Letter

Landau free energy of small clusters beyond mean-field approach

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Landau free energy determines the landscape of order parameter fluctuations that occur in a physical system at thermal equilibrium and, in particular, characterizes the critical phenomena. We propose a semianalytical approach based on the fluctuating local field method, which allows us to estimate Landau free energy for small clusters with discrete (Ising model) and continuous (Heisenberg model) order parameter.

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Introduction. Landau free energy (LFE) is a powerful tool for describing the critical phenomena and fluctuations of the order parameter in many quantum and statistical systems. This concept was first introduced by Lev Landau in 1937 to describe a second-order phase transition [1]. Near the transition point the free-energy potential $F_L(\beta, \eta)$ at certain inverse temperature β is expanded in Taylor series of an order parameter η up to fourth order assuming the inversion symmetry:

$$F_L(\beta, \eta) = C + a(\beta)\eta^2 + b(\beta)\eta^4 + \dots. \tag{1}$$

The potentials of a similar type are used to study various phases and material properties. For example, for the ferroelectric systems the Landau-Devonshire theory provides the phenomenological description of the relationship between the polarization and applied electric field, as well as other properties such as the dielectric constant and the strain of the material [2–7]. This concept is also important in the study of such statistical systems as molecular magnets [8], liquid crystals and nematic polymers, where it is known as Landau-de Gennes [9–11] theory. In the theory of collective quantum phenomena, the Ginzburg-Landau functional is widely used for the phenomenological description of superconductivity and Bose-Einstein condensation [12–15].

It is commonly accepted that the fourth-order expansion (1) is indeed a good approximation in many cases for the $F_L(\eta)$ dependence, given β. This is, e.g., supported by the experimental studies of ferroelectric and magnetic materials, where the coefficients in the expansion (1) can be extracted [16–19]. However an estimation of the temperature dependence of the polynomial coefficients $a(\beta)$, $b(\beta)$ is still a hard task. This dependence shows a nonanalyticity at the transition point for bulk materials. For small clusters, the sharp transition is suppressed by fluctuations, but the temperature dependence of the Landau coefficients is still nontrivial.

Landau free energy can be obtained from the numerical simulations. For small systems with a discrete order parameter it can be calculated directly by an enumeration of all states; however, the computational complexity grows exponentially with the system size. Methods based on the Monte Carlo approach, coarse-graining and molecular-dynamics simulations apply for a more general situation [20–23]. In particular, the Wang-Landau algorithm [24–28] proposed about 20 years ago allows us to calculate the Landau free energy for systems with both continuous and discrete order parameter.

Much less is achieved when it comes to analytical calculations. Actually the only method at hand is mean-field theory (MFT). In this approach the interacting system is replaced by the noninteracting one in a certain effective potential. MFT-like methods provide a basic tool for describing the collective behavior of correlated systems. However, the MFT description of critical phenomena is very limited, because the essentially important physics of fluctuations is almost neglected at the MFT level. Furthermore, it is quite hard to construct an improvement of the MFT result, because the theory does not contain an explicit small parameter.

The fluctuating local field (FLF) method was introduced several years ago for a more quantitatively accurate estimation of the thermodynamics properties of the classical lattices [29]. Later, the FLF method was applied to fermionic systems such as Hubbard chains [30] and two-dimensional clusters [31], [32], as well as to the disordered Ising model [33]. The main idea of this approach is to introduce the additional fluctuating degrees of freedom conjugated with the order parameter. This allows us to take into account the most important modes of the fluctuations in the system, regardless of their magnitude. The remaining part of the fluctuations is treated perturbatively. At the same time, similarly to the MFT, the FLF description greatly simplifies the form of the Hamiltonian of the system, which makes it possible to obtain good quantitative results without using complex technical procedures.

In this paper, we report that the FLF method allows us to reconstruct the landscape of Landau free energy of small classical lattices with a discrete (Ising) and continuous (Heisenberg) order parameter. We compare the results obtained with the numerically exact data as well as with the MFT predictions. We observe that the second-order FLF

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method outperforms the MFT one, both qualitatively and quantitatively.

Model and method. We consider the planar square Ising and Heisenberg periodized $L \times L$ site lattices with the nearest neighbor of the results obtained for a single mode interaction. Energy of the lattice spin configuration s takes the form:

$$E(s) = -J \sum_{\langle ij \rangle} (s_i, s_j), \tag{2}$$

where $(.,.)$ is a scalar product, the sum $\langle .. \rangle$ runs over nearest-neighboring sites i, j, and $J > 0$. For the Ising model s_i takes values ± 1, and for the Heisenberg case s_i is a three-component vector with $\|s_i\| = 1$.

The order parameter defined as $\eta(s) = N^{-1} \sum_i s_i$ is a three-component (single-component) vector for the Heisenberg (Ising) lattice. We define the Landau free energy:

$$F_L(\eta) = -\frac{1}{\beta} \ln \int_{\eta(s)=\eta} e^{-\beta E(s)} d^N s, \tag{3}$$

where $N = L^2$ is the number of sites. The integration (summation in the Ising case) goes over all these states with the order parameter equal to η.

In the following we consider the system (2) placed in the external field h. The energy of such a system reads:

$$E_h(s) = -J \sum_{\langle ij \rangle} (s_i, s_j) - \sum_i (h, s_i). \tag{4}$$

The partition function in the external field equals:

$$Z_h = \int e^{-\beta [F_L(\eta) - N(\eta, h)]} d\eta. \tag{5}$$

Mean-field approach. The main idea of the MFT-like methods is to replace the system (4) with a noninteracting one, placed in the effective field $\tilde{h}$. The energy of the noninteracting ensemble reads:

$$E_{\mathrm{MFT}} = -\sum_i (\tilde{h}, s_i), \; \tilde{h} = h + 4J\eta. \tag{6}$$

The noninteracting ensemble allows for a simple solution for the order parameter. This leads to a self-consistent equation, relating the external field h and the order parameter η,

$$\eta = \eta(h + 4J\eta). \tag{7}$$

Typically the solution of self-consistent equation is presented as a dependence $\eta(h)$. For our purposes we are interested in the inverse function, $h(\eta)$. This function appears to be single valued and well defined within the entire range of η.

Now the estimation for Landau free energy can be obtained. In the thermodynamic limit the partition function (5) can be approximated by the saddle-point value at $\eta = \bar{\eta}$. The first derivative of the integrand at the saddle point vanishes, that is:

$$\frac{\partial F_L}{\partial \eta}(\bar{\eta}) = Nh. \tag{8}$$

We substitute the dependence $h(\eta)$, defined from the Eq. (7), to the right-hand side of the latter formula. After that, the value of the antiderivative can be found by the straightforward integration:

$$F_L(\eta) = N \int_{|\bar{\eta}|<\eta} h(\bar{\eta}) d\bar{\eta}. \tag{9}$$

In the case of the Ising lattice, all calculations can be performed analytically. The relation between the external field and the order parameter takes the form $h = \frac{1}{\beta}[\operatorname{atanh} \eta - 4J\beta\eta]$. Landau free energy is equal to:

$$F_L(\eta) = \frac{N}{\beta} \left(\frac{1}{2} \ln (1 - \eta^2) + \eta \operatorname{atanh} \eta - 2J\eta^2 \right). \tag{10}$$

Fluctuating local field approximation. To introduce the fluctuation local field method, we write the partition function for the system (4) in the form

$$Z_h = \int d\nu \int e^{-\beta \left[E_h(s) + \frac{N}{2\lambda} \left(\frac{\lambda}{N} \sum_i s_i + h - \nu \right)^2 \right]} d^N s, \tag{11}$$

where the integration over the auxiliary variable ν is introduced. Likewise, the order parameter ν is a three- (single) component vector for the Heisenberg (Ising) system. As one can observe, the integration over ν leads, up to a prefactor, to the expression $Z_h = \int e^{-\beta E_h} d^N s$, corresponding to the partition function of (4).

That form of the partition function could be considered as an ensemble of the lattices placed in an external field. Interaction in these lattices is given by the expression:

$$\tilde{E}_h(s, \nu) = -\sum_i (\nu, s_i) + \frac{N(\nu - h)^2}{2\lambda} + \underbrace{\frac{\lambda}{2} \frac{\left(\sum_i s_i \right)^2}{N} - J \sum_{\langle ij \rangle} (s_i, s_j)}_{W}. \tag{12}$$

Compared to the system (2), the interaction between the spins includes now a long-range part $(\sum_i s_i)^2$. As one can observe, this part disfavors the spin ordering at the lattice.

One can formally integrate the partition function (11) over all the spin variables s_i:

$$Z_h = \int \tilde{Z}_h(\nu) d\nu = \int e^{-\beta F_{\lambda,h}(\nu)} d\nu. \tag{13}$$

The main idea behind the FLF approach is that the parameter λ can be at the particular value λ_0 taken in such a way that the free energy $F_{\lambda,h}$ can be calculated perturbatively. The series expansion is in powers of the spin-spin interaction part of (12), which is marked as W.

We choose such λ_0 that the new "artificial" long-range interaction $\propto (\sum_i s_i)^2$ compensates, on average, the term coming from the original Hamiltonian $\propto -\sum_{\langle ij \rangle} (s_i, s_j)$. At the mean-field level, each spin of the system (12) is subjected to the force $(\lambda \frac{N-1}{N} - 4J)\langle s \rangle$ from others. This suggests to take $\lambda_0 = \frac{4NJ}{N-1}$.

After choosing this value for λ_0, the thermodynamic perturbation theory [34] in powers of W can be used to calculate the approximation of $F_{\lambda_0,h}(\nu)$. In zeroth-order approximation, one deals with a noninteracting sites subjected to an external

field ν. Zeroth order gives:

$$F^0_{\lambda_0,h}(\nu) = -\frac{N}{\beta}\ln z_\nu + \frac{(N-1)(\nu-h)^2}{2J}. \tag{14}$$

The single-site partition function z_ν equals $z_\nu = 2\cosh\nu\beta$ and $z_\nu = 2\frac{\sinh\nu\beta}{\nu\beta}$ for the Ising and Heisenberg model, respectively.

Our choice of λ_0 leads to the vanished first-order correction, whereas the second-order gives:

$$F^2_{\lambda_0,h}(\nu) = -\frac{N}{\beta}\ln z_\nu + \frac{(N-1)(\nu-h)^2}{2J} + \underbrace{\frac{1}{2}\|g_\nu\|^2\sum_{i\neq j}\tilde{J}^2_{ij}}_{\langle W^2\rangle_{\mathrm{FLF}}}, \tag{15}$$

where $\|g_\nu\|^2 = \sum_{ij}(\frac{N^2}{\beta^2}\frac{\partial^2\ln z_\nu}{\partial\nu_i\partial\nu_j})^2$; the quantity $\tilde{J}_{ij}$ equals $J(1-\frac{4}{N-1})$ for the nearest neighbors and $-\frac{4J}{N-1}$ otherwise.

Free-energy flow. The partition function (11) could be expressed using the FLF in the following way:

$$Z_h = \int e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta, \tag{16}$$

where we introduce the new integration variable $\eta = \frac{\nu}{\lambda}$ and F_λ is free energy defined by (13) in the absence on external field $h = 0$. The reason we denote the integration variable by η is that the expression (16) can be seen as an extension of the formula (5) integrated in respect to the order parameter. These two formulas become identical at the limit $\lambda^{-1}\to 0$.

Let us consider a continuous change of λ^{-1} leaving Z_h invariant. This corresponds to certain flow of the function $F_\lambda(\eta)$. Our goal is to trace this flow between the point $\lambda^{-1} = \lambda_0^{-1}$, where we have the FLF result and $\lambda^{-1} = 0$. Knowledge of $F_\lambda(\eta)$ at the point $\lambda^{-1} = 0$ will give us the Landau free energy we are interested in.

Consider the infinitesimal shift $\lambda^{-1}\to\lambda^{-1}+\delta\lambda^{-1}$ and require that the partition function remains unchanged, so that $\delta Z_h = 0$. It gives:

$$\int(\partial_{\lambda^{-1}}F_\lambda)e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta = -\frac{Nh^2}{2}\int e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta. \tag{17}$$

To solve it, let us consider Schwinger-Dyson equations for the Z_h. Consider an infinitesimal shift of the integration variable $\eta\to\eta+\delta\eta$. This step should also preserve the partition function. Collecting the terms linear in $\delta\eta$, we obtain

$$\int\nabla F_\lambda\cdot e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta = Nh\int e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta, \tag{18}$$

where $\nabla = \frac{\partial}{\partial\eta}$ has three (one) components for the Heisenberg (Ising) model.

Expanding the second order in $\delta\eta$ gives:

$$\beta\int(\nabla F_\lambda - Nh)^2 e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta = -\int\Delta F_\lambda\cdot e^{-\beta[F_\lambda(\eta)-N(\eta,h)+\frac{N}{\lambda}\frac{h^2}{2}]}d\eta, \tag{19}$$

where $\Delta = (\nabla,\nabla)$ is the Laplace operator.

Expanding the parentheses in (19) and using the expressions (17) and (18), we obtain the equation

$$2\beta N(\partial_{\lambda^{-1}}F_\lambda) = (\Delta F_\lambda) - \beta(\nabla F_\lambda)^2. \tag{20}$$

This formula can be easily reformulated in terms of the density of states $g(\lambda^{-1},\eta) = e^{-\beta F_\lambda(\eta)}$, where it takes the form of the heat equation:

$$\partial_{\lambda^{-1}}g = \frac{1}{2\beta N}\Delta g. \tag{21}$$

Optimization problem. We deal with a Cauchy problem with the final condition given by FLF approximation:

$$\partial_{\lambda^{-1}}g(\lambda^{-1},\eta) = \frac{1}{2\beta N}\Delta g(\lambda^{-1},\eta)$$
$$g\big(\lambda_0^{-1},\eta\big) = e^{-\beta F_{\lambda_0}}. \tag{22}$$

It is important to observe that the FLF result F_{λ_0} describes the final state of the evolution under the heat equation. Modelling such a backward evolution is the ill-posed problem: Direct integration of (22) from $\lambda^{-1} = \lambda_0^{-1}$ to $\lambda^{-1} = 0$ appears to be very numerically unstable.

To get rid of possible instabilities, we introduce a finite-order polynomial approximation for the Landau free energy (1):

$$F_a(\eta) = a_0 + a_2\eta^2 + \cdots + a_p\eta^p. \tag{23}$$

Even polynomials of the order from $p = 4$ to 8 were used in practical calculations. For the Heisenberg system, this approximation was used within the range $|\eta|\leqslant 1$; outside this interval the density of states vanishes. For the Ising lattice, $F_a(\eta)$ was defined at the discrete grid $\eta = 0, \pm 2N^{-1}, \pm 4N^{-1}, \ldots, \pm 1$ (see the next section for details).

Given the initial density of states $e^{-\beta F_a}$, we solve the heat equation and compare the result for $g_a(\lambda_0^{-1},\eta)$ with the FLF prediction. The coefficients $a_0, a_2, \ldots$ are adjusted to minimize the tolerance $\|g_a(\lambda_0^{-1},\eta) - e^{-\beta F_{\lambda_0}(\eta)}\|$. A simple gradient-descent method was used to obtain the minimum.

Results. Here we consider the Ising and Heisenberg small ferromagnetic clusters of the size 4×4 and 6×6 with the interaction constant $J = 1$. For these systems, the reference data for the Landau free energy can be obtained numerically. In the case of the 4×4 Ising lattice, we used an exact enumeration; in other cases the Wang-Landau algorithm was employed to estimate the density of states.

For the Ising case the order parameter takes discrete values, and therefore the initial density of states could be expressed as

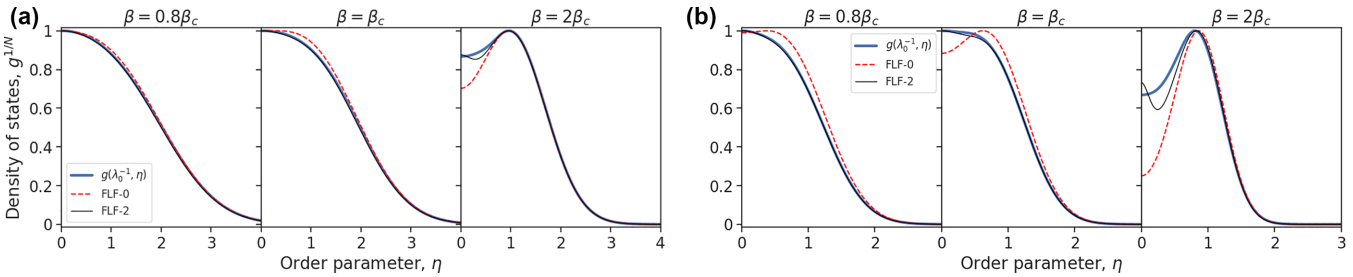

FIG. 1. Comparison of the evolved reference density of states $g(\lambda_0^{-1}, \eta)$ and the prediction by local fluctuating field method for the Ising (a) and Heisenberg (b) 6×6 periodic lattices. The curves labeled FLF-0 and FLF-2 refer to different orders of the FLF approximation.

delta functions sum. The evolved function reads:

$$g(0, \eta) = \sum_{\eta'} g(\eta')\delta(\eta - \eta')$$

$$\Downarrow$$

$$g(\lambda_0^{-1}, \eta) = \sqrt{\frac{N\beta}{4\pi\lambda_0}} \sum_{\eta'} g(\eta') \exp\left[-\frac{(\eta - \eta')^2 N\beta}{2\lambda_0}\right]. \tag{24}$$

For the Heisenberg lattice due to the spherical symmetry of the problem, the three-dimensional heat equation (22) can be reduced to a one-dimensional one by the replacement $g(\eta_r) \to \eta_r \cdot g(\eta_r)$, where η_r is a radial component of η. Since the states exist only for the order parameter $\eta \leqslant 1$, we suppose $g(0, \eta > 1) = 0$.

In Fig. 1, we present the evolved density of states $g(\lambda_0^{-1}, \eta)$. The FLF results are compared to the numerically exact reference data. The β_c refers to the critical inverse temperature predicted by the MFT. The predictions obtained by the fluctuation local field method are in a good agreement with the functions $g(\lambda_0^{-1}, \eta)$ obtained by evolving the initial condition $g(0, \eta)$. For relatively high temperatures ($\beta = 0.8\beta_c$), all curves almost coincide. In this case the FLF approximation perfectly captures the fluctuation arising in the system even at zeroth order. At low temperatures ($\beta = 2\beta_c$), the approximation also works well, but a visible difference appears between the orders of approximation. As expected, the second order gives a more accurate prediction, matching better with the density of states landscape.

In both cases the FLF method shows a qualitatively correct behavior for the $g(\eta)$ dependence. As β increases, the maximum position moves from the disordered state $\eta = 0$ to the polarized one with $\eta = 1$. The only qualitative artifact seen in the FLF-2 curves at low temperature is a local maximum at $\eta = 0$. It signals a divergence of the perturbation series at lower temperatures. However, within the range of temperatures considered in our calculation, this issue is not crucial.

Figure 2 shows the estimated Landau free energy obtained as a solution of the optimization problem. The results are compared with the numerical simulation, as well as with the MFT predictions. The MFT curves are calculated using the Eqs. (9) and (10). We used an expression (23) with degree $p = 4$ as an ansatz for the Ising model. For the Heisenberg model the Landau free energy curve shows a more complex behavior, so the $p = 4$ degree polynomial is not sufficient, and we increase its order to $p = 8$. The zeroth-order FLF and MFT curves show a similar accuracy. However, there are two quantitative issues about the MFT. First, it gives the results independent of the lattice size. Second, it predicts two local minima for the dependence $F(\eta)$ well below the transition point. However, such a picture is supported by the reference data for the Heisenberg model only. For the Ising case, $F(\eta)$ takes the minimal value at the edge of its domain, $\eta = \pm 1$. It should be also noted that we do not know a simple way to improve the MFT result. The FLF-0 curve has a dependence on the lattice size and reproduces the qualitative behavior of $F(\eta)$ in a correct way. The second-order correction greatly improves the FLF results for all types of lattices. An interesting feature of both cases is that for the Heisenberg model near the critical point $\beta = \beta_c$, the FLF-0 shows a minimum at $\eta \neq 0$, but the second-order FLF-2 eliminates this artifact.

Conclusion and outlook. Let us discuss the domain of applicability, limitations, and possible generalization of our method. First, in this paper we limited ourselves to small lattices. This is because we consider one mode of the fluctuation field ν, we can apply our results only to the systems with the homogeneous order parameter value, considering only small size systems. For larger systems the uniform dependency or the order parameter cannot catch all collective modes of fluctuations presented in the system. For medium-size lattices several Fourier modes η_k of the order parameter $\eta(r) = \sum_i \eta_k e^{ikr}$ should be estimated, corresponding to several modes of the fluctuating local field $\nu(r) = \sum_i \nu_k e^{ikr}$ [29]. Such a generalization of the formalism looks straightforward but makes numerical simulation harder.

In the most general case including infinite lattices, it is necessary to take into account the heterogeneity of the order parameter value $\eta(r)$ by switching from the Landau theory (1) to the Ginzburg-Landau functional [35]. To construct the Ginzburg-Landau functional, one basically should integrate over the high-energy degrees of freedom leaving only the variables related to the long-range fluctuations of the order parameter. This procedure can be carried out using the so-called cluster methods or coarse-grained modeling [22,23,36,37]. The key ingredient of this approach resembles the study presented in our paper—one performs calculations for a small lattice, called a cluster. The obtained collective properties of the cluster are later propagated to a large system. Thus the short-range phenomena are taken into account while solving the cluster model, and the entire system is described using the collective (coarse-grained) variables. In particular, constructing a Ginzburg-Landau functional, as well as coarse-

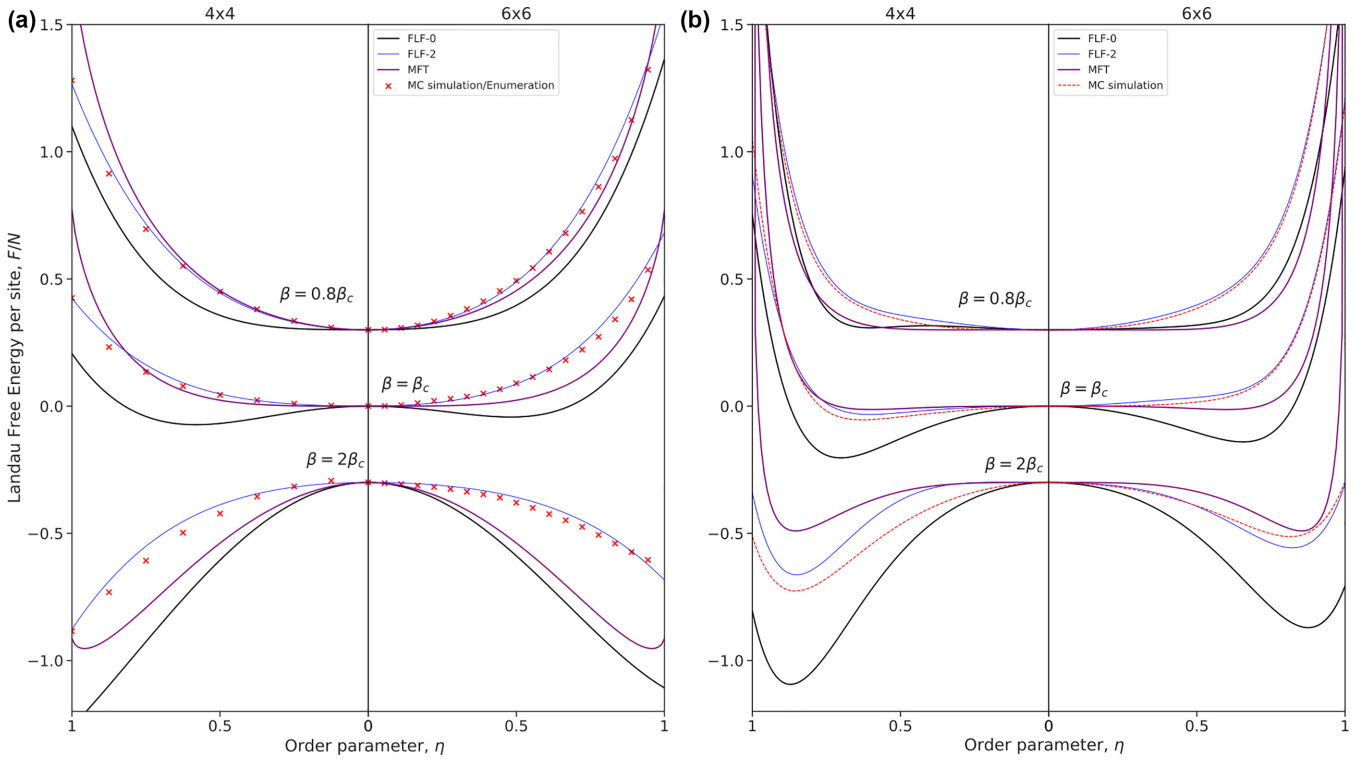

FIG. 2. Landau free energy obtained by the optimization procedure for the Ising (a) and Heisenberg (b) 4×4, 6×6 periodic lattices. The resulting curves are compared with the values obtained by numerical simulation. For better visualization, the curves are shifted by a constant for different temperatures.

grained equations of lattice motion, requires finding the Landau free energy of a cluster.

Since the fluctuation local field formalism allows us to calculate thermodynamical values such as free energy, magnetization [29], and Landau free energy, it could be also applied as a cluster solver for coarse-grained studies [38–40]. This makes possible extension of the present approach to fermionic systems particularly important, because it would contribute *ab initio* to computation, e.g., dynamics of large molecules [38,41].

In conclusion, we applied the fluctuation local field method to calculate Landau free energy landscape for the classical Heisenberg and Ising small periodical lattices. Our approach establishes an unambiguous relationship between the Landau free energy and the equations of the fluctuating local field method. We propose a way to reduce an arising ill-posed backward Cauchy problem for the heat equation to a minimization problem. This way, we formulate a controllable series of approximations for the Landau free energy of small systems. The scheme is benchmarked by a comparison with the results obtained by the numerically exact simulations.

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