Thermodynamics at less than the correlation volume

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Consider an infinite thermodynamic system A, an open subsystem A_V, with fixed volume V, of A, and an open subsystem $A_{V'}$, with fixed volume V', of A_V. Evidence is presented to support the following thermodynamic fluctuation rule: At any time, the probability of finding the thermodynamic state of $A_{V'}$ in some range, given the thermodynamic state of A_V, is independent of the thermodynamic state of A, *even if the volume V is less than the correlation volume of A.* This rule was confirmed by Monte Carlo simulation of the two-dimensional ferromagnetic Ising model. Both thermodynamic properties and the local correlation function were examined. Another rule, which states that, for a given state of A_V, the fluctuation probability distribution for the thermodynamic state of $A_{V'}$ depends on the volumes only as $\Delta t=(V')^{-1}-V^{-1}$ was also tested. It works well at volumes larger than the correlation volume, but was shown to break down at volumes less than the correlation volume. In addition, an easily justified rule stating that the average value of a density of a globally conserved additive quantity of a subsystem equals that of the infinite system was tested and found to work well. These rules are part of an effort to extend thermodynamic fluctuation theory to volumes less than the correlation volume.

I. INTRODUCTION

Thermodynamics has proved most effective in addressing a wide range of physical problems. Despite this generality, however, thermodynamics has not seen much application to subsystems of large systems near critical points. In this paper, we shall present tests of a set of general thermodynamic rules which attempt to extend "equilibrium thermodynamics," as presented by Tisza and Callen,[1,2] to subsystems of infinite systems near the critical point. Our primary concern is with what Callen[2] calls the second postulate of equilibrium thermodynamics, which deals with systems in contact. According to Lewis, this statement naturally involves rules of thermodynamic fluctuations.[3]

The rules of thermodynamic fluctuations of interest here were set down earlier.[4–6] Our extension of thermodynamics is based on a structure of "fluctuations inside fluctuations inside fluctuations...," an idea discussed by Kadanoff,[7] though not in the context of thermodynamics. Let A be an infinite d-dimensional system in thermodynamic equilibrium and with correlation volume ξ^d. Consider an open subsystem A_V, with fixed volume V, of A and an open subsystem $A_{V'}$, with fixed volume V', of A_V. Because of fluctuations, A_V and $A_{V'}$ are at some time in particular thermodynamic states with intensive parameters different from those of A. The most fundamental postulate[4–6] in the present research is that at any time the probability of finding the thermodynamic state of $A_{V'}$ in some range, given the thermodynamic state of A_V, is independent of the thermodynamic state of the infinite system A. In particular, this should hold even if V is less than ξ^d. *Therefore, the thermodynamic state of a subsystem at some time has a significance independent of the infinite system in which it is imbedded, even if its volume is less than the correlation volume of the infinite system.* This Markov rule is powerful since it enables one to, at least in principle, decompose a problem which near the critical point involves many scales of length into a set of problems each involving essentially only one.

A stronger statement of the Markov rule can be made on the basis of the ensemble of microstates of A_V corresponding to a given thermodynamic state of A_V. Though the thermodynamic state of A affects the frequency with which A_V is found in some particular thermodynamic state, *the ensemble of microstates of A_V corresponding to that thermodynamic state is independent of the state of A.*

In this paper results of direct Monte Carlo tests of the Markov rule are presented for systems with volumes less than the correlation volume ξ^d. The system simulated is the two-dimensional Ising model. The Markov rule is explored through both thermodynamic properties and the local correlation function; it is found to work very well. A preliminary report of these Ising-model simulations, without a test of the Markov rule, was given previously.[6]

There has been some discussion about the meaning of the thermodynamic state in fluctuating systems.[8] The position in this research is like that of Landau and Lifshitz[9] who define states by mechanical parameters, such as energy, particle number, or magnetization, which can be determined from microscopic quantities for subsystems at all volumes If necessary, equations of state derived from the thermodynamic limit can be used to assign values to other thermodynamic variables of subsystems.

Throughout this paper, states of systems are specified only with intensive parameters.

A second rule tested concerns the volume dependence of thermodynamic fluctuation probability distributions. It asserts that for a given state of A_V, the probability of finding the state of $A_{V'}$ in some range of states depends on V and V' only through $\Delta t=(V')^{-1}-V^{-1}$. This "translational invariance" rule allows thermodynamic

fluctuation probabilities to be deduced at all volumes from the large volume limit where the classical theory is applicable. In Ref. 6, this rule was shown to work well at volumes larger than the correlation volume, but here, where tests at smaller volumes were possible, it is found to break down at less than the correlation volume because of boundary effects.

A third rule tested is the statement that the average value of a density of a globally conserved extensive quantity of a subsystem equals the corresponding density of the infinite system. This rule is easily justified and is found to work well. This rule has been stressed in particular by Diósi and Lukács,[10] who included it in the fundamental postulates in their presentation of the new thermodynamic fluctuation theory.

Subsystem probability distributions near the critical point is a problem which was addressed also by Bruce and co-workers.[11] These authors feel that such probability distributions are an important link with the foundations of the universality hypothesis. A difference with our approach is that we are attempting to connect these problems to thermodynamics whereas Bruce *et al.*, use the tools of statistical mechanics and renormalization-group theory. The distributions in this paper can be probed directly by means of scattering experiments.[11]

An objective of this research, to connect the properties of small subsystems to the thermodynamic limit, is the same as that of finite-scaling theory in critical phenomena theory.[12] A difference is that in finite scaling the subsystem is generally assumed to be nonfluctuating and surrounded by an infinite uniform system. The temperature of the finite subsystem is assumed to be the same as that of the infinite reservoir.

Mathematically, the new thermodynamic fluctuation theory is based on a notion of distance, in the form of a Riemannian metric, between thermodynamic states. A thermodynamic metric was formally introduced by Weinhold,[13] and applied to thermodynamic fluctuation theory by myself[4,5,6,14] and by Diósi and Lukács,[10] and to thermodynamics in finite time by Salamon and co-workers.[15]

This paper is organized as follows. In Sec. II thermodynamic fluctuation theory is summarized. The connection between "drift" terms in the theory and global conservation laws is also discussed. Section III describes the Monte Carlo simulation program. Section IV presents the results of the simulation. The biggest success is the confirmation of the Markov assumption. The biggest remaining problem is that the translational invariance rule appears not to work at less than correlation volume because of boundary effects.

II. THERMODYNAMIC FLUCTUATION THEORY

In this section, rules of thermodynamic fluctuation theory are reviewed. The first rule, which is fairly standard,[9] defines the thermodynamic state of a finite subsystem at some time. For a magnetic system, such as the two-dimensional (2D) Ising model,[16] regardless of the subsystem volume, the energy per volume and the magnetization per volume have a mechanical meaning as well as a thermodynamic one. The basis of rule (1) is as follows.

(1) At some time, given a finite subsystem $A_{V'}$, with volume V', energy per volume u', and magnetization per volume m', all other intensive parameters of $A_{V'}$ shall be the same as those of an infinite system with the same densities.

There are alternatives to this rule.[8] The physical significance of rule (1), if any, is unclear; it is not explored in this paper.

For the second rule, consider an open subsystem A_{V2} of an open subsystem A_{V1} of a system A_{V0}. The volumes V_2, V_1, and V_0 of all three systems are fixed in time. The system A_{V0} is a subsystem of an infinite system A in thermodynamic equilibrium. Rule (2) is a Markov assumption about fluctuations.

(2) At some time, the probability of finding A_{V2} in some range of thermodynamic states, given the thermodynamic state of A_{V1}, is independent of the thermodynamic state of A_{V0}.

At first sight, the Markov assumption seems obvious since if A_{V2} is separated from any spin in A_{V0}/A_{V1} by a distance greater than the microscopic interaction range (one lattice site in the Ising model), A_{V2} will sample the state of A_{V0}/A_{V1} only through the intermediate system A_{V1}. A Markov assumption is certainly justified for the probability distribution of *microscopic* states since if the microscopic state of A_{V1} is given, the microscopic state of A_{V2} is known absolutely, regardless of the state of A_{V0}. It is by no means evident, however, that it should work for *thermodynamic* states where the detailed microscopic information is averaged out. It is conceivable that the ensemble of microscopic states of A_{V1} which have a certain value of (u_1,m_1) for a certain state of A_{V0} varies with the state of A_{V0}, particularly when the correlation length of A_{V0} is larger than V_1. If this is the case, the distribution of thermodynamic states of A_{V2} at a given state of A_{V1} would certainly depend on that of A_{V0} and the Markov assumption would fail.

One may make two more arguments about the Markov rule at less than the correlation volume. The first is that it is implausible since, near the critical point, spins are correlated over a long distance and the ensemble for a subsystem cannot be independent of the outside. This is the reason that the canonical distribution fails at less than the correlation volume. This argument is unsound since it ignores the constraint that we look at the state of A_{V2} only for a given state of A_{V1}. A better argument is that the Markov rule is plausible since long-range correlations are associated with long relaxation times and local equilibrium can be reached faster. This qualitative argument is, however, not entirely satisfactory since it brings dynamics into a statement about equilibrium fluctuations. The theoretical basis for the Markov rule is unclear, and the rule requires careful testing.

A. Classical theory

Denote by

$$P\left[\begin{matrix}a_2 & a_1\\ V_2 & V_1\end{matrix}\right]da_2 \tag{2.1}$$

the probability of finding the state of A_{V2} between a_2 and a_2+da_2 given that the state of A_{V1} is a_1. Here, "a" represents $(u,m)=(a^1,a^2)$. This probability density is given in the classical theory[9,17,18] as

$$P\left[\begin{matrix}a_2 & a_1\\ V_2 & V_1\end{matrix}\right]da_2=C_1\exp[S_1(a_2,a_1)]da_2\ , \tag{2.2}$$

where $S_1(a_2,a_1)$ is the entropy of A_{V1} when A_{V2} is in the state a_2, and C_1 is a normalization constant. The entropy is in units of Boltzmann's constant. An essential assumption for expressing $S_1(a_2,a_1)$ in terms of thermodynamic quantities is that A_{V2} and its reservoir A_{V1}/A_{V2} are each homogeneous thermodynamic systems with the only discontinuity occurring at the interface between them.

Expanding $S_1(a_2,a_1)$ to second order about its maximum value at $a_2=a_1$ yields[5]

$$P\left[\begin{matrix}a_2 & a_1\\ V_2 & V_1\end{matrix}\right]=\frac{1}{2\pi\Delta t_2}[g(a_1)]^{1/2}\times\exp\left[-\frac{1}{2\Delta t_2}g_{\mu\nu}(a_1)\Delta a_2^{\mu}\Delta a_2^{\nu}\right], \tag{2.3}$$

where $\Delta a_2^{\alpha}\equiv a_2^{\alpha}-a_1^{\alpha}$, $\Delta t_2\equiv V_2^{-1}-V_1^{-1}$,

$$g_{\mu\nu}(a_1)\equiv-\left.\frac{\partial^2 s}{\partial a^{\mu}\partial a^{\nu}}\right|_{a=a_1}, \tag{2.4}$$

$s=s(a)$ is the entropy per volume in the thermodynamic limit, and $g(a_1)\equiv\det\underline{g}(a_1)$. Repeated indices are summed over.

The assumption that the universe can be broken into two homogeneous systems A_{V2} and A_{V1}/A_{V2} is inadequate if V_2 is less than the correlation volume of A_{V1} since in this case A_{V2} sees itself at any time most likely surrounded by a "droplet" of A_{V1} whose state deviates widely from that of A_{V1}.[4,5] This failure of the classical theory makes it ineffective for fluctuation phenomena near the critical point.

B. New thermodynamic fluctuation theory

The new thermodynamic fluctuation theory[4–6,10] is based on the idea of a sequence of open concentric subsystems $A_{Vf}\subset A_{Vm}\subset A_{Vm-1}\subset\cdots\subset A_{V1}\subset A_{V0}\subset A$ of the infinite system A. Take the limit $m\to\infty$ and let the difference in volume between each adjacent system in the hierarchy go to zero. The limit to zero volume difference is a formal one necessary for the path-integral theory in this section. In reality, the volume difference must always be large enough to allow fluctuations in thermodynamic parameters to be regarded as continuous to a good approximation.

The key assumption in the new thermodynamic fluctuation theory is the Markov assumption, rule (2) stated above. It states that the probability density

$$P\left[\begin{matrix}a_i & a_{i-1}\\ V_i & V_{i-1}\end{matrix}\right] \tag{2.5}$$

for thermodynamic states of A_{Vi} depends on the outside only through A_{Vi-1}.

In the Gaussian approximation to the classical theory, Eq. (2.3), the probability density depends on V_1 and V_2 only as Δt_2. Rule (3) in the new theory states that this translational invariance holds in all volume regimes.

(3) The probability distribution in (2.5) depends on volume only as

$$\Delta t_i=V_i^{-1}-V_{i-1}^{-1}\ .$$

This rule allows the fluctuation probability distribution in any volume regime to be related to the distribution for large volumes, where it is given by the classical theory. In Ref. 6, rule (3) was found to work well at volumes larger than the correlation volume. In the research reported in this paper, where it was possible to investigate smaller volumes, it was found that rule (3) breaks down at volumes less than the correlation volume because of boundary effects.

It is essential to require internal consistency in the form of the Chapman-Kolmogorov equation. This is rule (4) in the theory,

$$\int P\left[\begin{matrix}a_i & a_{i-1}\\ V_i & V_{i-1}\end{matrix}\right]P\left[\begin{matrix}a_{i-1} & a_{i-2}\\ V_{i-1} & V_{i-2}\end{matrix}\right]da_{i-1}=P\left[\begin{matrix}a_i & a_{i-2}\\ V_i & V_{i-2}\end{matrix}\right]. \tag{2.6}$$

Given the probability distribution in Eq. (2.5) for small Δt_i and all V_{i-1}, the "short-time propagator," the thermodynamic probability distribution can be worked out at all volumes by repeated applications of the Chapman-Kolmogorov equation.

The fifth rule concerns the average energy and magnetization densities of a subsystem of an infinite system.

(5) For a subsystem A_{V0} of an infinite system A with energy and magnetization densities $a=(u,m)$, the ensemble average

$$\langle a_0\rangle=a\ . \tag{2.7}$$

Rule (5) is easy to justify physically and is consistent with the simulation results reported here. Let A have periodic boundary conditions. (In the limit as A becomes an infinite system, the nature of the boundary conditions is irrelevant, so long as A is not at the critical point.) Imagine A to be composed of a set of N identical open systems $A_{V0}^1,A_{V0}^2,\ldots,A_{V0}^N$. Let X denote either the constant extensive energy or magnetization of A and X_0^i the corresponding quantity of A_{V0}^i. Define $a_0^i=X_0^i/V_0$. It follows from the additivity of extensive quantities that at any time

$$a=N^{-1}\sum_{i=1}^{N}a_0^i\ . \tag{2.8}$$

By spatial translational invariance, imposed by the periodic boundary conditions for A, $\langle a_0^i\rangle$ is independent of i. On taking the ensemble average in Eq. (2.8), it then follows that $\langle a_0^i\rangle=a$.

It is essential in this argument that A be an infinite system, to which periodic boundary conditions can be applied without changing anything, and that X be a globally conserved, additive quantity. Rule (5) does not hold if A

is finite, as was demonstrated by the simulation. Also, for thermodynamic variables which are not densities of globally conserved additive quantities, such as temperature, rule (5) need hold only for large V_0 where fluctuations are Gaussian.

Rules (1)—(5) determine the new thermodynamic fluctuation theory. In path-integral notation,[5] with a two-parameter system,

$$P\begin{bmatrix} a_f & a \\ t_f & 0 \end{bmatrix} = g^{1/2}(a_f) \times \int\int D[a(t)] \exp\left[-\int_0^{t_f} \mathscr{L}(a,\dot{a})dt\right], \tag{2.9}$$

where

$$D[a(t)] \equiv \lim_{m\to\infty} \left[\left(\frac{1}{2\pi\tau}\right)^m \prod_{i=0}^{m-1} g^{1/2}(a_i)da_i\right], \tag{2.10}$$

$$\mathscr{L}(a,\dot{a}) \equiv \tfrac{1}{2}g_{\mu\nu}(\dot{a}^\mu - f^\mu)(\dot{a}^\nu - f^\nu) + \tfrac{1}{2}f^\mu{}_{;\mu} + \tfrac{1}{6}R(a), \tag{2.11}$$

and

$$f^\mu \equiv -\frac{1}{2}\frac{1}{\sqrt{g}}\frac{\partial}{\partial a^\nu}(\sqrt{g}g^{\mu\nu}). \tag{2.12}$$

The dot indicates derivative with respect to the "time" $t=1/V$, $t_f=1/V_f$, and $\tau=t_f/m$. $R(a)$ is the Riemannian curvature scalar of the manifold of thermodynamic states with metric $g_{\mu\nu}$, and the semicolon denotes the covariant derivative. Equation (2.9) has been set forth by several authors[19–23] as the most general solution to the Fokker-Planck equation and has been applied to irreversible thermodynamics.

The covariant drift in Eq. (2.12) is picked to guarantee that rule (5) holds. To see this, define the nonvector quantity

$$\langle \Delta a_f^\mu \rangle_{t_f} \equiv \int \Delta a_f^\mu P \begin{bmatrix} a_f & a \\ t_f & 0 \end{bmatrix} da_f \equiv t_f K^\mu(a) + O(t_f^{3/2}), \tag{2.13}$$

where $\Delta a_f^\mu = a_f^\mu - a^\mu$. The covariant drift vector f^μ is defined by[20]

$$f^\mu = K^\mu - \frac{1}{2}\frac{1}{\sqrt{g}}\frac{\partial}{\partial a^\nu}(\sqrt{g}g^{\mu\nu}). \tag{2.14}$$

As can be shown[20]

$$\langle \Delta \dot{a}_f^\mu \rangle_{t_f} \equiv \frac{d}{dt_f}\langle \Delta a_f^\mu \rangle_{t_f} = K^\mu(a)_{t_f}. \tag{2.15}$$

If in density coordinates we take $K^\mu=0$, which is necessary for rule (5), we get the expression for covariant drift given in Eq. (2.12). The fact that we should take density coordinates to be special in the theory is a point which has been emphasized by Diósi and Lukács.[10]

The expression for f^μ has the form in Eq. (2.12) only in density coordinates; on transforming coordinates, it should be transformed as a first rank contravariant tensor. The justification of Eq. (2.12) does not take into account boundary conditions of the manifold of thermodynamic states. Boundary conditions present an interesting problem, but one which will be deferred to the future.

In the form of the theory discussed in Refs. 4 and 5, rather than forcing rule (5) with drift, the guiding principle was that all coordinates be equivalent and that statements particular to specific coordinates should not be made. The covariant drift f^μ was set to zero. It was shown[5] that the curvature $R(a)$ can be interpreted as the correlation volume of an infinite system; this has been confirmed for several cases. This theory also gives fluctuation probability distributions superior to those of the conventional theory.[4,5]

III. DESCRIPTION OF THE SIMULATION PROGRAM

To test the rules discussed above, Monte Carlo simulations were carried out on the zero-field 2D ferromagnetic Ising model, with Hamiltonian

$$\mathscr{H} = -\sum_{\langle i,j\rangle} \sigma_i\sigma_j \tag{3.1}$$

and with critical temperature $T_c = 2.269\,185\,31\ldots$. The sum $\langle i,j\rangle$ is over nearest neighbors, and $\sigma_i = -1$ or $+1$. This model will be system A. A square subsystem of A was simulated with a lattice $A_{V0'}$, with number of spins $V_0' = N_0' \times N_0'$. During the simulation, the spins of $A_{V0'}$ were considered one at a time and flipped with the Metropolis probability

$$P(\Delta E,T) = \begin{cases} 1 & \text{if } \Delta E \le 0 \\ \exp(-\Delta E/T) & \text{if } \Delta E > 0, \end{cases} \tag{3.2}$$

where ΔE is the energy change which would result if the spin were flipped and T is the temperature of A. Periodic boundary conditions were used for $A_{V0'}$; if N_0' is much larger than the correlation length $\xi(a)$ of A, $A_{V0'}$ behaves as a subsystem of A.[24]

The Metropolis algorithm was implemented using multispin coding.[25] Random numbers were generated with Tautsworth's algorithm (R250) which is fast and has an essentially infinite cycle time.[26,27] The simulation program was run on Apple Macintosh microcomputers; the most frequently executed parts were written in Motorola 68 000 microprocessor assembly language and the rest in MacFORTH.

Metropolis Monte Carlo does not simulate dynamics correctly, a global temperature used to determine local spin-flip probabilities is an indication of this, but it does simulate the canonical distribution. This is sufficient here.

The program allowed three basic analysis modes. The first analyzed only the state a_0' of $A_{V0'}$. Since in this mode the greatest obstacle to good accuracy was slow relaxation times, particularly close to the critical point, time was spent on analysis only after every tenth complete sweep of $A_{V0'}$. At a temperature $T=2.35$, the program could update an average of 14 000 spins per second. An

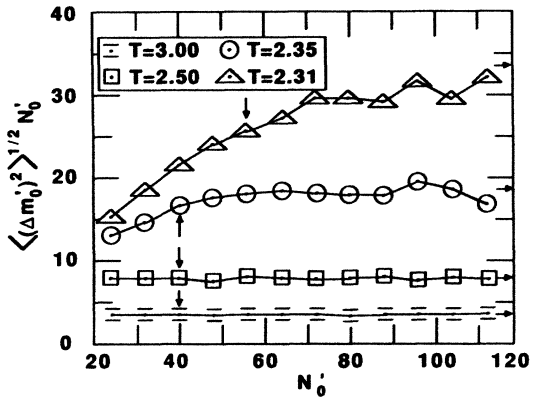

FIG. 1. Standard deviation of the magnetization density of $A_{V0'}$ times N_0' as a function of N_0' for four temperatures. As N_0' gets larger, these curves should reach constant limiting values related to the magnetic susceptibility through classical thermodynamic fluctuation theory. The expected limiting values were computed with series results (Ref. 28) and are shown by the arrows in the right margin. The results in this figure helped in the selection of a large enough N_0' in subsequent runs; values used at each temperature are shown by vertical arrows.

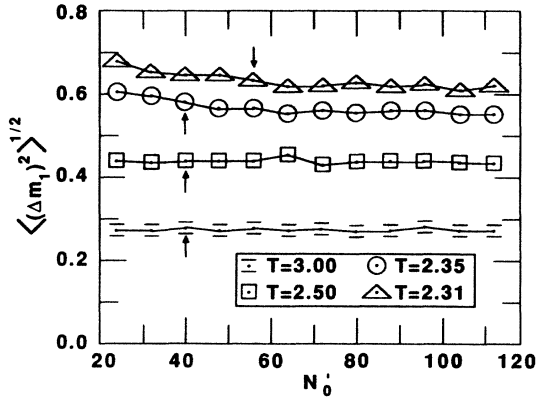

FIG. 2. Standard deviation of the magnetization density m_1 as a function of N_0' for a 10×10 sublattice A_{V1} of $A_{V0'}$. As N_0' gets large, these numbers should reach limits. Exact values for comparison are not known. These results were an aid in selecting a large enough N_0' in subsequent runs. Values used are shown in the figure.

overnight run could easily sweep and analyze a 40×40 lattice 300 000 times. Typically, the first 1000 sweeps in each run were discarded to allow the system to equilibrate.

Figure 1 (Ref. 28) shows $\langle(\Delta m_0')^2\rangle^{1/2}$ as a function of N_0' for four temperatures. For large N_0', the curves in Fig. 1 should reach constant values. The increased scatter for large N_0' results from the limited number of times large lattices could be swept in a reasonable period of time. The deviation from constant values at small volumes results from N_0' approaching the correlation length $\xi(a)$ and is an indication that $A_{V0'}$ is too small to mimic well a subsystem of A. For $T=2.31$, the curve was slow to reach a limiting value for large N_0' because T was close to the critical temperature. No smaller temperature was examined.

The second analysis mode analyzed the state of a square subsystem A_{V1} of $A_{V0'}$ after every twentieth sweep of $A_{V0'}$. Figure 2 shows the standard deviation of the magnetization density m_1 for $V_1=10\times10$, as a function of N_0'. If $N_0'\gg\xi(a)$, the fluctuation moments of A_{V1} should not depend on the size of $A_{V0'}$. This appears to be the case in Fig. 2. Limiting values are reached the fastest for states furthest from the critical point, where the correlation length is the smallest.

For any square subsystem A_V of $A_{V0'}$, the magnetization per volume m and the energy per volume u were computed from

$$m=V^{-1}\sum_{A_V}\sigma_i \quad \text{and} \quad u=-V^{-1}\sum_{A_V}\sigma_i\sigma_j\ , \tag{3.3}$$

where the later sum is over nearest neighbors. Each spin is linked to its nearest neighbors by four bonds. To each spin was assigned the energy in its left and upper bond; this rule determined which bonds crossing the boundary of A_V were counted in doing the energy sum.

Figures 1 and 2 were used to judge how large to take N_0' in subsequent runs. From the figures, it is clear that the fluctuation moments of a sublattice A_{V1} reach their limits faster than those of $A_{V0'}$. Since the analysis of interior lattices of $A_{V0'}$ was of interest in this paper, a small V_0' was picked. The vertical arrows in the figures show the values used in most of the runs.

In the third analysis mode, the state a_1 of A_{V1} was analyzed after every sweep of $A_{V0'}$. If a_1 fell into a "window" centered at $a_{1w}=(u_{1w},m_{1w})$ and with width Ω, defined by

$$a_{1w}^i-\Omega\langle(\Delta a_1^i)^2\rangle^{1/2}\le a_1^i\le a_{1w}^i+\Omega\langle(\Delta a_1^i)^2\rangle^{1/2}\ , \tag{3.4}$$

the state a_2 of a square subsystem A_{V2} at the center of A_{V1} was also analyzed. Figure 3(a) shows a schematic of the systems $A_{V0'}$, A_{V1}, and A_{V2}. The volumes of all three systems could be varied independently. For given T, a_{1w},

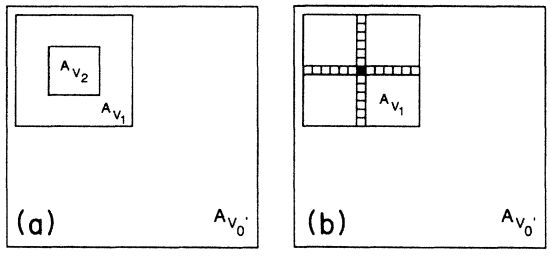

FIG. 3. Schematic sketch of the geometries used for analysis mode 3. The position of A_{V1} within $A_{V0'}$ was not important because periodic boundary conditions were used for $A_{V0'}$. (a) Configuration for analyzing thermodynamic properties. (b) Configuration for analyzing the local correlation function. Only odd values of N_1 were used. The central spin of A_{V1}, which is labeled with a black square, is σ_0. Spins were numbered from 0 to $(N_1-1)/2$. By symmetry, all four rows of A_{V1} should have the same correlation function and, so they were analyzed together.

V_1, and V_2, as Ω is made smaller, the fluctuation moments of a_2 should reach a limit. As will be shown in Sec. IV, a limit is indeed attained.

Analysis of A_{V1} after every sweep of A_{V0} added considerably to the running time because addressing specific individual spins is difficult to do efficiently in the multispin coding algorithm. At $T=2.5$, with $V_0'=40\times40$, $V_1=20\times20$, and $\Omega=0.04$, 6600 spins per second could be updated in the third analysis mode.

An alternate way of running mode 3 was to analyze the correlation function A_{V1} when a_1 falls into the window. The correlation function $G(r)$ is defined by[29]

$$G(r)=\langle\sigma_0\sigma_r\rangle-\langle\sigma_0^2\rangle\ , \tag{3.5}$$

where, in this paper, all of the spins were taken to lie along the same row or column. To analyze the *local* correlation function, the configuration shown in Fig. 3(b) was used. A bin was assigned to each value of r and values of $\sigma_r\sigma_0$ were accumulated in the appropriate bin as a_1 fell into the window.

IV. RESULTS

In this section, the simulation results are presented. For convenience, we shall call an analysis of the interior of A_{V1}, provided that a_1 falls in the window, a "snapshot" and the collection of snapshots taken in the course of a run for a given window an "album."

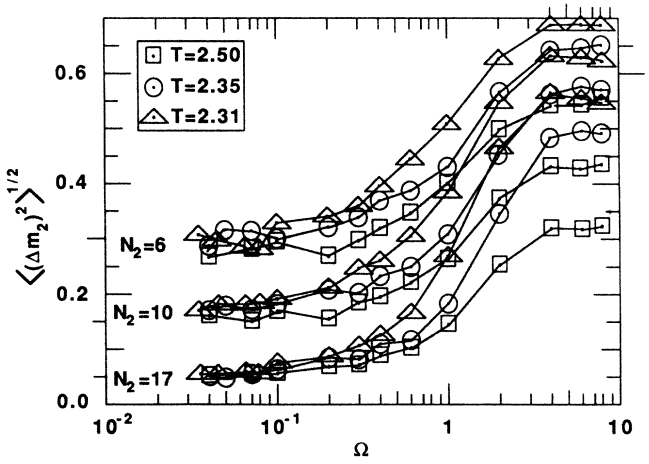

FIG. 4. Standard deviation of m_2 as a function of Ω for albums A for three values of N_2 and three values of T. The longest run for albums A was the one with $T=2.31$ and $\Omega=0.037$ which swept a 56×56 A_{V0} 290 000 times and included 0.025% of the sweeps in the window. Windows with $\Omega=8$ resulted in a snapshot after more than 99.5% of the sweeps. For comparison, the points in this figure with $\Omega=8$ were actually computed with mode 2, which includes all sweeps in the analysis of A_{V2}. For small Ω the curves reach limiting values independent of T, in accord with the Markov rule. The temperatures used in the figure, $T=2.5$, 2.35, and 2.31 have correlation lengths of 6.0, 16.3, and 31.9 lattice sites, respectively, so volumes less than the correlation volume of A were tested.

TABLE I. Window centers and volumes used for the sets of albums studied in this paper. In each set of albums, T, V_2, and Ω were varied. The energy density at the critical point is $-1.414\,213\,56\ldots$.

Albums	Energy center u_{1w}	Magnetization center m_{1w}	Volume V_1
A	−1.1074	0.50	20×20
B	−1.2000	0.25	14×14
C	−1.2000	0.00	30×30
D	−1.2000	0.00	20×20
E	−1.2660	0.00	25×25
F	−1.2660	0.00	7×7
G	−1.2660	0.00	13×13
H	−1.2660	0.00	19×19

A. Test of the Markov rule with thermodynamic properties

Let us present first an analysis of thermodynamic properties with mode 3, as shown in Fig. 3(a). Let us examine the approach to limits, as $\Omega\to0$, of fluctuation moments of A_{V2} for albums with windows centered at $a_{1w}=(-1.1074,0.5)$ and with $V_1=20\times20$. Call the set of such albums "albums A." Information about the sets of albums examined in this paper is presented in Table I.

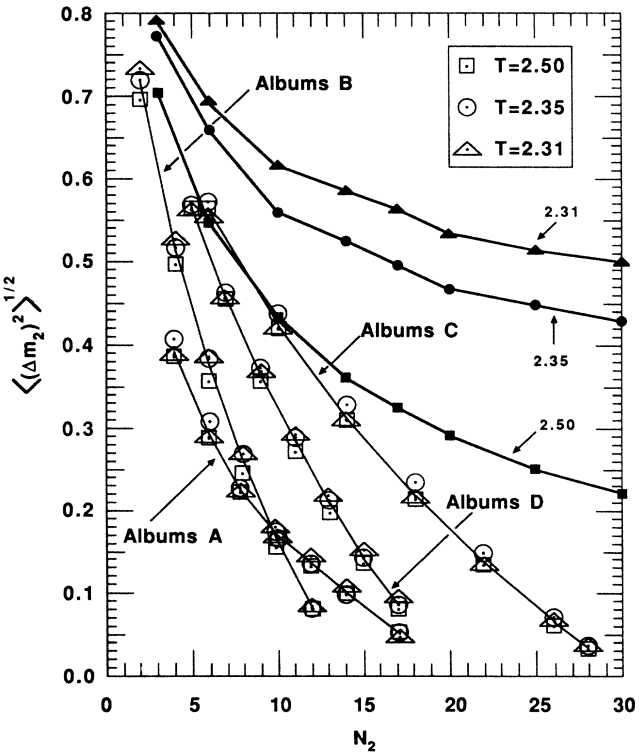

FIG. 5. Standard deviation of m_2 as a function of N_2 for four sets of albums (see Table I) and three T's in the limit of small Ω. Corresponding points are seen to fall on top of one another, confirming the Markov rule even at volumes less than the correlation volume. The solid points are values obtained at the three T's with the window wide open and all points accepted for analysis. The temperatures used in the figure, $T=2.5$, 2.35, and 2.31, have correlation lengths of 6.0, 16.3, and 31.9 lattice sites, respectively.

The temperature T, the volumes V_2, and the window width Ω were varied in albums A. For any given window, all values of V_2 were dealt with in a single run.

Figure 4 shows $\langle(\Delta m_2)^2\rangle^{1/2}$ as a function of Ω for three values of T and three values of V_2. The temperatures T were picked to give a good spread of correlation lengths for the infinite system A; $T=2.5$, 2.35, and 2.31 have correlation lengths of 6.0, 16.3, and 31.9 lattice sites, respectively.[30] As Ω gets smaller, each of the nine curves in Fig. 4 appears to reach a limiting value. For given a_{1w}, V_1, and V_2, the same limit appears to be approached, no matter what the value of T. This is consistent with the Markov rule.

For a comprehensive test of the Markov hypothesis, several values of a_{1w} and V_1 were tried in the limit of small Ω and the three values of T given above. The smallest values of Ω studied were typically around 0.03. Results are shown in Fig. 5. Each point shown is an average over six albums with $\Omega<0.07$. Typically, the standard deviations of these averages enclosed corresponding points with different T's. These data support the Markov hypothesis.

First and second fluctuation moments in the energy u_2 also satisfied the Markov rule for small Ω. Results are not shown here since the energy data do not vary as widely as the magnetization data and hence are not as interesting.

B. Test of the Markov rule with local correlation functions

The Markov rule was also tested using the local correlation function, with the configuration shown in Fig. 3(b). Figure 6 shows the approach to a limit for decreasing Ω of the local correlation function for albums E. In each case, within acceptable uncertainties, the limits seem to be the same.

It is apparent in Fig. 6 that the correlation between the central spin of A_{V1} and the edge spin diminishes as Ω gets smaller. To test this for generality, we made runs with the same window centers as albums E, but with varying volume V_1. Results are shown in Fig. 7. In each case the

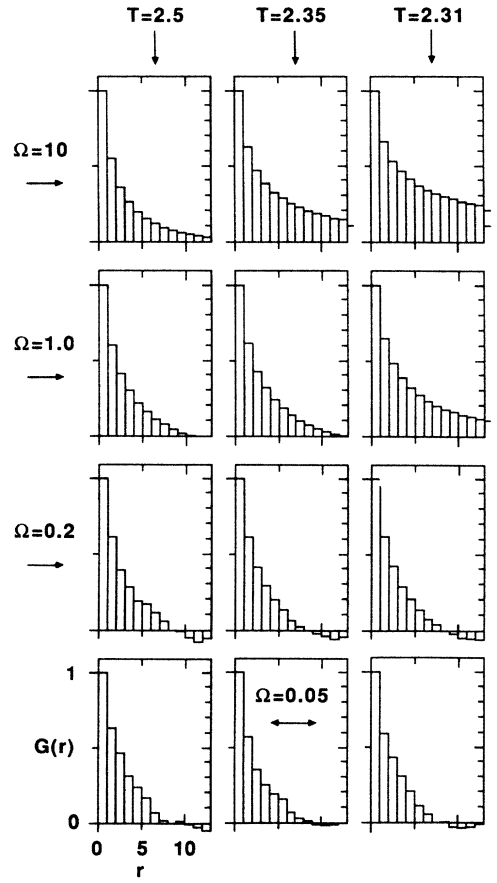

FIG. 6. Local correlation function of albums E as a function of the window width Ω for three temperatures T. All of the graphs have the same scales as the one in the lower left. For each T, though the initial correlation function is quite different, the same limiting correlation function seems to be reached. Long computation times were necessary to make this figure, the longest run in this research was the one with $T=2.5$ and $\Omega=0.05$ which swept a 48×48 lattice A_{V0} 720 000 times in the space of about 60 h. The window with $\Omega=10$ admitted almost all of the sweeps for analysis.

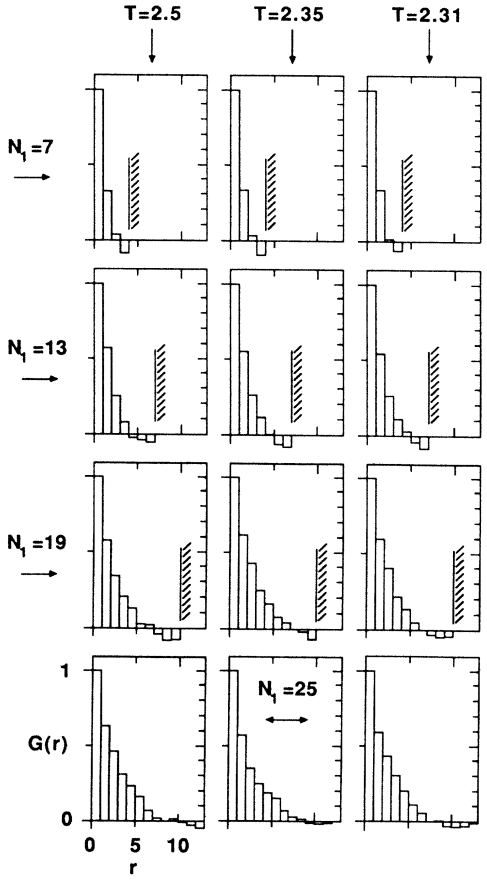

FIG. 7. Local correlation function of albums E–H as a function of N_1 for three temperatures T and $\Omega=0.05$. All of the graphs have the same scales as the one in the lower left. All the albums have the same window centers. For each N_1, the correlation with the central spin diminishes as the edge is approached. Note that these data support the Markov rule.

correlation of the central spin with the edges diminishes close to the edges. There is a small anticorrelation visible between center and edge spins. It is unclear whether this anticorrelation is real or a product of not having Ω small enough. Note that the data in Fig. 7 also support the Markov hypothesis.

C. Failure of translation invariance at less than the correlation volume

Rule (3) predicts that subsystem fluctuations depend on volumes only through $\Delta t_2 = V_2^{-1} - V_1^{-1}$. It was found to work well at volumes larger than the correlation volume.[6]

Figure 8 shows $\langle u_2 \rangle$ as a function of N_2 for small Ω for albums D. Clearly, $\langle u_2 \rangle$ depends on N_2 and deviates from $u_{1w} = -1.200$. By rule (5), for large V_1, $\langle u_2 \rangle$ must coincide with u_{1w} for all V_2. Translational invariance predicts then that this must hold at all volumes. For comparison, Fig. 8 also shows subsystem average energies with a wide open window for the temperature $T=2.405$ which has an average energy -1.200 for system A. The average energy does not depend on N_1, consistent with rule (5). These data force us to conclude that translational invariance does not hold in all volume regimes.

From the deviation of $\langle u_2 \rangle$ from u_{1w} in Fig. 8, it is clear that $\langle u_2 \rangle$ must depend on where the system A_{V2} is placed inside A_{V1}. We associate the breakdown in rule (3) to a failure of spatial translational invariance due to the boundaries of A_{V1}.

Figure 8 demonstrates again the Markov rule since the points for albums D with different T's fall on top of one another, within scatter, for different values of T.

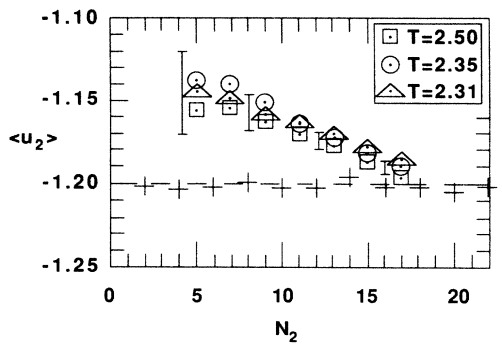

FIG. 8. Average values of u_2 as a function of N_2 for albums D for small values of Ω. Each point shown is an average over six points with $\Omega=0.07$. A rough error bar in each average is shown. $\langle u_2 \rangle$ deviates from the window central energy u_{1w}, demonstrating the failure of translational invariance at volumes near the correlation volume. The + points were taken for u_1, with $T=2.405$ and coincide with the window center. Note that the Markov rule is supported.

V. CONCLUSION

This research has implications for the foundations of the new thermodynamic fluctuation theory. Let us summarize the present status of the theory for various volume regimes.

Volumes larger than the correlation volume are characterized by the translational invariance rule, which states essentially that fluctuations at any volume level can be scaled to look like those in the large volume limit where the classical theory holds. At volumes larger than the correlation volume, the new theory appears to be a definite improvement over the classical theory, both formally, in the sense that it gives a proper covariant treatment of fluctuations, and in applications to model systems.[4,5,10]

At volumes less than the correlation volume, translational invariance fails because of boundary effects which the present form of the new thermodynamic fluctuation theory does not yet take into account. In contrast to the classical theory, however, the new theory offers a structure for addressing the small volume regime in the form of fluctuations inside fluctuations inside fluctuations.... It also predicts the volume at which the transition from the large volume regime to the small volume regime should take place. This is the Gaussian curvature of the Riemannian manifold of thermodynamic states, which, for systems with attractive or ferromagnetic interactions, appears to yield the correlation volume.[5,14]

In either regime, the dominant principle for thermodynamic understanding is the Markov rule, which is supported at all volumes by the computations reported in this paper. The Markov rule makes possible an extension of the present structure to small volumes; however, boundary effects must be taken into account.

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