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Evaluating and improving the cluster variation method entropy functional for Ising alloys

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The success of the “cluster variation method” ~CVM! in reproducing quite accurately the free energies of Monte Carlo ~MC! calculations on Ising models is explained in terms of identifying a cancellation of errors: We show that the CVM produces correlation functions that are too close to zero, which leads to an *overestimation* of the exact energy, E , and at the same time, to an *underestimation* of $2TS$, so the free energy $F \approx E - 2TS$ is more accurate than either of its parts. This insight explains a problem with “hybrid methods” using MC correlation functions in the CVM entropy expression: They give exact energies E and do not give significantly improved $2TS$ relative to CVM, so they do not benefit from the above noted cancellation of errors. Additionally, hybrid methods suffer from the difficulty of adequately accounting for both ordered and disordered phases in a consistent way. A different technique, the “entropic Monte Carlo” ~EMC!, is shown here to provide a means for critically evaluating the CVM entropy. Inspired by EMC results, we find a universal and simple correlation to the CVM entropy which produces individual components of the free energy with MC accuracy, but is computationally much less expensive than either MC thermodynamic integration or EMC. © 1998 American Institute of Physics.

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I. INTRODUCTION

The physics of phase transitions and phase stability of alloys is often couched in terms of statistical mechanics models on the generalized ~long-range pair and multibody interactions! Ising lattice and computed most accurately with Monte Carlo ~MC! methods.¹ These are time consuming calculations and usually are thus restricted to coarse grids of chemical potential and temperatures. Further, MC simulations do not give directly the values of important thermodynamic variables such as entropy and free energy, since these quantities cannot be written in terms of ensemble averages. Instead, these are obtained laboriously by integration of thermodynamic relations from a known starting point. To remedy this situation, one often uses the less accurate molecular field methods, most notably the cluster variation method ~CVM! of Kikuchi.² Despite its great simplicity, the CVM reproduces many of the features of phase diagrams obtained by the many-orders-of-magnitude more computer expensive MC method: For the fcc nearest-neighbor antiferromagnetic Ising Hamiltonian with coupling constant J and zero chemical field $h \approx 0$, the transition temperature T_c ³ from MC simulations is 1.74⁴ while CVM in the tetrahedron ~tetrahedron–octahedron! approximation gives 1.89 ~1.81!. This and other successes of the CVM² are even more surprising in light of the finding that the CVM correlation functions ~the thermal average of products of the Ising spin variables! differ considerably from the exact MC values: For example, in the nearest-neighbor fcc antiferromagnetic Ising model, the MC pair correlation functions⁵ at $T \approx 1.9$ and $h \approx 0$ are 0.208,

0.254, 0.036, 0.076 for the first to fourth neighbors, respectively, while the tetrahedron-CVM first neighbor correlation function is 0.188 and the tetrahedron–octahedron-CVM first and second neighbor correlation functions are 0.198 and 0.198. Thus, CVM correlation functions are substantially closer to zero ~i.e., more “random”! than the exact values. The error in tetrahedron-CVM first neighbor correlation function leads to a ; 10% error in both energy and entropy relative to MC ~see below!. However, despite such systematic discrepancies

simplicity of the CVM with the accuracy and flexibility of MC. A natural possibility is to use⁶ the correlation functions P_{MC} -or cluster probabilities! obtained from MC simulations in the CVM expression for free energy $F_{CVM}(P_{MC})$ in the hope of obtaining a more accurate free energy. We demonstrate that these methods⁶ are unlikely to succeed, as these approximations do not benefit from the cancellations of er-

Monte Carlo thus, $dE = 0$ in Fig. 1-b!, demonstrating that the energetic effect of short-range order in CVM is underestimated, and hence the CVM internal energy is more random than that of Monte Carlo. The entropy of CVM is overestimated @ $d(\mathcal{Z}TS)$

the “exact” Monte Carlo results in Fig. 1-a!, we may ascertain the errors in thermodynamic functions of the CVM. The differences dE , $d(\mathcal{Z}TS)$, and dF between the respective CVM and Monte Carlo functions are shown in Fig. 1-b!. In our CVM calculations, we have used only the CVM entropy expression with the disordered phase symmetry. Thus, in Fig. 1-b! differences with Monte Carlo for temperatures below the CVM transition ($T \leq 1.89$) are shown as dashed lines. Obviously, practitioners of CVM would correctly impose a lower symmetry on the entropy expression below the transition to the ordered phase and would not use the disordered phase symmetry in this temperature range. The reason we use the CVM disordered phase symmetry down to low temperature is due to our wish to combine CVM methods with MC, which as we describe in the next section, is problematic when using ordered expressions for CVM entropy.

As indicated in the Introduction, the CVM correlations functions \overline{P}_f are closer to zero than the MC values. By Eq. 2!, the CVM internal energy is less negative relative to

~2!, there is no error in energy ($dE \approx 0$). Thus, the error in free energy, shown in Fig. 2, is equal to the error in entropy: $dF \approx d(2TS)$. Since there is no error in energy in this method, there is no cancellation of errors. Hence, even though the exact Monte Carlo correlation functions are used in the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method, it produces less accurate free energies than standard CVM: For example, at $T=1.92$, the free energies as given by Monte Carlo, $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$, and CVM, are 22.109, 22.050, and 22.067, respectively. For comparison, CVM in the tetrahedron–octahedron approximation gives 22.094 for this temperature.

Other disadvantages of the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ approach are illustrated in Fig. 3, showing a comparison of the entropies as a function of temperature as calculated by MC (S_{MC}), by standard CVM $S_{\text{CVM}}(\mathbf{P}_{\text{CVM}})$, and by the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method $S_{\text{CVM}}(\mathbf{P}_{\text{MC}})$. The other two curves of Fig. 3 are discussed in Sec. C and III D below. One can again see that i) standard CVM (solid line) overestimates the entropy at high temperatures relative to Monte Carlo (open squares), ii) the CVM entropy of the disordered phase is not applicable at low temperatures, and iii) the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method underestimates the entropy at high temperatures, and at low temperatures this entropy takes on the unphysical values $S_{\text{CVM}}(\mathbf{P}_{\text{MC}}) < 0$. These unphysical values are a result of the fact that the expression for the disordered S_{CVM} allows negative values for many atomic configurations. For instance, in the fcc lattice, the simplest ordered configurations such as $L1_0$, $L1_1$, $L1_2$ have negative S_{CVM} values. These negative values of CVM entropy are likely to persist no matter what sized maximal cluster is used, and thus will always lead to difficulties with the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method at lower temperatures, since the CVM entropy will incorrectly tend to negative values rather than zero. Of course, one might argue that these ordered configurations only possess negative CVM entropy when evaluated with the CVM expression for the dis-

ordered phase, whereas when evaluated with the CVM expressions for the corresponding ordered phases, they will have non-negative entropies. However, this illuminates another potential problem with the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method: In Monte Carlo simulations, the presence of anti-phase boundaries and finite-sized domains of long-range order preclude one from unambiguously defining the distinction between sublattices and extent of long-range order present in the simulation. However, an ordered CVM expression for the entropy is written in terms of correlation functions and cluster probabilities for all the symmetry-distinct figures for the symmetry of the long-range ordered phase. Thus, the CVM ordered entropy expressions presuppose the domains of long-range order are infinite in size, and hence the distinction of various sublattices in the ordered phase is unambiguous. Thus, using the $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ method with ordered CVM entropy expressions is not practical because one does not know from the MC simulations precisely how to divide the MC simulations into sublattices of long-range order and hence one does not even know from the MC simulations which ordered CVM expression to use. Also one does not know at what temperature to change the symmetry of the CVM to the ordered entropy expression. Thus, an ideal method combining Monte Carlo and CVM would only use a single expression –e.g., the disordered CVM expression! for the entropy at both low and high temperatures. We next describe such a method called entropic Monte Carlo (EMC).

C. The entropic Monte Carlo method: A critical evaluation of CVM entropy

Lee⁷ has shown a practical way to determine the entropy of a Monte Carlo cell as a function of any state variable. We call this method entropic Monte Carlo (EMC). Though in his paper Lee applies the EMC method to the case of the energy as state variable in a quantized system, here we describe instead S_{EMC} in terms of the state variable $S_{\text{CVM}}(\mathbf{s})$ which is a continuous, not quantized, variable. Our strategy will be to calculate $S_{\text{EMC}}(S_{\text{CVM}})$ by the method of Lee, and then insert $S_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ into this expression, giving $S_{\text{EMC}}(S_{\text{CVM}}(\mathbf{P}_{\text{MC}}))$ which we write as $S_{\text{EMC}}(\mathbf{P}_{\text{MC}})$. We will show that this function reproduces very well S_{MC} . First, we describe how $S_{\text{EMC}}(S_{\text{CVM}})$ is calculated.

The EMC method is a self-consistent process in which each iteration is made from a series of Monte Carlo sweeps where the driving “energy” $E(\mathbf{s})$ of the Monte Carlo equations is not the true energy contained in the sample but an approximation to the entropy

$$E(\mathbf{s}) \approx E(S_{\text{CVM}}(\mathbf{s})), \quad (5)$$

which depends on the configuration \mathbf{s} through the function $E(S_{\text{CVM}})$, whose argument is the CVM entropy per site calculated with Eq. (3) for the cluster probabilities r

$$\exp\left\{2E_{\sim s_i}! \#W_{\sim i} \rightarrow j\right\} \cdot \exp\left\{2E_{\sim s_j}! \#W_{\sim j} \rightarrow i\right\}, \quad \sim 6!$$

where W

maximal cluster!, because the role of the energy driving the EMC calculations is played in Eq. (10) by the entropy itself.

Figure 4 shows a typical result $S_{EMC}(S_{CVM})$ of the EMC calculations, using a MC cell with $N = 12^3 = 1728$ sites. We also performed EMC calculations with different MC cells, with the results being slightly different for the larger negative values of S_{CVM} . The negative values of S_{CVM} correspond to configurations of atoms with higher symmetry, usually associated with smaller repeat units, thus explaining why the curve depends to some extent on the size and shape of the MC cell for the negative values of S_{CVM} : For instance, for an EMC cell with an odd number of sites (e.g., 11^3), one could never obtain the stoichiometric configuration $L1_0$ with its large negative CVM entropy. In fact, simple high-symmetry configurations such as $L1_0$, $L1_1$, $L1_2$ all have negative values of S_{CVM} . Examining the CVM entropy for all configurations with up to 16 atoms per cell,¹⁰ we found the configurations with the most negative CVM entropy had very small unit cells. The largest negative CVM entropy occurs for $L1_0$ for which $S_{CVM}(L1_0) \approx 2.134 \ln 2$.

The results $S_{EMC}(P_{MC})$ of EMC are shown in Fig. 3, where they are contrasted with the results of Monte Carlo, CVM, and $F_{CVM}(P_{MC})$.¹¹ By comparing $S_{EMC}(P_{MC})$ and $S_{CVM}(P_{CVM})$ with S_{MC} , we see that the EMC and CVM entropies are equally accurate at high temperatures. Remarkably however, the EMC method also produces extremely accurate entropies at low temperatures, in qualitative contrast with the $F_{CVM}(P_{MC})$ method. Thus, even though one only uses a single disordered expression for the CVM entropy in the EMC calculations, the EMC reproduces both high temperature (disordered) and low temperature (ordered) entropy values, with no need to change the CVM entropy expression at any point. Although the internal energy in EMC is exact (so this method does not benefit from the cancellation of errors noted in Sec. III A for the CVM!), we see that EMC does not need to be correct due to cancellation of errors. Instead, it is accurate because its individual terms (E and $2TS$) are accurate.

The EMC, like standard Monte Carlo, can be a computationally laborious procedure. However, our EMC calculations of $S(S_{CVM})$ suggest a very simple functional $\tilde{S}(S_{CVM})$ which is appealing because the correction does not require one to perform an EMC calculation. We next describe this simple correction.

D. An EMC-inspired new entropy functional

While $S_{CVM}(P_{MC})$ can be inaccurate, $S_{EMC}(P_{MC})$ is accurate but computationally expensive. Thus we will now develop a new functional $\tilde{S}(P_{MC})$ which is both accurate and inexpensive.

The EMC results of Fig. 4 permit one to guess the behavior of the exact entropy $S(S_{CVM})$ (in the limit $N \rightarrow \infty$) as a function of the CVM entropy obtained from a “good” maximal cluster (e.g., the tetrahedron or the tetrahedron-octahedron). This “true” entropy function $S(S_{CVM})$ should have the following properties:

i! The most positive $S_{CVM}(x)$ entropy $S_{CVM}^{MAX}(x)$ should correspond to the exact entropy for this case, i.e., the ideal

mixing entropy: $S(S_{CVM}^{MAX}) \approx S^0(x) \approx k_B \ln x \ln(1/x)$

ii! The slope of $S(S_{CVM})$ at the maximum value of $S_{CVM}^{MAX} \approx S^0$ should be unity because for nearly random configurations the CVM approaches the exact result: $dS/dS_{CVM}|_{S^0} \approx 1$.

iii! The most negative value of the CVM entropy should correspond to zero true entropy. Thus, $S(S_{CVM}^{MIN}) \approx 0$. The configuration with most negative CVM entropy can be found by examining all configurations up to some maximum unit-cell size, as described in Ref. 10. For instance, for the tetrahedron CVM, $L1_0$ has the most negative CVM entropy $S_{CVM}^{MIN} \approx S_{CVM}(L1_0)$

$S_{\text{CVM}}(\mathbf{P}_{\text{MC}})$ is negative. Also, the simple functional represented by $\tilde{S}(\mathbf{P}_{\text{MC}})$ effectively retains all of the improvements over $F_{\text{CVM}}(\mathbf{P}_{\text{MC}})$