Thermodynamics near the correlation volume

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I present and test three simple thermodynamic fluctuation rules which may in some cases hold for subsystems of infinite systems with volumes less than the correlation volume. Tests at volumes near the correlation volume are made in the two-dimensional square ferromagnetic Ising model by Monte Carlo simulation. Fluctuations into the metastable and spinodal regions are discussed. Aside from difficulties apparently resulting from the small volumes used in the simulations, the rules are found to work well.

Thermodynamics is generally done in the infinite-volume limit. The application of thermodynamics to finite subsystems of infinite systems has been less studied, particularly at volumes approaching the correlation volume. A preliminary report of such a study is given in this paper. I present and test three thermodynamic fluctuation rules which in some cases may hold down to microscopic volumes where there are no longer enough constituents in the system to justify a continuous thermodynamic approximation. In particular, these rules may hold at volumes less than the correlation volume.

The rules at issue in this paper have been presented before as part of a new thermodynamic fluctuation theory.[1,2] The aim here is to restate them with different emphasis and, for the first time, to test them *directly* down to volumes near the correlation volume in an interesting system, the two-dimensional (2D) square ferromagnetic Ising model. The computations will be made by the Monte Carlo method.

The first rule, which seems to be standard,[3] defines the thermodynamic state of a finite subsystem at some time. For a simple magnetic system,[4] regardless of the volume, the energy per volume and the magnetization per volume have a mechanical meaning as well as a thermodynamic one. This is the basis of Rule (1).

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

Consider now an open subsystem A_{V_2} of an open subsystem A_{V_1} of a system A_{V_0}. The volumes V_2, V_1, and V_0 of all three systems are fixed in time. The system A_{V_0} is part of an infinite system in thermodynamic equilibrium. Rule (2) deals with fluctuations.

(2) At some time, the probability of finding A_{V_2} in some range of thermodynamic states, given the thermodynamic state of A_{V_1}, is independent of the state of A_{V_0}.

Denote by

$$P\left(\begin{array}{c|c} a_2 & a_1 \\ V_2 & V_1 \end{array}\right) da_2 \qquad (1)$$

the probability of finding the state of A_{V_2} between a_2 and a_2+da_2 given that the state of A_{V_1} is a_1. Here, "a" represents (u,m). If V_2 is much larger than the correlation volume $\xi^d(a_0)$ of A_{V_0}, the probability density in Eq. (1) is given by the well-known formula[2,3]

$$P\left(\begin{array}{c|c} a_2 & a_1 \\ V_2 & V_1 \end{array}\right) = \frac{1}{2\pi\,\Delta t}\sqrt{g(a_1)}\exp\left(-\frac{1}{2\Delta t}g_{\mu\nu}(a_1)\Delta a_2^\mu\Delta a_2^\nu\right) , \qquad (2)$$

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

$$g_{\mu\nu}(a_1) \equiv -\left.\frac{\partial^2 s}{\partial a^\mu \partial a^\nu}\right|_{a=a_1} , \qquad (3)$$

$s=s(a)$ is the entropy per volume, and $g(a_1)\equiv \det g(a_1)$.

The probability density in Eq. (2) depends on V_1 and V_2 only as Δt. This translational invariance appears in the new thermodynamic fluctuation theory in all volume regimes.[1,2] I present it as the third universal thermodynamic fluctuation rule.

(3) The probability distribution in (1) depends on volume only as Δt.

With rules (1)–(3), and requirements of consistency, the new thermodynamic fluctuation theory can be constructed from Eq. (2) by using the mathematics of continuous Markov processes.[5]

Rules (1)–(3) were tested for the case where A_{V_0} is an infinite square 2D ferromagnetic Ising model with nearest-neighbor interactions and critical temperature $T_c=2.269$. The external magnetic field of A_{V_0} was set to zero throughout. I computed primarily second fluctuation moments, which, by rule (3), should depend on volume only as Δt. I proceeded by Monte Carlo simulation.[6] The system A_{V_0} was simulated by a finite grid $A_{V_0'}$, with periodic boundary conditions. If V_0' is large enough, $A_{V_0'}$ will behave as a finite subsystem of A_{V_0}. The systems A_{V_1} and A_{V_2} were studied as subsystems of $A_{V_0'}$.

For a given temperature T_0 of A_{V_0}, two different ways were used to ensure that V_0' was large enough. The first consisted in computing the heat capacity by means of a fluctuation formula, as described in Ref. 6, and comparing with exact results.[7] The second method was by computing the second fluctuation moments of an imbedded 10×10 subsystem. Provided V_0' is large enough, these moments should be independent of V_0'. It was found that $V_0'=40\times 40$ was large enough for temperatures explored in this work. This volume was used in all subsequent calculations.

The state of a finite subsystem may certainly fluctuate into the metastable region, but if this region can be handled as an analytic extension of the stable region, which is not clear,[8] there appears to be no impediment to applying rules (1)–(3) here, at least for fluctuations not so large as to force a phase transition. In the spinodal region there is no hope of applying thermodynamics in the sense of this paper. In an attempt to avoid this difficulty, I pose the following question: Does a fluctuating thermodynamic subsystem avoid the spinodal region?

To address this question, I simulated a subsystem A_{V_1} of an infinite system for three values of V_1 at $T_0 = 2.35$, where[9] $\xi(a_0) = 16$. I recorded (u_1, m_1) after every sweep of $A_{V_0'}$. One thousand sweeps of $A_{V_0'}$ were made for each V_1. The starting configuration was a random lattice; the first 200 cycles were discarded to allow $A_{V_0'}$ to equilibrate. 400 points for each V_1 are displayed in Fig. 1. Though the boundary of the spinodal region is not known, it seems that the spinodal region is avoided even for $V_1 = 10 \times 10$. For $V_1 = 10 \times 10$, it appears that roughtly 1% of the points do

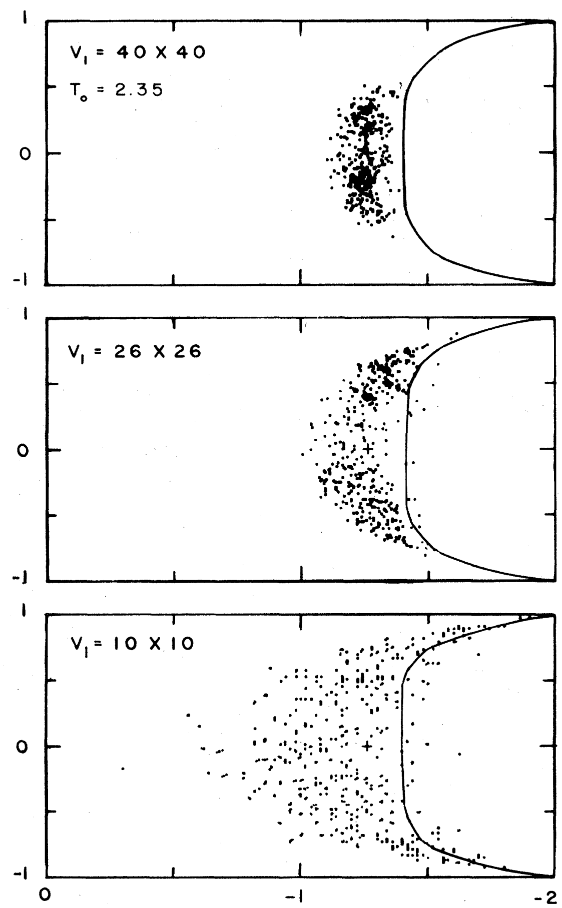

FIG. 1. Distribution of thermodynamic states (u_1, m_1) for $T_0 = 2.35$ and three values for V_1. The state a_0 of A_{V_0} is indicated with a "+" sign. The solid curve is the phase separation curve. The spinodal curve is not shown, but it appears that few points fall into the spinodal region.

make it into the spinodal region, but I believe that this failing of thermodynamics is due to the lack of spins in V_1 and has nothing to do with being less than the correlation volume of A_{V_0}.

One wonders what rule bars the thermodynamic state of a subsystem from the spinodal region. I make the following conjecture: *the probability of finding a subsystem in a state where its volume is less than its correlation volume is negligible.* Provided that the metastable region can be viewed as an analytic extension of the stable region, it appears that the correlation volume goes to infinity as the spinodal curve is approached. Thus, systems of all volumes are barred by this rule from crossing into the spinodal region.

I shall now focus on translational invariance [rule (3)] by introducing a subsystem A_{V_2} of A_{V_1} and examining fluctuations in a_2 for given values of a_1. To do this, A_{V_1} was allowed to fluctuate freely inside $A_{V_0'}$ and a "window" of width Ω was established such that the value of a_2 was recorded after a sweep of $A_{V_0'}$ if and only if

$$a_0^i - \Omega \langle (\Delta a_1^i)^2 \rangle^{1/2} \leq a_1^i \leq a_0^i + \Omega \langle (\Delta a_1^i)^2 \rangle^{1/2} . \quad (4)$$

I focused on testing rule (3), and centered the window at $a_0 (= \langle a_1 \rangle)$ to keep things as simple as possible. For given T_0, V_1, and V_2, as Ω gets smaller, the second fluctuation moments of a_2 should reach a limit. The inserts in Fig. 2 show the dependence of $\langle (\Delta u_2)^2 \rangle^{1/2}$ and $\langle (\Delta m_2)^2 \rangle^{1/2}$ on Ω for a specific case. A limit seems to be attained as Ω gets small. To simulate $V_1 = \infty$, a_2 was recorded after every sweep of $A_{V_0'}$.

For particular T_0 and V_1, a sequence of systems A_{V_2} was examined. The first 200 sweeps of $A_{V_0'}$ in each run were discarded. Results are shown in Fig. 2. As can be seen, second fluctuation moments with the same T_0 fall reasonably well on the same curves when plotted against Δt, in accordance with rule (3). First fluctuation moments also behaved properly. In each case, $\langle a_2 \rangle = \langle a_1 \rangle = a_0$.

The most significant deviation from rule (3) is in $\langle (\Delta m_2)^2 \rangle^{1/2}$ for cases where V_1 and V_2 are nearly equal to each other. The insert in Fig. 2 show such a case; the limit reached by $\langle (\Delta m_2)^2 \rangle^{1/2}$ as Ω goes to zero is about 20% too low. I believe that the explanation lies in large fluctuations of the magnetization m_2^ξ in the system A_{V_1}/A_{V_2} when V_1 and V_2 are nearly equal. It is easy to show that fluctuations cannot satisfy Eq. (2) all the way in the limit as V_2 goes to V_1, if V_1 is finite, because fluctuations in m_2^ξ and u_2^ξ would exceed their maximum possible values (i.e., with spins completely aligned or disaligned). It is also easy to show that for given Δt, fluctuations in m_2^ξ and u_2^ξ decrease with increasing V_1 and V_2; therefore, this effect appears to be associated with the small volumes used in this study.

The test above concentrated on rule (3), but it also provides evidence for rules (1) and (2). Rule (1) defines the thermodynamic state of a finite subsystem. Without this, rule (3) has no meaning. Hence, the success of rule (3) supports rule (1). Rule (2) is tested indirectly because fluctuations in a_2 behave correctly on constraining only a_1 and a_0. A direct test of rule (2) (the next step in this research) would vary a_0 at fixed a_1 and attempt to show that fluctuations in a_2 are not affected.

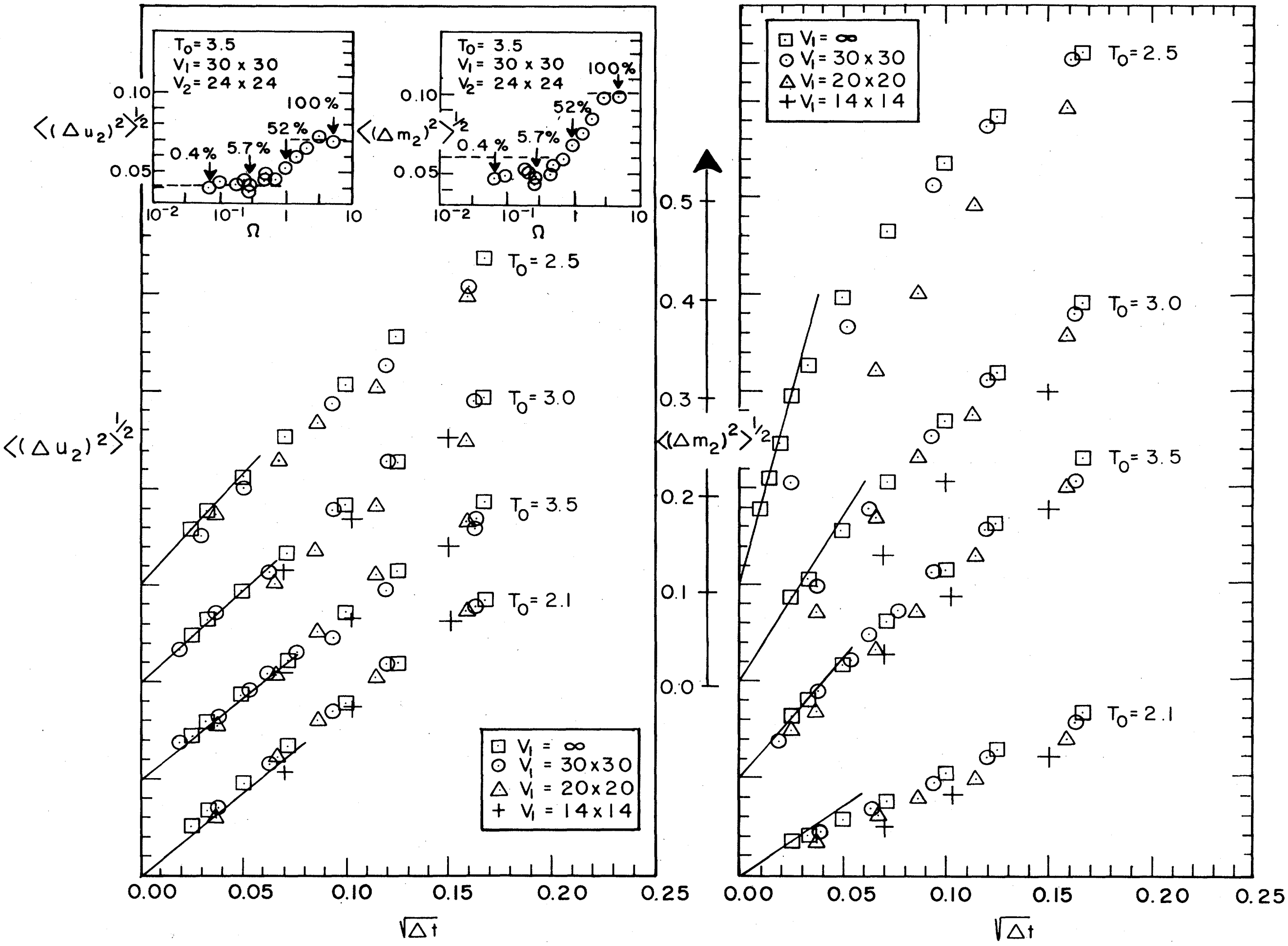

FIG. 2. Second fluctuation moments of a_2, at fixed a_1, as a function of $\sqrt{\Delta t}$ for several values of T_0 and V_1. As $\sqrt{\Delta t}$ goes to zero, each curve passes through the origin, which is located at a different position for each T_0 to facilitate plotting. The vertical scale for both graphs is given in the middle; the origin should be placed appropriately. The straight lines are exact results for small Δt, as deduced from Eq. (2). The length of the computer runs varied. The shortest run with a finite V_1 was for $T_0=2.1$ and $V_1=30\times 30$ where 4000 cycles were made with $\Omega=0.2$, which caught 5% of the sweeps in the window. The longest run was for $T_0=2.5$ and $V_1=20\times 20$ where 40 000 cycles were made with $\Omega=0.06$, which caught 0.3% of the points in the window. Points with the same T_0 fall reasonably well on the same curves. The inserts in the left figure show for a specific case how the fluctuation moments reach a limit as Ω is decreased. The dashed lines show the expected limiting values.

In conclusion, the test of thermodynamics for small subsystems of the 2D Ising model has turned up some good evidence in its favor. I had hoped to do more at volumes less than the correlation volume, but this requires temperatures closer to the critical point, larger grids, and much longer computer runs. It was beyond the scope of the present study.

I thank Mike Frame for useful conversations.

[1]G. Ruppeiner, Phys. Rev. Lett. **50**, 287 (1983).

[2]G. Ruppeiner, Phys. Rev. A **27**, 1116 (1983).

[3]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1977), Chap. XII.

[4]I use the language of magnetic systems only because such a system is of interest in this paper.

[5]In addition, it appears necessary to require explicitly that the average value of a_2, at fixed a_1, is a_1. This is done by introducing nonzero covariant drift into the new thermodynamic fluctuation theory and will be discussed in a forthcoming article.

[6]Extensive Monte Carlo calculations on the 2D Ising model were made by D. P. Landau, Phys. Rev. B **13**, 2997 (1976). I followed his basic method closely.

[7]B. M. McCoy and T. T. Wu, *The Two-Dimensional Ising Model* (Harvard, Cambridge, 1973).

[8]P. C. Hemmer and J. L. Lebowitz, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5B.

[9]M. E. Fisher and R. J. Burford, Phys. Rev. **156**, 583 (1967).