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Asymptotic Behavior of Fluctuations for the 1D Ising Model in Zero-Temperature Limit

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Fluctuation of the average spin for one-dimensional Ising spins with nearest neighbor interactions are studied. The distribution function for the average spin is calculated for a finite volume, finite temperature, and finite magnetic field. As the volume increases and the temperature diminishes at zero magnetic field, there are two limits in which the probability distribution shows quite different behaviors: in the thermodynamic limit as the volume goes to infinity for finite temperature, small deviations of the fluctuations are described by a Gaussian distribution, and in the limit as the temperature vanishes for a finite volume, the ground states are realized with probability one. The crossover between these limits is analyzed via a ratio of the correlation length to the volume. The helix–coil transition in a polypeptide is discussed as an application.

KEY WORDS: Fluctuations; 1D Ising model; exact results; distribution function; zero-temperature limit; first-order phase transition; helix–coil transition.

1. INTRODUCTION

A one-dimensional Ising model with short-range interactions undergoes no phase transition.[1–3] The free energy is analytic for finite temperature T and a magnetic field h. As the temperature decreases at $h=0$, correlations between spins extend over larger distances and short-range order of spin develops. In the limit as the temperature vanishes, for a finite system the correlations extend to the whole of the system, while the correlation length ξ increases toward infinity for an infinite system. Then spin fluctuations are definitely affected by boundary conditions, and spontaneous magnetization may occur. Indeed, it has been found that a finite-size scaling law for a first-order phase transition holds in the vicinity of the point $T=0$ and

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$h=0$.[4] Recently, Schonmann and Tanaka showed that in the limit $N \to \infty$ and $T \to 0$ at $h=0$, the one-dimensional nearest neighbor ferromagnetic Ising (1DNNFI) model with free boundary conditions presents a sharp transition between two different regimes[5]: the probability distribution of an average spin is described by the discrete measure concentrated on the numbers ± 1 for $\xi \gg N$, the normal distribution with a vanishing expectation value and a variance of order N^{-1} for $\xi \ll N$, and the limiting distribution which has a discrete and an absolutely continuous part, at the transition point $\xi = N$, where $\xi = e^{2\beta J}$ is an asymptotic form of the correlation length for the corresponding infinite system, and β and J are the inverse temperature and the interaction strength, respectively. For the description of the transition, they did not use the parameter[4] $y \equiv Ne^{-2\beta J}$ and actually used the parameter $\alpha \equiv (2\beta J)^{-1} \ln N$, which leads to the limit $y \to \infty$ for $0<\alpha<1$, to $y=1$ at $\alpha=1$, and to the limit $y \to 0$ for $\alpha > 1$ as N increases toward infinity. Therefore, they could not give a complete description of the crossover from the limiting distribution as y goes to infinity to that as y vanishes. The absolutely continuous part of the distribution at $\alpha = 1$ has not been written in an analytical form also. In this paper, we will study fluctuations of the average spin for the 1DNNFI system in Gibbs ensembles and obtain an analytical form of the distribution.

The 1DNNFI model finds many applications to, for example, polypeptides for the helix–coil transition, polymer chains with adsorption along the chain, two-level Markov chains, and so on.[6–9] For a bulk system thermodynamic properties as $T \to 0$ are obtained by taking the thermodynamic limit $N \to \infty$ first and then the limit $T \to 0$.[10] Since the free energy for the 1DNNFI system is analytic, the asymptotic distribution of an average spin can be described by the Legendre transform of the free energy with respect to a magnetic field. However, there are sometimes the cases that the correlation length goes beyond the length of a polypeptide for the helix–coil transition or of a polymer chain for the adsorption along the chain. In these cases, the large-deviation theory is invalid, so that the entropy function (or the asymptotic distribution function) cannot be derived from the free energy by Legendre transformation.[3] Investigating the fraction of helical amino acids for the helix–coil transition and the coverage of adsorption sites for the adsorption along the chain, we are interested in its probability distribution as well as its expectation value and its variance. Hence, it is worthwhile to calculate the probability distribution of an average spin for the 1DNNFI system with a finite volume. As far as I know, this calculation has not yet been done.

Critical phenomena on the band-splitting bifurcation of a chaotic dynamical system can be studied in terms of a two-level Markov chain.[9] Determined via observing a chaotic orbit for a finite time n, a probability for a point to be found on one side of two bands (or states) fluctuates. In the vicinity of a bifurcation point, the fluctuations of a probability distribute in the same form as those of an average spin for the 1DNNFI system in the limit $N \to \infty$ and $T \to 0$.[11] As a controlled parameter approaches the bifurcation point, the transition probability ε from one band (or state) to the other becomes smaller and the correlation time τ increases with $\tau \propto \varepsilon^{-1}$. The asymptotic behavior of the fluctuations of a probability for n and $\tau \gg 1$ has been investigated in numerical simulations.[9,12] In order to get asymptotic behaviors for $n \gg \tau \gg 1$, one must expend more CPU time in numerical calculations than to get those for $\tau \gtrsim n \gg 1$. However, the asymptotic behavior of the fluctuations for $\tau \gtrsim n \gg 1$ has not been studied, because of the absence of theory, while the numerical results for $n \gg \tau \gg 1$ are in good agreement with the theoretical results derived from the Legendre transform of the free energy for the 1DNNDI system.[9,12] For the study of critical phenomena on the band-splitting bifurcation, the results in this paper are useful not only for $n \gg \tau \gg 1$, but also for $1 \ll n \lesssim \tau$.

Section 2 gives a brief review and some definitions for the 1DNNFI system with periodic boundary conditions. In Section 3 we perform an exact calculation in the cluster expansion of the partition function. We obtain an analytical form of the distribution function for the average spin. The distribution function for the number of cluster surfaces is also calculated. In Section 4 we investigate the asymptotic behavior of the distribution functions for the average spin and the number of cluster surfaces in the limit as the volume goes to infinity and the temperature vanishes. Since an asymptotic form of the distribution function for the average spin is analytically obtained, we have a complete description of the crossover from the limiting distribution in the thermodynamic limit to that at the zero temperature. In Section 5 we discuss the helix–coil transition in a polypeptide consisting of N amino acid residues. We find that fluctuations of the fraction of helical amino acids for $N \sim 10^2$ show qualitatively different behaviors from those for $N \gg 10^2$: the helix–coil transition for $N \sim 10^2$ is analogous to the first-order phase transition, while it is the well-known one for $N \gg 10^2$. In appendices the asymptotic behavior of the distribution function for the average spin is investigated not only in ferromagnetic cases with different boundary conditions, but also in an antiferromagnetic case with periodic boundary conditions as the volume goes to infinity and the temperature vanishes.

2. DEFINITIONS

We consider a chain of Ising spins $\{\sigma\} \equiv (\sigma_1 \sigma_1 \cdots \sigma_N)$ with nearest neighbor interactions J. The Hamiltonian of the chain is written as

$$H(\{\sigma\}) = -J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} - h \sum_{i=1}^{N} \sigma_i \tag{2.1}$$

with suitable boundary conditions, where σ_i are Ising spins ($\sigma_i = \pm 1$). The corresponding Gibbs measure at inverse temperature β is given by

$$\rho_N(\{\sigma\}; \beta, h) = [\Xi_N(\beta, h)]^{-1} \exp[-\beta H(\{\sigma\})] \tag{2.2}$$

where

$$\Xi_N(\beta, h) = \sum_{\{\sigma\}} \exp[-\beta H(\{\sigma\})] \tag{2.3}$$

The partition function (2.3) can be written in terms of a 2×2 transfer matrix whose eigenvalues are

$$\lambda_{\pm} = e^{\beta J}\{\cosh(\beta h) \pm [\sinh^2(\beta h) + e^{-4\beta J}]^{1/2}\} \tag{2.4}$$

In the thermodynamic limit, the free energy $G_\infty(\beta, J)$ for finite temperature is independent of boundary conditions, given by

$$\begin{aligned} G_\infty(\beta, h) &\equiv -\lim_{N \to \infty} \frac{1}{N\beta} \ln \Xi_N \\ &= -\beta^{-1} \ln \lambda_+ \end{aligned} \tag{2.5}$$

For a spin configuration $\{\sigma\}$, the magnetization per site (i.e., the average spin) is given by

$$m(\{\sigma\}) \equiv \frac{1}{N} \sum_{i=1}^{N} \sigma_i \tag{2.6}$$

Now, we write

$$D_N \equiv \left\{ \frac{j}{N} \mid j = -N, -N+2, \ldots, N-2, N \right\} \tag{2.7}$$

Let $P_N(\mu; \beta)$ denote the probability that $m(\{\sigma\})$ takes a value $\mu \in D_N$ at $h = 0$. The Landau free energy ψ_N and the entropy function s_N are defined on D_N as

$$\psi_N(\mu; \beta, h) \equiv -\frac{1}{N\beta} \ln \left[\sum_{\{\sigma\}} e^{-\beta H(\{\sigma\})} \delta_\mu(m(\{\sigma\})) \right] \tag{2.8}$$

$$s_N(\mu; \beta) \equiv \frac{1}{N} \ln P_N(\mu; \beta) \tag{2.9}$$

where $\delta_\mu(x) = 1$ for $x = \mu$, and 0 for $x \neq \mu$. The partition function (2.3) can be written as

$$\Xi_N(\beta, h) = \sum_{\mu \in D_N} \exp[-N\beta\psi_N(\mu; \beta, h)] \tag{2.10a}$$

$$= \Xi_N(\beta, h=0) \sum_{\mu \in D_N} e^{N\beta\mu h} P_N(\mu; \beta) \tag{2.10b}$$

As N goes to infinity for $0 < \beta < \infty$, the ψ_N and s_N converge pointwise to continuous functions ψ_∞ and s_∞ on the interval $D_\infty \equiv [-1, +1]$, respectively.[3] For $N \gg 1$, we can use maximum term approximations in (2.10). Then it turns out that

$$G_\infty(\beta, h) = \min_\mu \psi_\infty(\mu; \beta, h) \tag{2.11a}$$

$$= G_\infty(\beta, h=0) - \max_\mu\{\mu h + \beta^{-1} s_\infty(\mu; \beta)\} \tag{2.11b}$$

Since $G_\infty(\beta, h)$ is analytic for $0 < \beta < \infty$ and $|h| < \infty$, $s_\infty(\mu, \beta)$ and $\psi_\infty(\mu; \beta, h)$ can be obtained by using the Legendre transformation. Fluctuations of the average spin can be characterized by the entropy function $s_\infty(\mu, \beta)$. The correlation length of spins can be written as

$$\xi(T) = [\ln(\lambda_+/\lambda_-)]^{-1} \tag{2.12}$$

In the limit $\beta \to \infty$ the eigenvalues (2.4) are degenerate at $h = 0$, and $\xi(T)$ diverges exponentially. Thus, the free energy $G_\infty(\beta, h)$ is nonanalytic at $T = 0$ and $h = 0$.[2] As β and N go to infinity, the fluctuations show different asymptotic behaviors between the cases $\xi(T) \gtrsim N$ and $\xi(T) \ll N$. For $\xi \ll N$ we can obtain the asymptotic form of $s_N(\mu; \beta)$ from $G_\infty(\beta, h)$. For $\xi(T) \gtrsim N$ the asymptotic behaviors are affected by boundary conditions, so that the free energy $G_\infty(\beta, h)$ cannot give true information about the fluctuations. However, it seems that the calculation of $s_N(\mu; \beta)$ is a hard task, using the transfer matrix method for calculating the partition function. In the next section, a cluster expansion method will be given to calculate $\Xi_N(\beta, h)$ and $P_N(\mu; \beta)$.

3. CLUSTER EXPANSION[2]

For simplicity, we assume periodic boundary conditions, $\sigma_{N+1} = \sigma_1$, in this section. Other cases with different boundary conditions are discussed in appendices.

[2] During the final stage of preparation of this manuscript I found out that some of the arguments in this section are the same as in the original work of E. Ising. See refs. 15.

A configuration $\{\sigma\}$ of N spins is completely specified by a linear sequence of alternating clusters of spins up ($\sigma_i = +1$) and those of spins down ($\sigma_i = -1$). The position of the boundary between adjacent clusters is represented by an index i that gives $\sigma_i \sigma_{i+1} = -1$. The symmetry of the periodic boundary conditions yields that the number of these boundaries is even. Let us consider a configuration $\{\sigma\}$ which consists of k clusters of spins up; we write $k=0$ if all spins are up or down. Assume that $2k$ indices labeling the boundaries are given in order of magnitude by[5]

$$1 \leqslant j_1 < j_2 < \cdots < j_{2k} \leqslant N \qquad (k \neq 0) \tag{3.1}$$

First we consider a case of $\sigma_1 = +1$. The numbers of spins up and of spins down are given by

$$\begin{aligned} N_+(\{\sigma\}) &= j_1 + (j_3 - j_2) + \cdots + (N - j_{2k}) \\ N_-(\{\sigma\}) &= (j_2 - j_1) + (j_4 - j_3) + \cdots + (j_{2k} - j_{2k-1}) \end{aligned} \tag{3.2}$$

respectively. The total magnetization can be written as

$$Nm(\{\sigma\}) = N_+(\{\sigma\}) - N_-(\{\sigma\}) \tag{3.3}$$

where $m(\{\sigma\})$ is the average spin per site. From (3.2) it follows that

$$N_\pm(\{\sigma\}) = \frac{N}{2}[1 \pm m(\{\sigma\})] \tag{3.4}$$

A statistical weight of the configuration (3.1) is completely determined by the number of clusters and the value of the average spin, not depending on details of the configuration.

Let us calculate the total number of the configurations for which the average spin takes a value $\mu \in D_N$. As $\sigma_1 = +1$, we have $\sigma_N = -1$ if $j_{2k} = N$, and $\sigma_N = +1$ if $j_{2k} < N$. Assume $j_{2k} = N$. The number of combinations that N_+ spins up are divided into k blocks is

$$\binom{N_+ - 1}{k - 1}$$

Similarly, the number of combinations that N_- spins down are divided into k blocks is

$$\binom{N_- - 1}{k - 1}$$

Therefore, the number of the configurations with k clusters of spins up is given by

$$\binom{N_+ - 1}{k-1}\binom{N_- - 1}{k-1} \qquad \text{for} \quad j_{2k} = N \quad \text{and} \quad \sigma_1 = +1 \tag{3.5a}$$

On account of the fact that σ_1 and σ_N belong to the same cluster for $j_{2k} < N$, it follows that the number of the configurations with k clusters of spins up is

$$\binom{N_+ - 1}{k}\binom{N_- - 1}{k-1} \qquad \text{for} \quad j_{2k} < N \quad \text{and} \quad \sigma_1 = +1 \tag{3.5b}$$

Hence, the number of the configurations with k clusters of spins up and $m(\{\sigma\}) = \mu$ for $\mu \in D_N$ can be written as

$$\frac{[N(1+\mu)/2]!}{k!\,[N(1+\mu)/2-k]!}\,\frac{[N(1-\mu)/2-1]!}{(k-1)!\,[N(1-\mu)/2-k]!} \tag{3.6}$$

From a symmetry argument for $\sigma_1 = -1$ we immediately obtain the number of the corresponding configurations. The total number of these configurations is given by

$$\begin{aligned} N_{2k}(\mu) &= \frac{Nk}{(N/2)^2(1-\mu^2)}\,\frac{[N(1+\mu)/2]!}{k!\,[N(1+\mu)/2-k]!}\,\frac{[N(1-\mu)/2]!}{k!\,[N(1-\mu)/2-k]!} \\ &\qquad \text{for} \quad k \geqslant 1 \\ &= \delta_1(\mu) + \delta_{-1}(\mu) \qquad \text{for} \quad k = 0 \end{aligned} \tag{3.7}$$

The whole contribution of the configurations to the partition function is

$$W_{2k}(\mu) = N_{2k}(\mu)\,e^{N(\beta + \mu h)}e^{-4k\beta J} \qquad \text{for} \quad k \geqslant 0 \tag{3.8}$$

Therefore we can write the partition function (2.3) in the cluster expansion[6]

$$\Xi_N(\beta, h) = \sum_{\mu \in D_N} \{W_0(\mu) + W_2(\mu) + W_4(\mu) + \cdots\} \tag{3.9}$$

The distribution function $P_N(\mu; \beta, h)$ and the Landau free energy $\psi_N(\mu; \beta, h)$ can be written as

$$P_N(\mu; \beta, h) = \left[\sum_{\mu \in D_N}\sum_{k=0}^{k_0} N_{2k}(\mu)e^{-4k\beta J}e^{N\beta\mu h}\right]^{-1}\sum_{k=0}^{k_0} N_{2k}(\mu)e^{-4k\beta J}e^{N\beta\mu h} \tag{3.10}$$

$$\psi_N(\mu; \beta, h) = -(J + \mu h) - \frac{1}{N\beta}\ln\left[\sum_{k=0}^{k_0} N_{2k}(\mu)e^{-4k\beta J}\right] \tag{3.11}$$

where $k_0 \equiv N(1-|\mu|)/2$. Fluctuations of the number of cluster surfaces (i.e., boundaries between spins up and spins down) are described by the distribution functions

$$\Theta_N(2k; \beta, h) = [\Xi_N(\beta, h)]^{-1} \sum_{\mu \in D_N} W_{2k}(\mu) \tag{3.12a}$$

$$\vartheta_N(2k; \mu, \beta) = \left[\sum_{k=0}^{k_0} N_{2k}(\mu) e^{-4k\beta J}\right]^{-1} N_{2k}(\mu) e^{-4k\beta J} \tag{3.12b}$$

Since the ratio $W_{2(k+1)}(\mu)/W_{2k}(\mu)$ monotonically decreases for $1 \leqslant k \leqslant k_0$, the number of cluster surfaces under the constraint $m(\{\sigma\}) = \mu$ is most probable at the value

$$2k_N(\mu) = \frac{z^2}{1 + Ne^{-4\beta J} + [(1 + Ne^{-4\beta J})^2 + z^2(1 - e^{-4\beta J})]^{1/2}} \tag{3.13}$$

where we wrote

$$z \equiv Ne^{-2\beta J}(1-\mu^2)^{1/2} \tag{3.14}$$

4. ASYMPTOTIC BEHAVIORS FOR $N \gg 1$

The results obtained in the previous section are evaluated in the limit as the volume goes to infinity and the temperature vanishes.

4.1. Finite Temperature

Let us derive the free energy (2.5) from the partition function (3.9). As N goes to infinity, Eq. (3.13) gives $k_N(\mu) \sim O(N)$ for $|\mu| < 1$. We have

$$\begin{aligned} x_\infty &\equiv \lim_{N \to \infty} \frac{2k_N}{N} \\ &= \{[1 + (1-\mu^2)(e^{4\beta J} - 1)]^{1/2} - 1\}/(e^{4\beta J} - 1) \qquad \text{for} \quad |\mu| < 1 \end{aligned} \tag{4.1}$$

In order to evaluate Eq. (3.11) in the thermodynamic limit we use Stirling's approximations in (3.7) and maximum value approximations in the summation of k. Then it follows that

$$\psi_\infty(\beta; \mu, h) = -J(1 - 2x_\infty) - \mu h + \beta^{-1}[K(x_\infty; \mu) - K(0; \mu)] \tag{4.2}$$

where we wrote

$$K(x; \mu) \equiv x \ln x + \tfrac{1}{2}(1 + \mu - x) \ln(1 + \mu - x) + \tfrac{1}{2}(1 - \mu - x) \ln(1 - \mu - x) \tag{4.3}$$

After some calculations we can write the entropy function (2.9) as

$$\begin{aligned} s_\infty(\mu, \beta) = &\ln\{[1+(1-\mu^2)(e^{4\beta J}-1)]^{1/2}+1\} \\ &-\mu \ln\{[1+(1-\mu^2)(e^{4\beta J}-1)]^{1/2}+\mu\} \\ &-\tfrac{1}{2}(1-\mu)\ln(1-\mu^2) - 2\beta J(1-\mu) - \ln(1+e^{-2\beta J}) \end{aligned} \tag{4.4}$$

and see that the large-deviation theory (2.11) holds.[3] Equation (4.4) can be directly obtained from the Legendre transformation of $G_\infty(\beta, h)$ with respect to h.[13]

Let us consider fluctuations of the number of cluster surfaces.[6] Large deviations of these fluctuations are characterized by

$$\phi(x) \equiv \lim_{N\to\infty} \frac{1}{N} \ln \Theta_N(2k = Nx; \beta, h) \tag{4.5a}$$

$$\phi_\mu(x) \equiv \lim_{N\to\infty} \frac{1}{N} \ln \vartheta_N(2k = Nx; \mu, \beta) \tag{4.5b}$$

Since $2k_N(\mu) = Nx_\infty$ in the thermodynamic limit, $\phi_\mu(x)$ takes the maximum value $\phi_\mu(x) = 0$ at $x = x_\infty$. Indeed, we can write

$$\phi_\mu(x) = 2\beta J(x_\infty - x) + K(x_\infty; \mu) - K(x; \mu) \tag{4.6}$$

The substitution of a maximum value approximation for the summation of μ in (3.12a) leads to

$$\phi(x) = \beta J(1-2x) + \beta\mu_* h + K(0; \mu_*) - K(x; \mu_*) - \ln \lambda_+ \tag{4.7a}$$

where we wrote

$$\mu_* \equiv \frac{2(1-x)\sinh(\beta h)}{x\cosh(\beta h) + [x^2 + (2-x)^2 \sinh^2(\beta h)]^{1/2}} \tag{4.7b}$$

The most probable value of the density of cluster surfaces is given by

$$x = x_* \equiv \frac{1}{e^{4\beta J}-1}\left[\frac{\cosh(\beta h)}{[\sinh^2(\beta h) + e^{-4\beta J}]^{1/2}} - 1\right] \tag{4.8}$$

at which the $\phi(x)$ is maximum.

4.2. In the Limit $T \to 0$

For $\xi(\tau) \ll N$ the thermodynamic limit must be taken first and then the limit $\beta \to \infty$ taken.[10] The most probable value of the density of cluster surfaces x_N becomes

$$x_\infty \simeq (1-\mu^2)^{1/2} e^{-2\beta J} \to 0 \tag{4.9}$$

in this limit. It means that as the temperature vanishes, the clusters grow and collapse and their number decreases exponentially in β. The entropy function (4.4) can be written as

$$s_\infty(\mu; \beta) \simeq e^{-2\beta J}[(1-\mu^2)^{1/2} - 1] + O(e^{-4\beta J}) \tag{4.10}$$

Therefore, it turns out that

$$\frac{dP_N(\mu; \beta, h=0)}{d\mu} \simeq \left(\frac{N}{2\pi}\right)^{1/2} \exp(-\beta J) \exp\{N[\exp(-2\beta J)][(1-\mu^2)^{1/2} - 1]\} \tag{4.11}$$

This asymptotic form of the distribution function is the same as obtained for a two-level Markov process by Fujisaka *et al.*[9] When β approaches infinity with a fixed N, the probability distribution (3.10) takes the following form:

$$\frac{dP_N(\mu; \beta \to \infty, h)}{d\mu} = \begin{cases} \delta(\mu - 1), & h > 0 \\ \frac{1}{2}[\delta(\mu-1) + \delta(\mu+1)], & h = 0 \\ \delta(\mu+1), & h < 0 \end{cases} \tag{4.12}$$

where we wrote $\delta(x-a) \equiv N\delta_a(x)$, which becomes a Dirac δ-function as $N \to \infty$. The ground state which brings out the alignment of all spins is realized with probability one. Hence, a different order of the limiting operation leads to a different limit.

Let us introduce the parameter

$$y \equiv Ne^{-2\beta J} \tag{4.13}$$

The asymptotic behavior of the fluctuations can be systematically described by taking the limit as N goes to infinity with a fixed y. First we consider the case of $h = 0$. The most probable value of the number of cluster surfaces is finite in this limit:

$$\lim_{\substack{N \to \infty \\ y \text{ fixed}}} 2k_N(\mu) = y(1-\mu^2)^{1/2} \tag{4.14}$$

Note that Eq. (4.14) gives the same result as Eq. (4.9). The W_{2k} for $k \lesssim O(y)$ can give finite contributions to the partition function (3.9). For $1 \leqslant k \ll N$, we can write

$$N_{2k}(\mu) \simeq N \frac{1}{k!\,(k-1)!} \left[\left(\frac{N}{2}\right)^2 (1-\mu^2)\right]^{k-1} \tag{4.15}$$

Therefore, we have

$$\sum_{k=1}^{k_0} N_{2k}(\mu) e^{-4k\beta J} \simeq N e^{-4\beta J} \sum_{k=0}^{\infty} \frac{1}{(k+1)!\,k!} \left[\left(\frac{y}{2}\right)^2 (1-\mu^2) \right]^k \tag{4.16a}$$

$$= d\mu\, y^2 z^{-1} I_1(z) \qquad \text{as} \quad N \to \infty \text{ with a fixed } y \tag{4.16b}$$

where z is given by Eq. (3.14) and $I_\nu(z)$ is a modified Bessel function of the first kind. Inserting (4.16) into (3.10), we obtain

$$\frac{dP_\infty(\mu; y, h=0)}{d\mu} = \left\{ \delta(\mu-1) + \delta(\mu+1) + \frac{y^2}{z} I_1(z) \right\} \Big/ 2\cosh y \tag{4.17}$$

The probability distribution (4.17) has prominent peaks at $\mu = \pm 1$ for $y \lesssim 1$ as shown in Fig. 1. Substituting the asymptotic form of $I_1(z)$ for $z \gg 1$ yields that

$$\frac{dP_\infty(\mu; y, h=0)}{d\mu} = [\exp(-y)][\delta(y-1) + \delta(\mu+1)] + \left(\frac{y}{2\pi}\right)^{1/2} (1-\mu^2)^{3/4} \exp\{y[(1-\mu^2)^{1/2} - 1]\} \tag{4.18}$$

As the first term is negligible for $y \gg 1$, Eq. (4.18) coincides with Eq. (4.11). Since the term of k clusters of spins up W_{2k} is proportional to y^{2k}, the

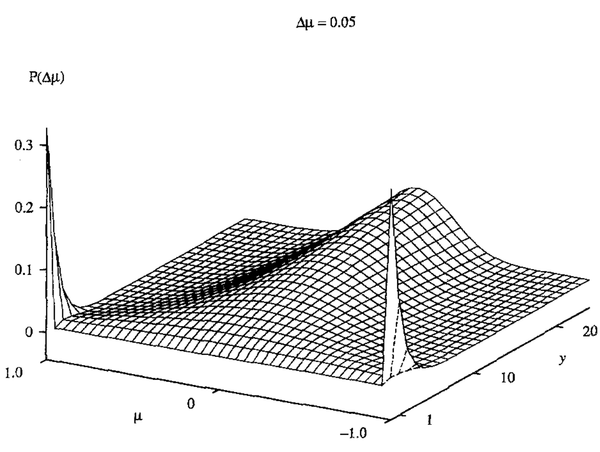


Fig. 1. Probability distribution $P(\mu; y, h=0)\,\Delta\mu$ with $\Delta\mu = 0.05$.

power series expansions for y of $\cosh y$ and $I_1(z)$ give the distribution functions $\Theta_\infty(k)$ and $\vartheta_\infty(k)$:

$$\Theta_\infty(2k; y, h=0) = \frac{y^{2k}}{(2k)!\cosh y} \qquad (k \geqslant 0) \tag{4.19a}$$

$$\vartheta_\infty(2k; \mu, y) = \frac{(z/2)^{2k-1}}{k!\,(k-1)!\,I_1(z)} \qquad (k \geqslant 1 \text{ and } |\mu| < 1) \tag{4.19b}$$

In the derivation of Eq. (4.19a) we have used

$$\sum_{\mu \in D_N} N_{2k}(\mu) \simeq \frac{2N^{2k}}{(2k)!} \qquad \text{for} \quad N \gg k$$

Note that the $\vartheta_\infty(2k; \mu, y)$ depends only on the variables k and z explicitly. Schonmann and Tanaka studied the distribution of an average spin and of the number of cluster surfaces at $y=1$ and $h=0$. Equations (4.17) and (4.19b) do not agree with their results.[5] This disagreement comes from difference of the boundary conditions. Some cases with different boundary conditions are discussed in Appendix A.

Let us consider the case of $h \neq 0$. Since the distribution function (4.12) is nonanalytic at $h=0$, we investigate the asymptotic behavior of the distribution functions (3.10) and (3.12a) in the following limit:

$$N \to \infty \qquad \text{with} \quad Ne^{-2\beta J} = y \quad \text{and} \quad N\beta h \equiv a \text{ fixed} \tag{4.20}$$

Using

$$\lim_{\substack{N \to \infty \\ y,\, a \text{ fixed}}} e^{-N\beta J} \Xi_N(\beta, h) = 2\cosh[(a^2+y^2)^{1/2}]$$

we can write

$$\frac{dP_\infty(\mu; y, a)}{d\mu} = \frac{e^a\delta(\mu-1) + e^{-a}\delta(\mu+1) + y^2 z^{-1} e^{\mu a} I_1(z)}{2\cosh[(a^2+y^2)^{1/2}]} \tag{4.21}$$

Inserting (4.15) into (3.8) and performing the integration of μ in (3.12a), we have

$$\Theta_\infty(2k; y, a) = \frac{1}{k!}\left(\frac{\pi a}{2}\right)^{1/2}\left(\frac{y^2}{2a}\right)^k I_{k-1/2}(a) \Big/ \cosh[(a^2+y^2)^{1/2}] \qquad (k \geqslant 0) \tag{4.22}$$

Note that the numerator of the lhs in (4.22) is obtained in the Neumann expansion of $\cosh[(a^2+y^2)^{1/2}]$.

5. DISCUSSION

We have studied the asymptotic behavior of fluctuations of an average spin for the 1DNNFI system as the volume increases toward infinity and the temperature vanishes. When the correlation length goes beyond the size of the system, the fluctuations are definitely affected by boundary conditions and are distributed in a form quite different from a Gaussian distribution. For example, in the case with free boundary conditions, the distribution function for the average spin has three peaks, two δ peaks at $\mu = \pm 1$ and one broad peak, for a zero magnetic field. See Fig. 2. A small magnetic field h brings out a big change of the mass for each δ peak. Hence the most probable value of an average spin changes discontinuously at $h = 0$. This is characteristic of a first-order phase transition. Similar behavior may be shown in fluctuations of the fraction of helical amino acids in a polypeptide for the helix–coil transition.

Let us consider a polypeptide consisting of N amino acid residues, each of which is assumed to be in a helical state (h) or coil state (c), depending on whether or not the NH group of the ith residue in question is hydrogen bonded to the CO group of the $(i-4)$th residue.[8] In the nearest-neighbor interaction model of Zimm and Bragg[7] the statistical weight matrix for the ith residue is given by

$$\begin{array}{cc} & \begin{array}{cc} \mathrm{h} & \mathrm{c} \end{array} \\ \begin{array}{c} \mathrm{h} \\ \mathrm{c} \end{array} & \begin{pmatrix} s & 1 \\ \sigma s & 1 \end{pmatrix} \end{array} \tag{5.1}$$

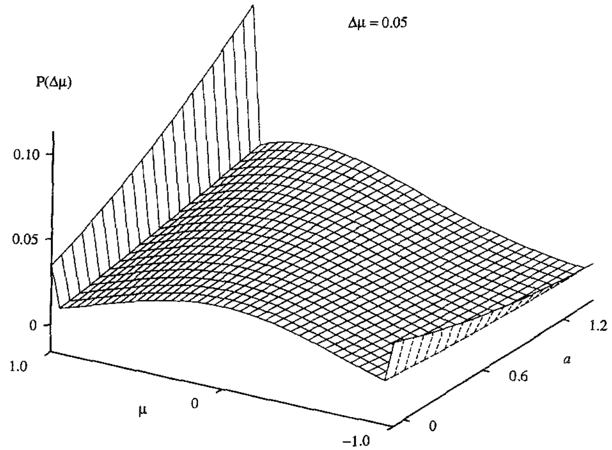


Fig. 2. Probability distribution $P(\mu; y, a)\,\Delta\mu$ with $\Delta\mu = 0.05$ at $y = 3.5$. The probability distribution for $a < 0$ can be obtained from the relation $P(\mu; y, a)\,\Delta\mu = P(-\mu; y, -a)\,\Delta\mu$.

The statistical weight σ describes the situation in which three consecutive residues have certain restricted, i.e., α-helical, conformation but no hydrogen bond. Usually the σ has a small value, such as $\sigma = 10^{-4}$. We assume that the first residue is always in the coil state and the last is free.[14] For the configurations that the polypeptide has k clusters of helical residues and N_h residues in the helical state, the total statistical weight can be written as

$$W_N(N_h; k) = \binom{N_c}{k}\binom{N_h - 1}{k-1} s^{N_h}\sigma^k \qquad \text{for} \quad k \neq 0 \tag{5.2}$$

where $N_h + N_c = N$. The fluctuations of the fraction of helical amino acids are described by the probability distribution

$$P_N(\theta \equiv N_h/N; s, \sigma) \equiv \sum_{k=0}^{k_0} W_N(\theta; k)/\Xi_N(s, \sigma) \tag{5.3}$$

where $\Xi_N(s, \sigma)$ is the partition function. Putting

$$a \equiv N(s-1)/2 \qquad \text{and} \qquad y \equiv N\sqrt{\sigma} \tag{5.4}$$

we can write

$$\Xi_\infty(a, y) = e^a[\cosh u - (a/u)\sinh u] \tag{5.5}$$

in the limit as N goes to infinity with fixed a and y, where $u \equiv (a^2 + y^2)^{1/2}$. Then we have

$$\frac{dP_\infty(\theta; a, y)}{d\theta} = \frac{e^{-a}\delta(\theta) + 2y^2z^{-1}(1-\theta)e^{(2\theta-1)a}I_1(z)}{\cosh u - (a/u)\sinh u} \tag{5.6}$$

with $z \equiv 2y[\theta(1-\theta)]^{1/2}$. Figure 3 shows the probability distributions (5.3) for $\sigma = 10^{-4}$ and $N = 200$ and 2000. For $N = 200$ the probability at $\theta = 0$ is dominant for $s < 1$ and becomes very small for $s > 1$ after a drastic change near $s = 1$. The probability distribution on the interval $0 < \theta < 1$ is rather flat for $s < 1$, has a very broad peak for $s \sim 1$, whose position moves from left to right and approaches $\theta = 1$ as s increases, and has a sharp peak near $\theta = 1$ for $s > 1$. Hence, the helix–coil transition for $N = 200$ is analogous to the first-order phase transition. For $N = 2000$ it seems that the probability distribution has always a single peak, which is very sharp when s is apart from the transition point $s = 1$ and becomes broad near the transition point. The peak position is at the point $\theta = 0$ for $s < 1$, moves rapidly from left to right near the transition point, and approaches $\theta = 1$ for $s > 1$, as s increases. Thus the helix–coil transition for $N = 2000$ is continuous and diffusive. Note that Eq. (5.6) gives an approximate probability for a finite N and in general not a correct one, so that the probability is not normalized. This is caused by using different types of approximations for the numerator and the denominator in Eq. (5.6). Indeed, the value of the probability is sensitive to the large-N approximation in the exponential part. The approximation Ξ_∞ deviates from Ξ_N by a multiplicative factor of $O(1)$ for $N \sim u^2$. Nevertheless, Eq. (5.6) still describes in qualitatively correct way the features of the probability distribution for the helix–coil transition, normalized by a suitable constant (see Fig. 4.)

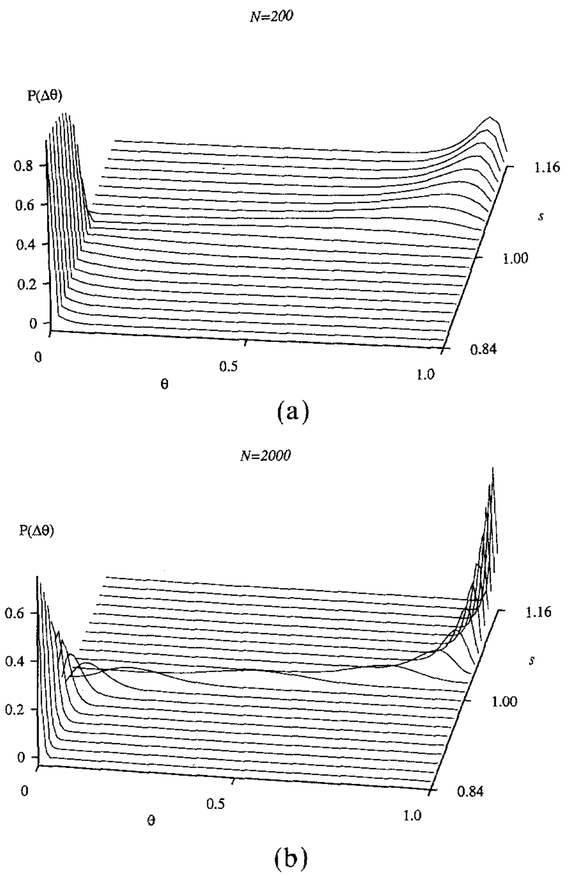


Fig. 3. Probability distribution $P(\theta; s, \sigma)\,\Delta\theta$ for (a) $N = 200$ and (b) $N = 2000$. Parameter values are $\sigma = 10^{-4}$ and $\Delta\theta = 0.02$ for $N = 200$ and $\Delta\theta = 0.01$ for $N = 2000$. As $s \simeq 1$, the $P_N(\theta; s, \sigma)\,\Delta\theta$ has two peaks for $N = 200$ and a single peak for $N = 2000$.

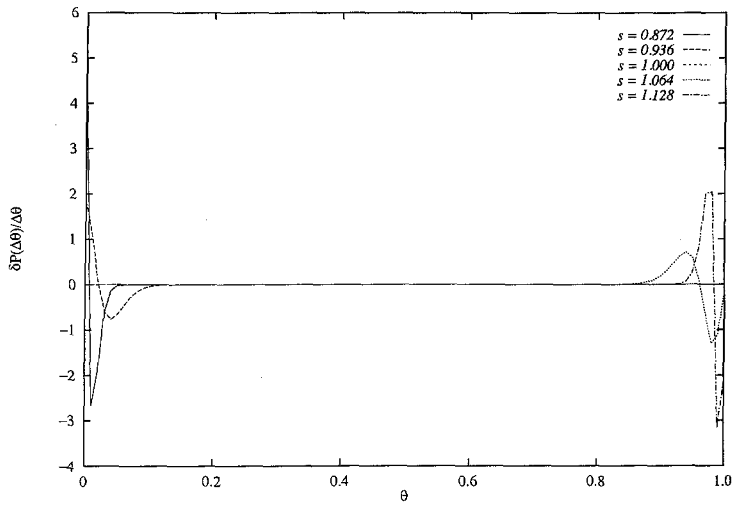


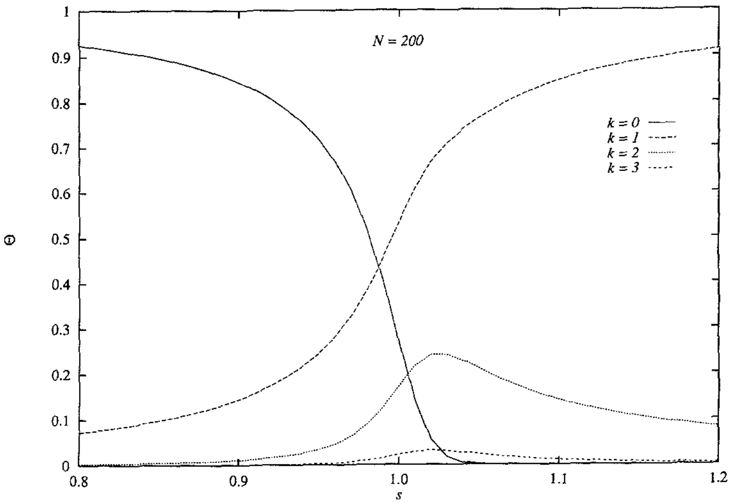
Fig. 4. Differences between the probability distributions (5.3) and (5.6) for $N=2000$ and $\sigma=10^{-4}$. Here $\delta P(\Delta\theta)\equiv P_N(\theta;s,\sigma)\,\Delta\theta-P_\infty(\theta;s,\sigma)\,\Delta\theta$, where $\Delta\theta=0.01$. The position of a peak for the $P_\infty(\theta;s,\sigma)\,\Delta\theta$ tends to shift slightly from that for the $P_N(\theta;s,\sigma)\,\Delta\theta$ to the right.

The distribution function for the number of helical clusters can be easily calculated from the power series expansion of the partition function for σ:

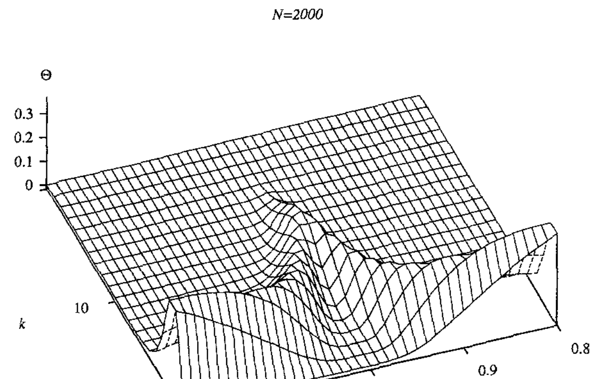
$$\Theta_N(k;s,\sigma)=\frac{1}{k!}\sigma^k\left[\frac{\partial^k}{\partial\sigma^k}\Xi_N(s,\sigma)\right]_{\sigma=0}\Big/\Xi_N(s,\sigma)$$

$$\simeq\frac{1}{k!}\left(\frac{\pi a}{2}\right)^{1/2}\left(\frac{y^2}{2a}\right)^k[I_{k-1/2}(a)-I_{k+1/2}(a)]\Big/e^{-a}\Xi_N(a,y) \qquad (5.7)$$

Figure 5 gives the probability distribution of the number of helical clusters in the cases $N=200$ and 2000. For $N\sqrt{\sigma}\lesssim 1$ $(N=200)$ we can expect that the polypeptide is in a random coil state with no helical cluster for $s<1$ and in a state with one helical cluster for $s>1$. Even near the transition point we have only one or two helical clusters. For $N\sqrt{\sigma}\gg 1$ $(N=2000)$ the number of helical clusters increases and the probability of a small number is negligible as s approaches the transition point. In conclusion, the helix–coil transition in a polypeptide with a large N of $O(\sigma^{-1/2})$ is qualitatively different from that found in the thermodynamic limit.



(a)



(b)

Fig. 5. Probability distribution $\Theta_N(k; s, \sigma)$ for (a) $N=200$ and (b) $N=2000$.

APPENDIX A. BOUNDARY CONDITIONS AND FLUCTUATIONS

We study fluctuations of an average spin for 1DNNDI systems with different boundary conditions. In the limit $N \to \infty$ with $Ne^{-2\beta J} = y$ fixed the distribution function for the average spin is strongly affected by boundary conditions, as the correlation length grows up to $O(N)$. We consider the Hamiltonian

$$H(\{\sigma\}) = -J \sum_{i=0}^{N} \sigma_i \sigma_{i+1} - h \sum_{i=1}^{N} \sigma_i \tag{A.1}$$

with the following boundary conditions: (1) $(++)$ boundary, $\sigma_0 = \sigma_{N+1} = +1$. (2) $(+-)$ boundary, $\sigma_0 = +1$ and $\sigma_{N+1} = -1$. (3) Free boundaries, $\sigma_0 = \sigma_{N+1} = 0$. (4) A finite chain embedded in an infinite chain. Using the transfer matrix

$$\mathbf{T} = \begin{pmatrix} e^{\beta(J+h)} & e^{\beta(-J+h)} \\ e^{-\beta(J+h)} & e^{\beta(J-h)} \end{pmatrix}$$

we get the partition functions

$$\begin{aligned} \Xi_N^{(++)}(\beta, h) &= e^{-\beta h}(S_{11} S_{11}^{-1} \lambda_+^{N+1} + S_{12} S_{21}^{-1} \lambda_-^{N+1}) \\ \Xi_N^{(\text{free})}(\beta, h) &= (S_{11} + S_{21})(S_{11}^{-1} e^{\beta h} + S_{12}^{-1} e^{-\beta h}) \lambda_+^{N-1} \\ &\quad + (S_{12} + S_{22})(S_{21}^{-1} e^{\beta h} + S_{22}^{-1} e^{-\beta h}) \lambda_-^{N-1} \end{aligned} \tag{A.2}$$

etc., where S_{ij} and S_{ij}^{-1} are elements of regular matrices such that

$$\mathbf{S}^{-1}\mathbf{T}\mathbf{S} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \quad \text{and} \quad \mathbf{S}^{-1}\mathbf{S} = \mathbf{S}\mathbf{S}^{-1} = \mathbf{1}$$

Here, the superscript on Ξ_N denotes the boundary conditions.

The whole of the statistical weights for configurations with $m(\{\sigma\}) = \mu$ and k clusters of spins down is given for $N \gg k$ by

$$W_{2k}^{(++)}(\mu) \simeq \frac{N}{2}(1+\mu)\frac{1}{k!\,(k-1)!}\left[\left(\frac{N}{2}\right)^2 (1-\mu^2)\right]^{k-1} e^{-4k\beta J} e^{(N+1)\beta J + N\beta\mu h} \tag{A.3a}$$

in the case (1), and

$$W_{2k-1}^{(+-)}(\mu) \simeq \frac{1}{[(k-1)!]^2}\left[\left(\frac{N}{2}\right)^2 (1-\mu^2)\right]^{k-1} e^{-2(2k-1)\beta J} e^{(N+1)\beta J + N\beta\mu h} \tag{A.3b}$$

in the case (2). In the limit (4.20) the distribution function (3.10) can be written as

$$
\begin{aligned}
\frac{dP_{\infty}^{(++)}(\mu; y, a)}{d\mu} &= \frac{e^{a}\delta(\mu-1)+(1+\mu)\,y^2(2z)^{-1}e^{\mu a}I_1(z)}{\cosh u+(a/u)\sinh u} \\
\frac{dP_{\infty}^{(+-)}(\mu; y, a)}{d\mu} &= \frac{e^{\mu a}I_0(z)}{(2/u)\sinh u} \\
\frac{dP_{\infty}^{(\mathrm{free})}(\mu; y, a)}{d\mu} &= \frac{e^{a}\delta(\mu-1)+e^{-a}\delta(\mu+1)+ye^{\mu a}I_0(z)+y^2z^{-1}e^{\mu a}I_1(z)}{2[\cosh u+(y/u)\sinh u]}
\end{aligned} \tag{A.4}
$$

where $u \equiv (a^2+y^2)^{1/2}$. In the case (4), the distribution function is given by

$$
\begin{aligned}
P_N^{(\mathrm{embed})}(\mu; \beta, h) = \lambda_+^{-(N+1)} \sum_k [&S_{11}S_{11}^{-1}e^{\beta h}W_{2k}^{(++)}(\mu)+S_{11}S_{12}^{-1}e^{-\beta h}W_{2k-1}^{(+-)}(\mu) \\
&+S_{21}S_{11}^{-1}e^{\beta h}W_{2k-1}^{(-+)}(\mu)+S_{21}S_{12}^{-1}e^{-\beta h}W_{2k}^{(--)}(\mu)]
\end{aligned} \tag{A.5}
$$

As the limit (4.20) is taken, Eq. (A.5) becomes

$$
\begin{aligned}
\frac{dP_{\infty}^{(\mathrm{embed})}(\mu; y, a)}{d\mu} = \frac{1}{2e^{u}}\Bigg[&\left(1+\frac{a}{u}\right)e^{a}\delta(\mu-1)+\left(1-\frac{a}{u}\right)e^{-a}\delta(\mu+1) \\
&+\frac{y^2}{u}e^{\mu a}I_0(z)+\left(1+\frac{\mu a}{u}\right)\frac{y^2}{z}e^{\mu a}I_1(z)\Bigg]
\end{aligned} \tag{A.6}
$$

Note that the coefficients $S_{i1}S_{1j}^{-1}$ in (A.5) cannot be replaced into $S_{i1}S_{1i}^{-1}S_{j1}S_{1j}^{-1}$ because the correlation between the spins on both ends of the embedded chain is strong.

It is easy to calculate the distribution function for the number of cluster surfaces. Expanding the numerators and denominators on the rhs of (A.4) into power series of y, we can write the distribution functions $\theta_{\infty}(k)$ and $\Theta_{\infty}(k)$ in the cases (1)–(3). We have, for example,

$$
\theta_{\infty}^{(+-)}(2k-1; \mu, y) = \frac{1}{[(k-1)!]^2}\left(\frac{z}{2}\right)^{2(k-1)}\Big/ I_0(z) \tag{A.7a}
$$

$$
\Theta_{\infty}^{(\mathrm{free})}(l; y, a) = \begin{cases} \dfrac{C}{k!}\left(\dfrac{\pi a}{2}\right)^{1/2}\left(\dfrac{y^2}{2a}\right)^{k} I_{k-1/2}(a) & \text{for } \; l=2k \\[2ex] \dfrac{C}{k!}\left(\dfrac{\pi a}{2}\right)^{1/2} y\left(\dfrac{y^2}{2a}\right)^{k} I_{k+1/2}(a) & \text{for } \; l=2k+1 \end{cases} \tag{A.7b}
$$

with $C^{-1} \equiv \cosh u + (y/u)\sinh u$. Note that $\Theta_{\infty}^{(\mathrm{free})}(l; y, a=0)$ gives a Poisson distribution, which agrees with the result of ref. 5. As the coefficients of W_k in (A.5) depend on y, we cannot use a bare expansion of the denominator on the rhs of (A.6) in the case (4). From (A.3), (A.5), and (A.7b), we can write

$$\Theta_{\infty}^{(\text{embed})}(l; y, a) = \begin{cases} \dfrac{1}{k!}\left(\dfrac{\pi a}{2}\right)^{1/2}\left(\dfrac{y^2}{2a}\right)^{k} e^{-u}\left[I_{k-1/2}(a)+\dfrac{a}{u}I_{k+1/2}(a)\right] & \text{for } l=2k \\ \dfrac{1}{k!}(2\pi a)^{1/2}\left(\dfrac{y^2}{2a}\right)^{k+1}\dfrac{1}{u}e^{-u}I_{k+1/2}(a) & \text{for } l=2k+1 \end{cases} \tag{A.8}$$

APPENDIX B. ANTIFERROMAGNETIC CASE ($J<0$)

We study the asymptotic behavior of the fluctuations of the average spin for the system (2.1) with $J<0$ as N and $\beta|J|$ go to infinity. The term $W_{2k}(\mu)$ at $k=k_N(\mu)$ is maximum in the cluster expansion (3.9). For N and $\beta|J| \gg 1$ we can write

$$\begin{aligned} 2(k_0-k_N) &\simeq N(1-|\mu|)^2(\mu^2+e^{-4\beta|J|})^{1/2}-|\mu|] \\ &\simeq \begin{cases} (2|\mu|)^{-1}(1-|\mu|)^2\, Ne^{-4\beta|J|} & \text{if } \ |\mu| \gg e^{-2|J|} \\ Ne^{-2\beta|J|}\{[(\mu e^{2\beta|J|})^2+1]^{1/2}-|\mu|\,e^{2\beta|J|}\} & \text{if } \ |\mu| \lesssim e^{2\beta|J|} \end{cases} \end{aligned} \tag{B.2}$$

i.e., k_N approaches k_0 exponentially as $\beta|J| \to \infty$ with fixed N. The main contributions to the partition function come from W_{2k} of small $j \equiv k_0-k$. The statistical weight (3.8) can be written as

$$W_{2k_0+2j}(\mu) \simeq B(\mu)\left(\frac{N|\mu|}{e}\right)^{N|\mu|}\frac{1}{(N|\mu|+j)!\,j!}\left(\frac{z}{2}\right)^{2j} e^{N\beta[(1-2|\mu|)|J|+\mu h]} \tag{B.2}$$

for N and $k_0 \gg j$, where the $B(\mu)$ and z are given by

$$B(\mu) \equiv \frac{2}{1+|\mu|}\left(\frac{1-\mu^2}{4\mu^2}\right)^{N|\mu|/2}\left(\frac{1+|\mu|}{1-|\mu|}\right)^{N/2} \tag{B.3a}$$

$$z \equiv (1-|\mu|)\, Ne^{-2\beta|J|} \tag{B.3b}$$

Inserting (B.2) into (3.10), we have

$$P_N(\mu; \beta, h) \propto B(\mu)\left(\frac{2N|\mu|}{ez}\right)^{N|\mu|} I_{N|\mu|}(z)\, e^{N\beta(-2|\mu J|+\mu h)} \tag{B.4}$$

for N and $\beta|J| \gg 1$. Using Stirling's approximations in (B.2), we can write Eq. (B.4) for $N|\mu| \gg 1$ as

$$P_N(\mu; \beta, h) \propto B(\mu) \exp\left[N\beta(-2|\mu J| + \mu h) + \frac{N(1-|\mu|)^2 e^{-4\beta|J|}}{4|\mu|}\right] \tag{B.5}$$

Inserting (B.5) into (2.9) gives the entropy function

$$\begin{aligned} s_N(\mu; \beta) \simeq & -2\beta|\mu J| - |\mu| \ln(2|\mu|) + \frac{1}{2}(1+|\mu|)\ln(1+|\mu|) \\ & -\frac{1}{2}(1-|\mu|)\ln(1-|\mu|) + \frac{(1-|\mu|)^2}{4|\mu|} e^{-4\beta|J|} - \ln(1+e^{-2\beta|J|}) \end{aligned} \tag{B.6}$$

which agrees with the Legendre transform of the free energy, given by Eq. (4.4),[13] for $|\mu| \gg e^{-2\beta|J|}$. Equation (B.6) is singular at $\mu = 0$, as is Eq. (4.4) in the limit $\beta|J| \to \infty$. Therefore, small deviations of the fluctuations are described by a non-Gaussian distribution. We set $y = Ne^{-2\beta|J|}$ and $l = N\mu$, and consider (B.4) in the limit $N \to \infty$ with fixed y and l. In this limit, we have the following:

$$B(\mu)\left(\frac{2N|\mu|}{ez}\right)^{N|\mu|} e^{-2N\beta|\mu J|} = 2\left(\frac{y}{2}\right)^{|l|}$$

$$\Xi_N(\beta, h) e^{-N\beta|J|} = \begin{cases} 2\cosh[y\cosh(\beta h)] & \text{for} \quad N = \text{even and } \beta h \sim O(1) \\ 2\sinh[y\cosh(\beta h)] & \text{for} \quad N = \text{odd and } \beta h \sim O(1) \end{cases}$$

Hence, we find that the small deviations for N and $\beta|J| \gg 1$ can be described by the probability distribution function

$$P_N(l; \beta, h) = \begin{cases} e^{l\beta h} I_{|l|}(y)/\cosh[y\cosh(\beta h)] & \text{if} \quad N \text{ and } l \text{ are even} \\ e^{l\beta h} I_{|l|}(y)/\sinh[y\cosh(\beta h)] & \text{if} \quad N \text{ and } l \text{ are odd} \end{cases} \tag{B.7}$$

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