New Monte Carlo Estimates of Critical Interfacial Amplitudes and the Universality of Amplitude Ratios

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Critical interfacial tension amplitudes can be obtained without the usual difficult task of calculating the related excess free energy. This permits for the first time practical Monte Carlo calculations with very large lattices. By use of up to $128\times128\times128$ for the simple-cubic Ising model, a new amplitude is obtained and is larger than previous estimates with smaller lattices. This resolves the long-standing large disagreements between experiments and theory on the universality of the related amplitude ratios.

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The modern theory of critical phenomena[1] has made significant contributions to a broad range of important complex physical problems involving many degrees of freedom. One of the more important theoretical concepts has been universality, which provides the framework for a detailed description of singular behavior near the critical point. If universality holds, then one can understand and predict properties of complex systems by studying much simplified models which are in the same universality class. There now exist numerous comparisons of experimental measurements on the critical exponents and various combinations of critical amplitudes with theoretical predictions. Although, on the whole, the agreements have been satisfactory, there are, however, long-standing unresolved anomalies where the differences have been shown to be statistically significant.

We consider here the important example of the amplitude ratios[2] involving the critical interfacial tension amplitude τ_0 and the correlation-length amplitude ξ_0. The ratio $\tau_0\xi_0^2/k_BT_C$ enters into theoretical descriptions of nucleation[3] and wetting,[4] topics of broad fundamental and applied interests. A demonstration of the universality of this ratio would also be a test of scaling[5] and the two-scale-factor universality concept.[6] Recent reviews on the Ising universality class in three dimensions indicate a clear disagreement between theoretical calculations of the Ising model and experimental measurements on fluids and fluid mixtures.[7,8] This disagreement remains unresolved because the absence of an exact solution to the three-dimensional Ising model prevents conclusive comparisons of theory and experiments. A wide range of theoretical estimates based on approximate methods[9] produced values which are different from the experimental values. In principle, Monte Carlo simulation estimates of the interfacial tension can produce numerically exact results for any finite lattice. In practice, one is limited to small lattices and one must extrapolate to the thermodynamic limit to obtain the amplitude. There have been a number of Monte Carlo calculations, with increasing lattice sizes, but still using lattices of $16\times16\times16$ or less. These calculations are based on direct estimates of the excess free energy and are computationally demanding, thus preventing practical calculations of very large lattices.[10,11] In this Letter, the simple (but yet unexploited) relation between the interfacial excess free energy and the interfacial excess energy is shown to permit estimate of the interfacial tension amplitudes without calculation of interfacial excess free energy. With this approach, large simple-cubic nearest-neighbor ferromagnetic Ising-lattice model calculations are obtained, allowing a much broader exploration of the scaling function[12] and revealing a rather slow convergence toward the asymptotic limit. The amplitude obtained is in agreement with previous Monte Carlo estimates of the same lattice sizes but significantly larger when lattices larger than before are used. The approaches to the asymptotic limit are consistent with logarithmic terms in the scaling function. The extrapolated amplitude produces ratios which are in agreement with experimental results within statistical uncertainty. The long-standing disagreements are resolved and universality is confirmed.

The interfacial tension near criticality (T_c) in the thermodynamic limit for a L^d cubic-lattice system vanishes as $\tau(t,L\approx\infty)=\tau_0 t^\mu$, where $t=(1-T/T_c)>0$, μ is the interfacial tension critical exponent, and τ_0 is the amplitude. The excess interfacial energy density is simply related to τ by

$$\delta U(t,L\approx\infty)/L^{d-1}=d[\beta\tau(t,L\approx\infty)]/d\beta = \tau_0 t^\mu(1+\mu T/tT_c), \qquad (1)$$

where $\beta=1/k_BT$. This implies that

$$\tau_0=[\delta U(t,L\approx\infty)/L^{d-1}][t^\mu(1+\mu T/tT_c)]^{-1} \qquad (2)$$

and any measurement of the excess interfacial energy density will yield an estimate for τ_0. $\delta U(t,L)$ can be defined as the excess $\delta U(t,L)=U_{ap}(t,L)-U_p(t,L)$, the difference between a system with an interface imposed by an antiperiodic boundary condition and a system without an interface with a periodic boundary condition. The excess interfacial energy can be accurately obtained by standard Monte Carlo ensemble averaging. The scaling function for δU can be obtained from the finite-size scaling function for τ,[13]

$$L^{\mu/\nu}\tau(t,L)=\tau_0 L^{\mu/\nu}t^{\mu}\Sigma(L^{1/\nu}t)=\tau_0 X^{\mu}\Sigma(X), \tag{3}$$

with $X=L^{1/\nu}t$. From Eq. (1) and the assumption of hyperscaling, the scaling function is

$$\delta U(t,L)=\tau_0 X^{\mu}\{\Sigma(X)(1+\mu T/tT_c)+L^{1/\nu}(T/T_c)d\Sigma(X)/dX\}$$

and for $t\approx 0$,

$$\delta U(t,L)=\tau_0 X^{\mu}(1+[\mu/t][T/T_c])\{\Sigma(X)+[X/\mu]d\Sigma(X)/dX\}. \tag{4}$$

Very little is known about $\Sigma(X)$ for $X\approx\infty$, except that $\Sigma(X\approx\infty)\approx 1$. By demanding consistency with Eq. (1) for $X\approx\infty$, I argue that $\Sigma(X)$ must satisfy the limit $\{\Sigma(X)+[X/\mu]d\Sigma(X)/dX\}\approx 1$, for $X\approx\infty$. We now obtain

$$\delta U(t,L)/X^{\mu}(1+[\mu/t][T/T_c])=\tau_0\{\Sigma(X)+[X/\mu]d\Sigma(X)/dX\}.$$

This is a scaling function of X and converges to τ_0 for $X\approx\infty$. I therefore define a scaling function,

$$\tau_0(X)=\delta U(X)/X^{\mu}(1+[\mu/t][T/T_c]), \tag{5}$$

with $\tau_0=\tau_0(\infty)$, in the small-t limit. I have studied this scaling function with standard Monte Carlo methods.[14]

$\tau_0(X)$ has been studied for a wide range of L and t near 0, by use of about a million Monte Carlo steps per spin for $d=3$. The results given in Fig. 1 contain L up to 128 and $0.001<t<0.0075$. $\mu=1.26$ (LeGuillou and Zinn-Justin[15]) and $J/k_BT_c=0.221\,655$ (Pawley *et al.*[16]) were used. [Statistical errors were estimated by standard procedures of averaging over different (5–10) Monte Carlo runs.] The range of X^{μ} used is about 5 times larger than before. In earlier Monte Carlo studies (using direct calculation of excess free energy),[11] $X\approx 1.0$ was used to obtain τ_0/k_BT_c of 1.2 ± 0.1 in agreement with the present method. This is also consistent with the first Monte Carlo study[10] of interfacial tension, where smaller values of X yield 1.05 ± 0.05.

Figure 1 indicates that even with $X^{\mu}\approx 7$, the amplitude estimate is still increasing. This implies a very slow convergence of the scaling function. I have assumed an $(X^{\mu})^{-1}$ convergence and plotted $\tau_0(X)/k_BT_c$ vs $(X^{\mu})^{-1}$ in Fig. 2. This provides a good description of the large-X data and extrapolates to a value of 1.58 ± 0.05. Although I have no rigorous theoretical basis for an $(X^{\mu})^{-1}$ convergence, I am motivated by the possibility of logarithmic subdominant terms in the scaling function $\Sigma(X)$, similar to those found in the exact calculation of the Ising model for two dimensions.[17] The numerical results are consistent with

$$\Sigma(X)=1+[A/X^{\mu}][1+b\ln(1+\{X/c\})]$$

and, for $X/c\gg 1$,

$$\tau_0(X)\approx\tau_0(\infty)\{1+[Ab/\mu X^{\mu}]\}, \tag{6}$$

with $\tau_0(\infty)/k_BT_c=1.58\pm 0.05$ and

$$\{Ab/\mu\}\{\tau_0(\infty)/k_BT_c\}\approx 0.66\pm 0.12.$$

These are approximate fits to the numerical data and should not be taken as claims to the actual functional form for the scaling function. Nevertheless, they provide hints as to the asymptotic behavior which may be of use in more rigorous analytic studies. Note that for small X,

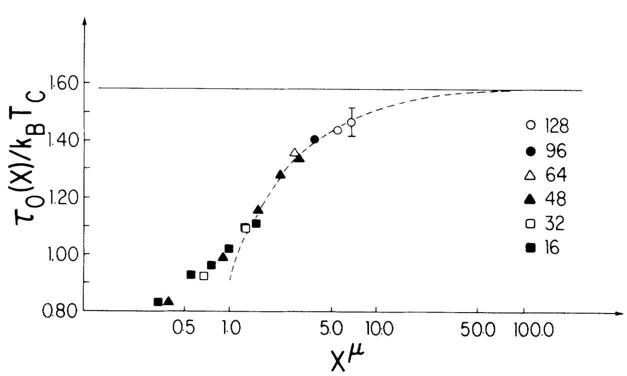

FIG. 1. Monte Carlo results for $\tau_0(X)/k_BT_c$ vs $\log X^{\mu}$ for $L=16$ to 128. Dashed line is Eq. (6). See text.

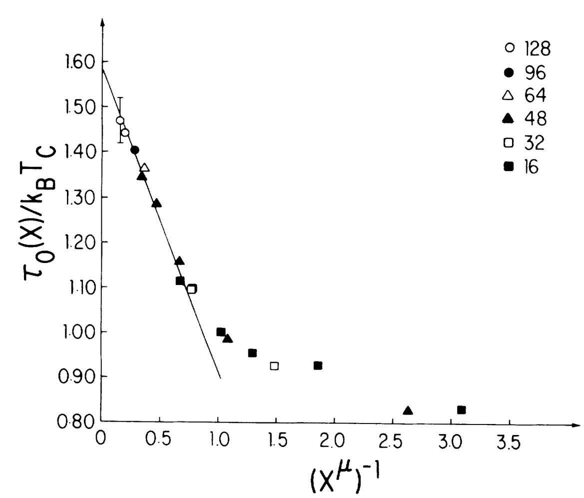

FIG. 2. Monte Carlo results for $\tau_0(X)/k_BT_c$ vs $(X^{\mu})^{-1}$ for $L=16$ to 128. Solid line is Eq. (6). See text.

the previously proposed approximant (based on data of $X \approx 1.0$) is recovered.[13] In that form, there are no logarithmic corrections. Even given the uncertainty of the extrapolation, a lower bound of $\tau_0(\infty)/k_B T_c > 1.5$ is assured on the assumption that the scaling function's approach to the large-X limit is smooth and monotonic.

The proposed universal amplitude ratio[2] is $U_I^{\pm} = \tau_0/k_B T_c (\xi_0^{\pm})^{d-1}$, where $\xi_0^{\pm}$ denotes the correlation-length amplitude for $T \gtrless T_c$. Recent detailed reviews of experimental data indicate a value of $U_I^+ \approx 0.386$,[8] $U_I^- \approx 0.757$,[7] and previous Monte Carlo estimates are 0.27 ± 0.023 and 0.284 ± 0.018 for U_I^+ of the simple-cubic and body-centered-cubic Ising lattices, respectively.[11] The correlation amplitudes were taken from series analysis.[18] Using my present estimates for $\tau_0/k_B T_c$ of 1.58, I obtained ratios of 0.36 ± 0.01 and 0.846 ± 0.027 for U_I^+ and U_I^-, respectively. These are differences of only about 7% from 0.386 and 11% from 0.757, within the spread of the experimental values.[7,8]

Using my new estimate for τ_0, I have also compared theoretical estimates with experimental values for two other amplitude ratios involving the interfacial tensions. See Table I. The first[5] is

$$\beta^2 C = C^-(\tau_0/k_B T_c)/[4B^2 \xi_0^-].$$

$B = 1.569$ and $C^- = 0.209$ are critical amplitudes for the order parameter[19] and susceptibility.[18] The second[6] is $Y^{\pm} = (\tau_0/k_B T_c)/[A^{\pm}]^{(d-1)/d}$, with $A^+ = 0.142$ (Sykes *et al.*[20]) and $A^- = 0.278$, assuming $A^+/A^- = 0.51$.[21] These are specific-heat critical amplitudes. The overall agreements with experiments are satisfactory. The differences are about 10%, except for $\beta^2 C$, where 17% is indicated. Note, however, that the present estimate for this ratio is in very good agreement with the Fisk and Widom result[5] of 0.135, calculated with $\beta = 0.325$. The universality can be considered to be confirmed within the combined experimental[7,8] and estimated numerical errors of the Monte Carlo calculations.

I have shown that the interfacial tension amplitudes can be obtained from the study of the excess interfacial energy without the need to calculate interfacial tension. This makes possible practical calculations for very large lattices, providing information on the scaling function and a more reliable extrapolation to the asymptotic limit.

TABLE I. Comparisons of amplitude ratios between experiments and Monte Carlo results. See text.

	$\beta^2 C$	U_I^+	U_I^-	Y^+	Y^-
Experiments					
Reference 7	0.114		0.757		3.62
Reference 8		0.386		5.65	3.71
Monte Carlo, present work	0.137 ± 0.004	0.36 ± 0.01	0.846 ± 0.027	5.80 ± 0.2	3.70 ± 0.12

The new amplitude for the three-dimensional Ising model provides new amplitude ratios which are in agreement with experiments and support universality. This method does not provide other information such as the proposed universal finite-size scaling amplitude[11] at $T = T_c$ and the interfacial tension far from T_c. It complements previously proposed methods for the study of interfacial tension.[10,11] Extensions of similar ideas to other critical free energy quantities are possible and will be considered elsewhere.

I have not provided a rigorous theoretical explanation for the apparent occurrence of logarithmic terms in the scaling function. One possible source is that the Ising interface near and below the critical temperature is rough and in the Kosterlitz-Thouless phase.[22] This may provide the marginal operator responsible for the logarithmic terms. Such speculations are under active numerical investigations. I hope that these numerical results will motivate further theoretical research.

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