering cross sections, multiple scattering is important. This fact, of course, is what makes the determination of surface structural information so difficult. However, multiple scattering is *not* a fundamental obstacle to the study of phase transitions. Multiple scattering is short ranged:[1] It introduces a length scale into the measurement of the order of the electron mean free path (typically several atomic spacings). As long as the correlation length is much larger than this length (that is, sufficiently close to T_c), the inverse width of diffraction features, for example, will scale the same way as the correlation length. The electron mean free path is short enough that it should not obscure critical behavior that might otherwise have been observed. Moreover, integrated LEED features measure the exponent α independent of the amount of multiple scattering.

Some of these ideas were sketched in short papers by us[2] and have appeared in various forms earlier, particularly regarding resistivity[3-5] but also with applications to scattering,[6,7] etc.[8] Our goal here is to present a thorough treatment from the perspective of someone interested in critical properties of surfaces and to provide detailed illustrations by our Monte Carlo simulations of the structure factor. In Sec. II we discuss why finite-resolution LEED measurements allow the exponent α to be measured. In Sec. III we discuss the crossover of finite-resolution LEED experiments to infinite-resolution ones, and suggest how one might determine the exponents β, γ, and ν by varying instrumental resolution (in a way analogous to finite size scaling). In Sec. IV we illustrate our ideas by applying them to Monte Carlo data from lattice-gas phase transitions in two different universality classes—a $(\sqrt{3} \times \sqrt{3})R\,30°$ and a $p(2 \times 2)$ order-disorder transition. In Sec. V we present a short summary.

II. DERIVATION OF ENERGYLIKE SINGULARITY

In this section we show that the scattered intensity measured as a function of temperature in experiments such as LEED exhibit an energylike singularity near the critical temperature T_c. We expand on the arguments presented in earlier shorter papers.[2] We are interested in the extra spots induced by ordered overlayers of adsorbed atoms or by reconstruction of the top layer(s) of atoms of the substrate. These spot intensities are temperature dependent because they are determined by correlation functions of these atoms. In the lattice-gas picture and the kinematic approximation LEED intensities are weighted sums of the pairwise correlation functions $\langle n(\mathbf{r})n(\mathbf{r}')\rangle$. Because of the large scattering cross section that makes LEED surface sensitive, the actual intensities will also generally depend on multisite correlation function via multiple scattering. While one can minimize their contribution by various experimental techniques,[9] we show below that their presence does not alter our arguments for the sort of measurement we propose. An important feature of real LEED instruments is that they are sensitive to correlations within only a finite ("instrumental") range,[10] for example, L_i. LEED intensities are thus *finite* sums of correlation functions. If we neglect multiple scattering and assume for simplicity a sharp cutoff, LEED intensities are proportional to $I(k)$:

$$I(\mathbf{k}) = \sum_{\substack{\mathbf{r} \\ 0 \le r \le \infty}} \sum_{\substack{\mathbf{r}' \\ 0 \le r' \le L_i}} e^{i\mathbf{k}\cdot\mathbf{r}'} \langle n(\mathbf{r})n(\mathbf{r}+\mathbf{r}')\rangle . \qquad (2.1)$$

In what follows we present the argument that the temperature singularities of $I(k)$ and of the more general sums of correlation functions associated with LEED intensities are the same as that of the energy. The essence of this argument is that both the energy and $I(k)$ are derivatives of the free energy with respect to coefficients of short-range terms in the Hamiltonian which do not change its symmetry. To show this explicitly, we consider the scaling form of the (reduced) free energy per site, $f = -F/Nk_BT$. A result of the phenomenological theory of second-order phase transitions is that f can be decomposed into an analytic part and a singular part,

$$f = f_a + f_s , \qquad (2.2)$$

with the leading singularity of f_s determined by the specific-heat exponent α

$$f_s = \begin{cases} a_+ |t|^{2-\alpha}, & T > T_c \\ a_- |t|^{2-\alpha'}, & T < T_c , \end{cases} \qquad (2.3)$$

where $t \equiv (T - T_c)/T_c$ and $\alpha' = \alpha$ by scaling. The average (reduced) energy is the partial derivative of f with respect to T,

$$E = \frac{\partial f}{\partial T} = \frac{\partial f_a}{\partial T} \pm b_\pm |t|^{1-\alpha} . \qquad (2.4)$$

The actual LEED intensity, including multiple scattering, is an average of

$$\widehat{I}(\{n(\mathbf{r})\}) = \sum_{\substack{\mathbf{r} \\ 0 \le r \le \infty}} \left[\sum_{\substack{\mathbf{r}' \\ 0 \le r' \le L_i}} I^{(1)}(\mathbf{r}')n(\mathbf{r})n(\mathbf{r}+\mathbf{r}') + \sum_{\substack{\mathbf{r}' \\ 0 \le r' \le L_i}} \sum_{\substack{\mathbf{r}'' \\ 0 \le r'' \le L_i}} I^{(2)}(\mathbf{r}',\mathbf{r}'')n(\mathbf{r})n(\mathbf{r}+\mathbf{r}')n(\mathbf{r}+\mathbf{r}'') + \cdots \right] . \qquad (2.5)$$

Note the use of $\widehat{I}$ to distinguish from its expectation value I [cf. Eq. (2.1)], the measured intensity. We can imagine a term like this in the Hamiltonian of Eq. (1.1). If we extend Eq. (1.1) by adding a term $g\widehat{I}(\{n(\mathbf{r})\})$, then

$$I = \frac{\partial f_s}{\partial g}\bigg|_{g=0} .$$

Equation (2.3) gives the temperature dependence of f at $g=0$. In general $\widehat{I}(\{n(\mathbf{r})\})$ will not have the same symmetry as the physical Hamiltonian. This means that we must allow for new critical behavior when $g \ne 0$. The dependence of f on g and T is expected to have the general crossover form

$$f_s(T,g) = |\tilde{t}|^{2-\alpha} X_\pm(\tilde{g}|\tilde{t}|^{-\phi}) ,$$

where ϕ is the leading crossover exponent and $X_\pm(z)$ is a crossover function. The (nonlinear) scaling fields $\tilde{g}$ and $\tilde{t}$ can be expanded about $g=0$ and $t=0$ as

$$\tilde{t} = t + c_1 g + \mathcal{O}(gt, t^2, g^2) ,$$
$$\tilde{g} = g + c_2 t + \mathcal{O}(gt, t^2, g^2) ,$$
with

$$t \equiv \frac{T}{T_c(g=0)} - 1 .$$

An important point is that in the absence of any special symmetry of I, the thermal scaling field contains a term linear in g. For example when g is irrelevant, i.e., $\phi < 0$

$$f_s \propto \left| \frac{T}{T_c(g)} - 1 \right|^{2-\alpha} ,$$

and thus

$$c_1 = -\frac{1}{T_c} \frac{dT_c}{dg}\bigg|_{g=0} .$$

Given the above form for $f_s(T,g)$ the leading singularity in the temperature dependence of I is

$$I_s = \pm c_1(2-\alpha)|t|^{1-\alpha} X_\pm(0) + |t|^{2-\alpha-\phi} X'_\pm(0) + \cdots . \qquad (2.6)$$

The $|t|^{2-\alpha-\phi}$ term is only of concern when $\phi > 0$, that is when the field g is relevant. The field g will only be relevant (excluding exceptional cases) when the term gI

breaks some symmetry of the physical Hamiltonian. We will argue that when no information about the phase of the order parameter can be obtained from I, I can be found by differentiating with respect to a field g' conjugate to a term $\hat{I}'(\{n(\mathbf{r})\})$, which does *not* break the symmetry of the Hamiltonian.

The ideal infinite-system Hamiltonian is invariant with respect to the space group of coordinate transformations $\{A_i\}$ of the substrate: $\mathbf{r}' = A_i \mathbf{r}$. Since $\hat{I}(\{n(\mathbf{r})\})$ is automatically invariant with respect to the lattice translations, $\{T_i\}$, $[\hat{I}(\{n(\mathbf{r})\}) = \hat{I}(\{n(T_i\mathbf{r})\})]$, for symmorphic groups we need only consider the point-group operations $\{R_i\}$. (These arguments can be generalized to nonsymmorphic groups.) The term

$$g'\hat{I}'(\{n(\mathbf{r})\}) = g' \sum_{i=1}^{m} \hat{I}_i(\{n(\mathbf{r})\}) ,$$

where $\hat{I}_i(\{n(\mathbf{r})\}) = \hat{I}(\{n(R_i\mathbf{r})\})$ and m is the number of point-group elements, has the same symmetry as the physical Hamiltonian. The average I will have the same singularity as the energy [Eq. (2.3)] because g' is now generally irrelevant. Above T_c, by definition, the symmetry of the correlation functions giving $I_i = I_j$ is unbroken, so that $I = I'/m$. Below T_c we have assumed that no information about the ordered phase can be obtained from I_i, so again $I_i = I_j$. (If $I_i \neq I_j$ the diffraction pattern would depend on the ordered phase.) Lack of phase information can arise from (at least) two sources. Either the correlation function symmetry which is broken is a translational symmetry [as in the $\sqrt{3} \times \sqrt{3}$ and $p(2 \times 2)$ order-disorder transitions discussed in Sec. IV], or the LEED instrument (as is typically the case) averages over all orientations (domains) of the ordered phase. If phase information can be obtained from I (which is possible when the number of components of the order parameter is greater than one), then the $|t|^{2-\alpha-\phi}$ term of Eq. (2.6) must be considered. The origin of this term in field theory is discussed by Brézin *et al.*[11] This argument for the energy singularity of I fails in the exceptional cases where a non-symmetry-breaking term like $\hat{I}'$ is relevant (for example the X-Y model with cubic anisotropy). The virtual interactions implicit in $\hat{I}'$ must be short ranged to be irrelevant; if one decays as $1/r^{d+\sigma}$, irrelevancy requires $\sigma > 2 - \eta$.[12] As instrument response functions are typically Gaussian,[10] this condition is usually satisfied. So, given these conditions, the temperature dependence of an arbitrary LEED intensity close to T_c will be of the same form as the temperature dependence of the energy; that is,

$$I(T) = I_a(T) + I_s(T) = A_0 - A_1 t \mp B_\pm |t|^{1-\alpha} + \cdots ,$$
$$(2.7)$$

where we have included the first two terms of the analytic part. Of course as the instrumental resolution becomes infinite this temperature dependence can cross over to another type, as discussed below. The ratio B_+/B_- is universal—independent of both instrument and system details.

On a real surface there are quenched defects in the form of random steps and impurities which limit the range of long-range order. This will limit the range of validity of Eq. (2.7) to reduced temperatures where the system's correlation length is less than some characteristic size. For example, divergences in the derivative of I with respect to temperature will be rounded. One problem which then arises is how to estimate the perfect system T_c. In finite systems a natural estimate of T_c is the temperature of the peak in the specific heat. The convergence of this estimate is well understood.[13] The singular structure of the specific heat is the same as that of I, so the analogous estimate of T_c is the inflection point of the integrated intensity. This correspondence justifies a common practice.[14]

In first-order transitions with discontinuities in the energy,[15] the short-range order of the two phases are discontinuously different and so any measure of the short-range order will mirror this discontinuity; fits with Eq. (2.7) will yield α close to 1.

In summary, the poor resolution of LEED compared to x-ray experiments, or the sensitivity of LEED to multiple scattering, does not prohibit its use as a probe of critical phenomena. Any LEED measurement which shows a second-order phase transition can be used to study the critical exponent α and the amplitude ratio B_+/B_-. For experiments carried out at fixed coverage rather than at fixed chemical potential (the usual case in studies of chemisorbed systems because they are not, typically, in equilibrium with the gas phase) and away from maxima in phase boundaries, there is an important caveat: Fisher renormalization.[16,17] In these cases exponents are replaced by their "Fisher-renormalized" values. In particular the α in Eq. (2.7) is replaced by $-\alpha/(1-\alpha)$.[16] As a result the fitted α can change from positive to negative, making it more difficult to determine. This problem can be circumvented by performing experiments near maxima in temperature-coverage phase boundaries—where the temperature region where Fisher renormalization is observed becomes small.[16]

III. SCALING FUNCTION FORMULATION

Usually LEED experiments are envisioned as methods for measuring the structure factor of surfaces. The structure factor $S(\mathbf{k}, T)$, is the Fourier transform of the surface-atom pair correlation function

$$S(\mathbf{k}, T) = \sum_{\mathbf{r}} \sum_{\mathbf{r}'} \langle n(\mathbf{r}) n(\mathbf{r} + \mathbf{r}') \rangle e^{i\mathbf{k} \cdot \mathbf{r}'} , \qquad (3.1)$$

i.e., the form of Eq. (2.1) with $L_i = \infty$. It is what would be measured by a LEED instrument with *infinite spatial resolution* in the kinematic (single scattering) limit. When there is long-range positional order on the surface, $S(\mathbf{k}, T)$ will contain a series of delta functions at positions $\mathbf{k} = \mathbf{g}$, where the vectors $\mathbf{g}$ characterize the long-range order (i.e., the locations of the "extra" spots). For convenience we define a reduced $\mathbf{k}$-dependent susceptibility $\mathcal{X}(\mathbf{k}, T)$ as the structure factor without the delta functions,

$$\mathcal{X}(\mathbf{k}, T) = S(\mathbf{k}, T) - \sum_{\mathbf{g}} m_\mathbf{g}^2(T) \delta(\mathbf{k} - \mathbf{g}) . \qquad (3.2)$$

The coefficients $m_\mathbf{g}$ give the amplitudes of the long-range

order and hence are proportional to the order parameters of the surface. In an order-disorder phase transition, a subset of the m's will vanish as the temperature is raised. Near a second-order phase transition, m_g is expected to approach zero as $t^{2\beta}$, and $X(\mathbf{k},T)$ is expected[18] in the limit $k\to 0$ and $k\xi$ fixed to have the (scaling) form

$$X(\mathbf{k},T)=\xi^{\gamma/\nu}X_{\pm}(k\xi) , \qquad (3.3)$$

where by k we mean $|\mathbf{k}-\mathbf{g}|$, $\xi=\xi_0|t^{-\nu}|$ is the correlation length, and $X_{\pm}$ are universal functions (of a single variable). As $t\to 0$, the susceptibility $X(0,T)$ diverges like $t^{-\gamma}$ and the width of the structure factor vanishes like t^{ν}. We begin with systems which scale isotropically,[19] commenting subsequently on anisotropic effects encountered in our studies of specific structure factors. We assume in this section some familiarity with the idea of scaling functions and their expansions in the various limits; for readers wanting background material, excellent references are available.[18,20]

It is not immediately clear that this interpretation of a LEED measurement is consistent with what was said in the previous section—that diffraction intensities show energylike singularities. In the following we show how they can be consistent. The essential point is that $S(\mathbf{k},T)$ comes from an infinite-ranged sum (in $\mathbf{r}$ space) of correlation functions, while LEED intensities are finite-ranged sums. That is, a measured LEED intensity is (in the kinematic limit) an integral of $S(\mathbf{k},T)$ over $\mathbf{k}$. The exponents γ, β, and ν and the scaling functions $X_{\pm}$ must have properties so that any integral of $S(\mathbf{k},T)$ has an energylike singularity. The Fisher-Langer[3] approximate to $X_{\pm}(y)$,

$$X_{\pm}(y)=C_1y^{-\gamma/\nu}(1+C_2^{\pm}y^{-(1-\alpha)/\nu}\pm C_3y^{-1/\nu}) , \qquad (3.4)$$

which is valid in the limit $y\to\infty$ ($k\neq 0,t\to 0$), ensures (by construction) that integrals away from the spot center (with $|\mathbf{k}|$ small, however) will have the energy singularity. This form has been verified in $4-\epsilon$ dimensions, for example.[11] Thus let us consider an integral of $X(k,T)$ of radius k_I including a point $\mathbf{g}$,

$$I_X(k_I,T)=2\pi\xi^{\gamma/\nu}(2\pi)^{-2}\int_0^{k_I}dk\,kX_{\pm}(k\xi)$$
$$=\xi^{(\gamma/\nu)-2}Y_{\pm}(k_I\xi) , \qquad (3.5)$$

where $Y_{\pm}(x)=(2\pi)^{-1}\int_0^x dy\,yX_{\pm}(y)$. Now we will show that for this to be consistent with integrals of S having an energylike singularity we must have $2\beta=2\nu-\gamma$ and also that $Y_{\pm}$ must have a particular asymptotic expansion. From the definitions of X and δ

$$I_S(k_I,T)=I_X(k_I,T)+m^2(T) . \qquad (3.6)$$

In the limit of small k_I and t we can rewrite this using Eq. (3.5):

$$I_S(k_I,T)=\xi_0^{(\gamma/\nu)-2}|t|^{2\nu-\gamma}Y_{\pm}(k_I\xi_0|t|^{-\nu})+m_{\pm}^2|t|^{2\beta} , \qquad (3.7)$$

(where $m_+=0$, by definition). We now assume that for large x, $Y_{\pm}(x)$ has the form

$$Y_{\pm}(x)\sim D_0^{\pm}x^{\omega_0}\left[1+\sum_{i=1}^{\infty}D_i^{\pm}x^{-\omega_i}\right] \qquad (3.8)$$

For small t we have assumed that $I_S(t)$ must have an energylike singularity. Expanding both sides of Eq. (3.7) thus yields

$$A_0\mp A_1|t|\mp B_{\pm}|t|^{1-\alpha}=m_{\pm}^2|t|^{2\beta}+D_0^{\pm}k_I^{\omega_0}|t|^{2\nu-\gamma-\omega_0\nu}\left[1+\sum_{i=1}D_i^{\pm}k_I^{-\omega_i}|t|^{+\omega_i\nu}\right] . \qquad (3.9)$$

To obtain a term independent of t on the right-hand side, we must have $\omega_0=(2\nu-\gamma)/\nu$ and $A_0=D_0^{\pm}k_I^{2\beta/\nu}$. To eliminate the $|t|^{2\beta}$ singularity from the right-hand side we must further have $2\beta=2\nu-\gamma$ (a familiar hyperscaling result), $\omega_1=\omega_0=2\beta/\nu$, $D_0D_1^-=-m_-^2$, and $D_1^+=0$. Similarly, $\omega_2=(1-\alpha)/\nu$, $\omega_3=1/\nu$ with $B_{\pm}=\pm D_0D_2^{\pm}k_I^{\omega_0-\omega_2}$, and $A_1=\mp D_0D_3^{\pm}k_I^{\omega_0-\omega_3}$. Thus $Y_{\pm}(x)$ has the asymptotic form

$$Y_{\pm}(x)\sim D_0x^{2\beta/\nu}(1+D_1^{\pm}x^{-2\beta/\nu}+D_2^{\pm}x^{-(1-\alpha)/\nu}$$
$$+D_3x^{-1/\nu}+\cdots) . \qquad (3.10)$$

If now instead of integrating X we integrate S, we see that it too will satisfy the scaling relation in the limit of small k_I,

$$I_S(k_I,T)=|t|^{2\beta}Z_{\pm}(k_I\xi) , \qquad (3.11)$$

where $Z_-(0)$ is the amplitude of the $|t|^{2\beta}$ term in the order parameter and $Z_+(0)=\xi_0^{-2\beta/\nu}Y_+(0)=0$. When $k_I=0$ one recovers the infinite-sum diffraction picture; when $k_I\neq 0$ the singularity crosses over to the finite-sum,

energy-singularity picture. When the correlation length is smaller than the resolution of the LEED instrument, the structure-factor approach is appropriate; when the correlation length becomes larger (something easy to arrange experimentally), the energy singularity is seen as described in Eq. (2.7).

The requirement that the structure factor have an energylike singularity at T_c when $k\neq 0$ led to the introduction of the Fisher-Langer form of the large-y expansion of $X(y)$. However the structure factor is accurately represented by $|t|^{-\gamma}X(k\xi)$ only in the limit of small k, whereas the energy singularity, as discussed in the preceding section, occurs at all nonzero k. Thus the corrections to scaling which occur at finite k must have similar large-y expansions. Including the first corrections to scaling, the structure factor is approximated by the form[21]

$$S(\mathbf{k},T)\simeq|t|^{-\gamma}\left[X(k\xi)+\sum_i a_i|t|^{\Delta_i}X_i(\mathbf{k}\xi)\right] , \qquad (3.12)$$

where we have allowed for the possibility that the corrections to scaling are not isotropic in the scaling limit by

letting the (universal) scaling functions X_i have vector arguments. The exponents Δ_i are the usual gap exponents associated with various irrelevant fields; the constants a_i are nonuniversal. So, to ensure the energylike singularity of $S(\mathbf{k}, T)$ as T approaches T_c, the large-$|\mathbf{y}|$ limits of $X_i(\mathbf{y})$ must be similar to Eq. (3.4):

$$X_i(\mathbf{y}) = C_1^i |\mathbf{y}|^{-(\gamma - \Delta_i)/\nu} [(1 + C_2^{i\pm}(y) |\mathbf{y}|^{-(1-\alpha)/\nu}$$
$$\pm C_3^i(y) |\mathbf{y}|^{-1/\nu})] , \quad (3.13)$$

where $y = \mathbf{y} / |\mathbf{y}|$.

IV. ILLUSTRATIONS OF FEASIBILITY

To illustrate explicitly how integrals over the structure factor, and hence LEED, give information about the singularities in the energy at a phase transition, we have calculated with Monte Carlo techniques the structure factor and energy of two different triangular lattice gases. The ordered states in the two cases, a $(\sqrt{3} \times \sqrt{3})R\,30°$ and $p(2 \times 2)$ structure, are expected to disorder in two universality classes which can be distinguished by differences in the singularity of the temperature dependence of the energy. They are also common phases of adsorbed atoms on the close-packed faces of fcc and hcp single crystals.[22]

On the basis of the ideas of the preceding sections we expect that sufficiently close to T_c the temperature dependence of the integrated intensity $I(T)$ will be proportional to the temperature dependence of the energy $E(T)$. That is,

$$I(T) \approx uE(T) + w, \quad T \approx T_c; \; k_I \gg \xi^{-1} \qquad (4.1)$$

where u is negative. The temperature range over which this proportionality is valid decreases as the k_I decreases (and the resolution of the instrument increases!). In the limit of very small integration radius and infinite system size the temperature dependence of the integrated structure factor, as discussed above, crosses over into very different behavior,

$$\lim_{k_I \to 0} I(T) \approx \begin{cases} a \, |t|^{2\beta}, & T < T_c \\ 0, & T > T_c . \end{cases} \qquad (4.2)$$

Of course Monte Carlo simulations (and experiments) on finite systems give only approximations to this behavior. For example for a lattice gas with N sites instead we have[13]

$$\lim_{k_I \to 0} I(T) \propto \begin{cases} N^2 \left[|t|^{2\beta} + \dfrac{c}{N} |t|^{-\gamma} \right], & T < T_c, \; \sqrt{N} \gg \xi \\ N^{2-\eta/2}, & T = T_c \\ Nt^{-\gamma}, & T > T_c, \; \sqrt{N} \gg \xi , \end{cases} \qquad (4.3)$$

where η is the anomalous dimension of the critical point. The amplitude of the structure factor away from positions of long-range order (in $\mathbf{k}$ or T) is proportional to N. When one integrates the structure factor over any finite region of $\mathbf{k}$ space the result is proportional to N^2, regardless of whether one includes $\mathbf{k} = 0$ or not. So the order of magnitude of the integrated structure factor is of the same

order of magnitude above T_c as below, and Eq. (4.1) can be valid. At the critical point of the infinite system the energy converges to its infinite system values as $N^{-(1-\alpha)/2\nu}$.

The phase diagram for the triangular lattice gas with only nearest-neighbor repulsions has been studied by a variety of methods.[23-25] At low temperatures and at particle densities greater than $(5 - \sqrt{5})/10 \; (=0.276...)$,[25] the commensurate $(\sqrt{3} \times \sqrt{3})R\,30°$ phase appears with the second-neighbor sites preferentially occupied and a threefold degenerate ground state at $\frac{1}{3}$ monolayer coverage. It is believed (known at $T = 0$) that this ordered state can disorder via a second-order transition in the three-state Potts universality class.[26,27] We concentrate here on the temperature dependence of the structure factor at a chemical potential of $\frac{3}{2}$ of the nearest-neighbor energy. This line of constant chemical potential crosses the phase boundary near its peak (close to a density of $\frac{1}{3}$). A contour plot of logarithm of the structure factor around a $\sqrt{3} \times \sqrt{3}$ diffraction spot at a temperature approximately 5% above T_c is shown in Fig. 1. In Fig. 1 the horizontal axis points radially away from the zone center; that is, k_a and k_r are the azimuthal and radial components of the wave vector. All the structure-factor information presented here was obtained from Monte Carlo calculations on a 3888-site lattice. The lattice was hexagonally shaped (with periodic boundary conditions) rather than rhomboidal so that more of the infinite system symmetries were present in the finite system. Typically 2×10^5 Monte Carlo steps/site were used in computing averages. Because of the periodic boundary conditions the structure factor is nonzero at only a discrete number of points (387
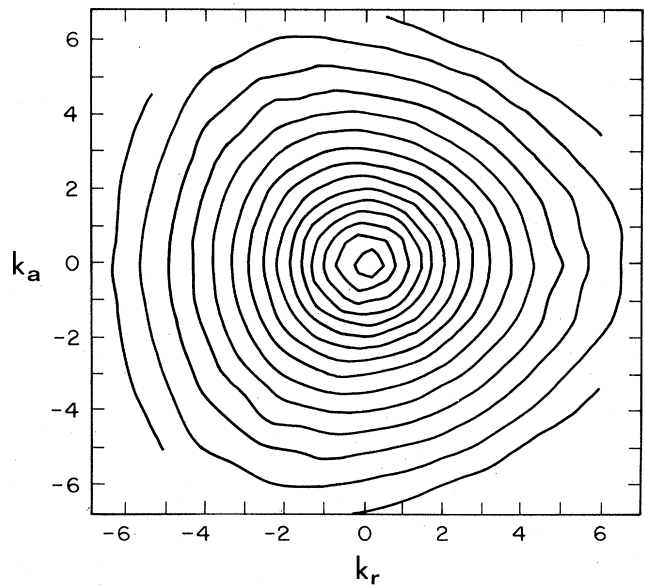

FIG. 1. Contour plot of the structure factor, the kinematic LEED intensity, of a $(\sqrt{3} \times \sqrt{3})R\,30°$ overlayer, about 5% above T_c $(0.355E_1)$. Contour increments are in a (common) logarithmic scale separated by 0.1, starting with 3.2 at the outermost contour. Center of the SBZ is to the left; k_r and k_a, the radial and azimuthal components of the wave vector, are in units of $\pi/27a$.

points in Figs. 1 and 3). Expressed alternatively, there are 36 intervals of length $\pi/27a$ between the origin and a corner of the surface Brillouin zone (SBZ), i.e., a $(\sqrt{3} \times \sqrt{3})$ inner-spot position. Here a is the lattice constant of the triangular lattice.

Figure 2 shows the temperature dependence of the structure factor summed in an approximately circular region of radius $5\pi/27a$ (i.e., 2.3% of the SBZ area). Superimposed on it is the energy scaled according to Eq. (4.1). (The parameters u and w were fixed by a least-squares fit.) Clearly for this temperature range and integration radius any information about the singularities of the energy is contained in $I(T)$. Evidently this integration radius satisfies the condition $k_I \xi \gg 1$ for the temperature range considered. As the integration radius is decreased the fit becomes progressively worse, as expected. For integration radii of $6\pi/27a$ and $7\pi/27a$ (i.e., 4.6% of the SBZ area) the fit is similar, although the amplitude of the singularity compared to the temperature-independent term decreases. For different systems the size of k_I needed to make the energy singularity dominate in the temperature range considered will vary; it is easily determined, however, by varying k_I.

The second triangular lattice gas we have examined is the one with first- and second-neighbor repulsions. At low temperatures and at particle densities greater than about 0.187 (Ref. 28) the $p(2 \times 2)$ structure orders, with third-neighbor sites preferentially occupied and a fourfold degenerate ground state at $\frac{1}{4}$ monolayer coverage. For this study we chose the second-neighbor interaction E_2 to be half of the nearest-neighbor repulsion E_1, and the chemical potential to be 1.4 times the nearest-neighbor interaction. The case of $E_2 = E_1/10$ has been considered by Glosli and Plischke[29] and the case of $E_2 = E_1$ by Saito.[30] A continuous disordering transition of the $p(2 \times 2)$ struc-

FIG. 3. Contour plot of the structure factor of a $p(2 \times 2)$ overlayer, about $2\frac{1}{2}$% above T_c $(0.354E_1)$. Contour increments are as in Fig. 1 starting with 3.0 at the outermost contour; k_a and k_r are in units of $\pi/27a$. Center of the SBZ is again to the left.

ture is expected to be in the four-state Potts universality class.[27] Figure 3 shows a contour plot of the structure factor approximately $2\frac{1}{2}$% above T_c around a $p(2 \times 2)$ diffraction condition. (Compare the triaxial symmetry of Fig. 2 with the biaxial symmetry of Fig. 4.) The temperature dependence of the structure factor, integrated as before, is shown in Fig. 4 and compared with the calculation of the energy. Again $I(T)$ clearly reproduces any information about the energy singularity contained in $E(T)$.

Another way of analyzing the integrated structure factors is on the basis of Eq. (3.11). Plots of $t^{-2\beta}S(k_I, T)$ versus $k_I t^{-\nu}$ should be independent of k_I if the scaling
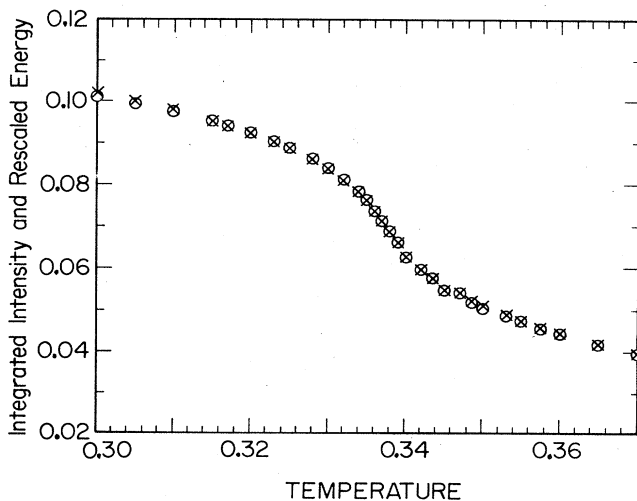

FIG. 2. Structure factor integrated over 2.3% of the SBZ (radius of 5 mesh lengths in Fig. 1) (circles) vs T, plotted with the rescaled energy ($\times$'s) for the $\sqrt{3} \times \sqrt{3}$ overlayer. Rescaling involves multiplication by a negative number and shifting by a constant. The energylike behavior of the integrated structure factor near T_c is evident.
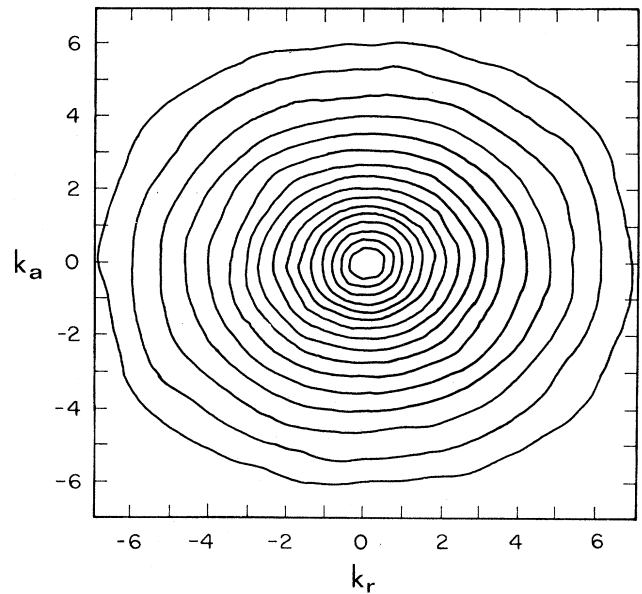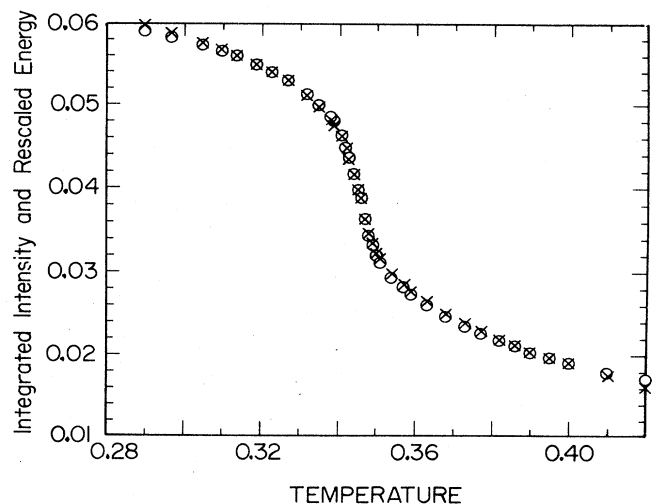

FIG. 4. Same as Fig. 2, for a $p(2 \times 2)$ overlayer.

function X is isotropic. An experimenter then might vary his instrumental resolution, and find the exponents β and ν for which this occurs. In analogy with the successes of finite-size scaling this might allow the exponents β and ν to be determined when they are unavailable directly from log-log plots of m_g and ξ. However, the structure factors for the lattice-gas model considered here were not isotropic (see Figs. 2 and 4). As these anisotropies make significant contributions to the integrals of S, Eq. (3.11) is not valid for k on the order of $\pi/4a$. For the $\sqrt{3}\times\sqrt{3}$ lattice gas the source of the anisotropy is probably a correction to scaling as described by Eq. (3.12). This type of correction to scaling comes from the presence of an irrelevant field.[31] The lowest-order field that couples to the anisotropy of the $\sqrt{3}\times\sqrt{3}$ structure factor is the triaxial chiral field considered by Huse and Fisher.[32] We fit our Monte Carlo data at small k to the form

$$\chi(T)[1-k^2\xi^2(T)-c(T)(k_r^3-3k_a^3k_r)]\;,$$

where k_r and k_a are the components of **k** in the radial and azimuthal directions, respectively. We find that $c(T)/\xi^3(T)$ vanishes as t^Δ with $\Delta=1.0+0.2$.[33] On the other hand, the scaled structure factor for the $p(2\times2)$ order-disorder transition seems to be anisotropic: Fitting to $\chi(T)[1-k_r^2\xi_r^2(T)-k_a^2\xi_a^2(T)]$ yields $\xi_a/\xi_r\approx1.2$ as $T\to T_c$.[33] The lowest-order term in the Landau-Ginzburg-Wilson Hamiltonian of this lattice-gas model which distinguishes it from that of the (isotropic) four-state Potts model is of the form[34]

$$\sum_{j=1}^{3}(\mathbf{g}_j\cdot\nabla\phi_j)^2\;,\qquad(4.4)$$

where the $\phi_j(\mathbf{r})$ are the three components of the order-parameter field, and the $\mathbf{g}_j$ are the three "primitive" reciprocal-lattice vectors of the $p(2\times2)$ ordered state. If the scaled $p(2\times2)$ structure factor is not isotropic, then this transition might belong to a different universality class, as would occur if term (4.4) is relevant (or even if it is irrelevant but has large enough amplitude). Alternatively, it might be marginal, perhaps in the same manner that simple lattice anisotropy is marginal in the Ising model.[35]

Ultimately we arrive at the problem of extracting critical properties from the integrated spectra. With the many adjustable parameters of Eq. (2.7), multivariable least-squares fits can be very delicate. The problems involved in determining effective exponents are well known from the nearly identical problem (especially in view of Figs. 2 and 4) of analyzing the specific-heat divergence.[36,37] Nonetheless, Bretz[38] and Tejwani et al.[39] have studied the critical properties of the specific heat of a $\sqrt{3}\times\sqrt{3}$ overlayer using a thermal range comparable to that available from chemisorbed systems. (Their work provides ample illustration of the difficulties in obtaining "expected" critical exponents.[40])

There are more parameters in Eq. (2.7) than the data justify. To reduce free parameters, we typically fix $\alpha'=\alpha$, in accordance with scaling. The issue of whether to include the background term in specific-heat analyses becomes here whether to allow the linear term. Obviously, a

fitted value of α will be smaller when the linear term is allowed. The difference is sizable, of order 0.1 (for reasonable values of other parameters) for the $p(2\times2)$ structure and about 0.2 for the weaker $\sqrt{3}\times\sqrt{3}$ anomaly. The question of thermal fitting range is familiar also. Near T_c data is distorted by finite-size rounding and so should be excluded. Far from T_c corrections to scaling enter. In the scaling regime the effective exponent will be insensitive to variations in the upper and lower thermal cutoffs. Unfortunately, for the size system in most surface experiments, the maximal thermal range is not much more than a decade; hence, scaling is difficult to check. A new parameter in our case is the integration radius about the extra spot; in units of the grid spacing of $\pi/27a$, we consider integration radii $k_I=1-7$. For too small k_I, Eq. (2.7) might not be valid in the temperature range of the data. As suggested by Figs. 2 and 4, the effective α' for the energy and for $k_I=5$ are usually nearly identical (i.e., within 0.01), for both layers.

Our effective specific heat exponents for the $p(2\times2)$ and $\sqrt{3}\times\sqrt{3}$ overlayers (expected to have α's of $\frac{2}{3}$ and $\frac{1}{3}$, respectively) are tabulated in Table I. There was generally little dependence on the upper thermal cutoff when it was varied between 0.12 and 0.18. The average value is given with the variation in the final digit indicated in parentheses. Decreasing the thermal cutoff below 0.12 for the smaller k_I made the effective exponents closer to those for the larger k_I. This is consistent with the idea that the range of validity of Eq. (2.7) decreases with decreasing k_I. For small k_I, when Eq. (2.7) is less representative, the variations are largest. The dependence on the lower cutoff is more significant, but the effective α seems to stabilize by 0.02 for all k_I. To check whether this cutoff is sensible, we computed energy using a lattice with half the length scale L and examined the thermal range over which it differed from the energy of the larger lattice. (The thermal rounding occurs over $\delta t\sim L^{-1/\nu}$.) We found that rounding is expected for $t<0.01-0.02$. Without the linear term for the $p(2\times2)$ overlayer, our values are comparable to those found by Saito[30] [$\alpha'=0.65$, $\alpha=0.59$ (or 0.62 if one point is discarded)] and by Binder[41] ($\alpha'=0.66$, $\alpha=0.57$) from log-log plots of energy of the four-state Potts model (where T_c and the energy at T_c are known exactly). If we fixed B_+/B_-, we could find the linear term. For three- and four-state Potts models (as well as Ising), duality predicts that $B_+=B_-$.[42] Since the $(\sqrt{3}\times\sqrt{3})$ and $p(2\times2)$ overlayers are expected to belong to these universality classes, respectively, we used this result and found the effective α decreases somewhat. For the $(\sqrt{3}\times\sqrt{3})$ overlayer we find rather large values of α, ≥0.50, but still notably less than those of the $p(2\times2)$ case for comparable fitting procedures. The values of T_c obtained from the fits [0.338(1)] are close to the best transfer matrix estimate of 0.335.[43] In his studies of the energy of the three-state Potts model, Binder[41] found $\alpha'=0.38$, $\alpha=0.39$. Selke and Yeomans[44] obtained $\alpha=0.45\pm0.05$ from log-log plots of the specific heat (without background removal), similar to our results. With the linear ("background") term included in the fit, α drops considerably to the neighborhood of $\frac{1}{3}$. We finally remark on the general trend for α to increase as the tem-

TABLE I. Values of effective exponent α for $p(2\times2)$ and $\sqrt{3}\times\sqrt{3}$ overlayers, obtained without or with linear terms, for the energy (E) and $k_I = 1$, 3, 5, and 7, and for three lower thermal cutoffs. See text for comments.

	Without linear terms			With linear terms		
	0.01	0.02	0.03	0.01	0.02	0.03
$p(2\times2)$						
1	0.81(2)	0.83(2)	0.84(2)	0.60(4)	0.65(6)	0.71(3)
3	0.65(2)	0.67(1)	0.67(1)	0.45(3)	0.52(2)	0.53(3)
5	0.59(1)	0.61(0)	0.62(0)	0.45(2)	0.53(1)	0.52(2)
7	0.57(1)	0.59(0)	0.59(1)	0.45(1)	0.53(1)	0.52(2)
E	0.56(1)	0.58(1)	0.59(1)	0.44(1)	0.50(1)	0.53(1)
$(\sqrt{3}\times\sqrt{3})R30°$						
1	0.77(3)	0.78(3)	0.79(4)	0.49(8)	0.51(9)	0.56(8)
3	0.58(2)	0.60(2)	0.62(1)	0.30(5)	0.36(4)	0.39(4)
5	0.52(1)	0.54(1)	0.55(1)	0.29(4)	0.35(2)	0.39(4)
7	0.49(1)	0.51(1)	0.52(1)	0.27(3)	0.29(5)	0.33(6)
E	0.49(1)	0.50(1)	0.51(1)	0.28(2)	0.34(1)	0.36(2)

perature analyzed gets farther from T_c.

While our primary orientation was to study lattice-gas systems of relevance to chemisorption, we also briefly considered several familiar magnetic models for calibration purposes. In these cases we only computed the structure factor along the radial direction and assumed circular symmetry to get $I(k_I, T)$. For the three-state Potts model on a 36×36 square lattice, $\alpha \sim 0.43$; for a four-state Potts model on a triangular lattice half the size used for the lattice-gas studies $\alpha \sim 0.70\pm0.03$ with no linear term. With a linear term the fits in both cases became very sensitive to k_I and the deduced α's generally much smaller. Presumably the number of data points is inadequate for this fit. We also considered two first-order transitions, for which α is formally 1. For an eight-state Potts model on a 24×24 square lattice, fits yield $\alpha \sim 0.85\pm0.03$ with a linear term and 0.90 ± 0.01 without; direct fits to the energy yielded similar results. Of more physical interest was a $p(2\times2)$ overlayer on a honeycomb lattice. In several other calculations we found evidence that this model, relevant to O/Ni(111),[45] was first order, at least for a wide range of interaction parameters. Here we find, allowing B_+ and B_- to vary independently, $\alpha \sim 0.89$; if we arbitrarily fix their ratio at unity, we have $\alpha \sim 0.97$.

V. SUMMARY AND DISCUSSION

One of the goals of surface science is to understand the forces responsible for surface order. Unfortunately the experimental probes available usually only give indirect information about these forces. By examining the temperature dependence of some experimentally obtained quantity one could hope to extract information about the temperature dependence of the various correlation functions of surface atoms, and thus obtain information about the Hamiltonian [such as Eq. (1.1)] describing the simple excitations of the surface. Unfortunately the most natural tool for such studies, LEED, couples in a very complicated way to surface correlation functions because of multiple scattering.[1] At surface phase transitions, however, the symmetries of the correlation functions change. These changes manifest themselves in LEED diffraction features in ways that are quite independent of the detailed dependence of LEED on the correlation functions themselves. In particular, the main point of this paper is that a LEED intensity, or any other measurement, that is sensitive to only short-ranged correlations (and insensitive to the symmetry of the correlations), is expected to show the same singularity at a phase transition as that of the energy.

One (perhaps even practical) application of this idea has been to the transition of the Si(111) surface from a (7×7) (reconstructed) low-temperature state to the unreconstructed ["(1×1)"] high-temperature state.[46] In this experiment the temperature dependence of the *total* diffracted current was monitored. It was found that the abruptness of the change in this current (that is, the magnitude of the peak of the specific heat) depended sensitively on the method by which the surface was cleaned of impurities, whereas no other method has yet detected a difference. Presumably the different preparation methods led to different characteristic length scales. Thus, study of this transition characterizes the surface without knowledge of how the measurement depends on the surface order.

We note finally that the variation of effective exponent values in Table I is a consequence mainly of the relatively limited range in reduced temperature available for analysis. This limitation results from the finite size of our simulations, chosen to be comparable to the length scale to which various surface imperfections limit real chemisorption systems. While we have suggested in this paper that one can *study* surface phase transitions with short-range probes, we are obliged to make the following counterpoint: To improve exponent estimates will require substantial improvements in sample quality.

ACKNOWLEDGMENTS

puter facilities were supplied by the University of Maryland Computer Science Center. We are grateful to Professor O. E. Vilches for the unpublished draft cited in Ref. 40 and a helpful conversation with one of us (T.L.E.)

APPENDIX

The scaling function $F_\pm(x)$ for the spin-spin correlation function of the Ising model is defined by

$$\lim_{\substack{t\to0^\pm \\ r\to\infty \\ r/\xi \text{ fixed}}} \langle\sigma(0)\sigma(\mathbf{r})\rangle = \frac{F_\pm(r/\xi(T))}{r^{1/4}} . \qquad \text{(A1)}$$

The structure factor of the Ising model is simply

$$S(\mathbf{k},T) = \sum_{\mathbf{r}} \langle\sigma(0)\sigma(\mathbf{r})\rangle e^{i\mathbf{k}\cdot\mathbf{r}} .$$

In the limit of small t, this sum can be replaced by an integral. For the square lattice case, following Tracy and McCoy,[47] we obtain the leading contribution to the structure factor per site

$$S(k,T) \sim 2\pi\xi^{7/4} \int_0^\infty du\, u^{3/4} F_\pm(u) J_0(k\xi u) .$$

Integrating this structure factor on a circular region of ra-

dius k_I centered on $\mathbf{k}=0$ yields

$$I(k_I,T) = (2\pi)^{-2} \int_0^{k_I} dk\, k \int_{-\pi}^{\pi} d\phi\, S(k,T)$$

$$\sim \xi^{-1/4} \int_0^\infty du\, u^{-5/4} F_\pm(u) k_I \xi u J_1(k_I \xi u) .$$

The above equation is of the form of Eq. (3.11) with $\beta=\frac{1}{8}$, $\nu=1$, and

$$Z_\pm(x) = x\xi_0^{-1/4} \int_0^\infty du\, u^{-1/4} F_\pm(u) J_1(xu) . \qquad \text{(A2)}$$

The large-x (small-t) behavior of $Z_\pm(x)$ can be obtained by considering the small-u behavior $F_\pm(u)$:[47]

$$F_\pm(u) = F(0)\{1 \pm \tfrac{1}{2}u[\ln u + (\gamma_E - \ln 8)] + \cdots \} \qquad \text{(A3)}$$

[γ_E is Euler's constant and $F(0) = 0.703\,380\,16$]. Combining Eqs. (A2) and (A3) (and replacing $x^{\alpha=0}$ by $\ln x$) yields

$$Z_\pm(x) = \xi_0^{-1/4} d_1 x^{1/4} (1 \mp d_3 x^{-1} \ln x \mp d_4 x^{-1} + \cdots) , \qquad \text{(A4)}$$

where the d_i's can be evaluated in the manner implicit in Tracy and McCoy's derivation of the C_i's of Eq. (3.4).[48] We find

$$d_1 = 2\pi^{-1} C_1 = 2^{11/4}\pi^{-1} F(0)[\Gamma(\tfrac{7}{8})]^2 \cos(3\pi/8) = 0.684\,366\ldots ,$$

$$d_3 = \tfrac{1}{3} C_2 = \tfrac{1}{3}[\Gamma(\tfrac{11}{8})/\Gamma(\tfrac{7}{8})]^2 \tan(3\pi/8) = 0.535\,547\ldots , \qquad \text{(A5)}$$

$$d_4/d_3 = (C_3/C_2) + \tfrac{4}{3} = \tfrac{4}{3} - \gamma_E + 2\ln 2 - \psi(\tfrac{11}{8}) + \frac{\pi}{2}\tan(7\pi/8) = 1.579\,099\ldots .$$

Here (unlike in the text) we have defined d_3 and d_4 in Eq. (A4) such that they are positive; these terms have the opposite sign of the corresponding coefficients in the expansion of χ. Thus the large argument expansion for the integrated structure factor has the same form (with k_I replacing k) as the large argument expansion of the structure factor (the Fisher-Langer expansion) even though the singularity at $k=0$, which the Fisher-Langer expansion does not describe, has been included in the integral. Hence the integral displays the energy singularity for nonvanishing k_I.

We can also obtain an explicit expression for the contribution to Z of the squared magnetization, and hence $d_1 d_2^-$, by replacing $u^{3/4} F_\pm(u)$ with $2^{3/8} u$ in Eq. (A2).[47]

Since $\int_0^\infty J_1(ux)du = x^{-1}$, the resulting term $d_1 d_2^-$ is $2^{3/8}$; the squared magnetization thence is $2^{3/8}\xi_0^{-1/4}$, where $\xi_0^{-1} = 4E/k_B T_c = 1.762\,747\ldots .$

Finally we cast our results in the form of Sec. III:

$$I = d_1 k_I^{1/4} \pm d_1 d_3 \xi_0^{-1} k_I^{-3/4} |t| \ln|t|$$

$$\mp d_1 k_I^{-3/4} \xi_0^{-1}[d_4 + d_3\ln(k_I\xi_0)] |t| . \qquad \text{(A6)}$$

In closing, we point out that Eq. (A6) demonstrates for the square Ising model that I decreases monotonically with increasing temperature. Therefore, a previously reported[49] peak in I near T_c in the same model must be spurious.

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[49]P. A. Bennett and M. B. Webb, Surf. Sci. **104**, 74 (1981).