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Gaussian Ensemble as an Interpolating Ensemble

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We consider a noncanonical ensemble which involves a sample thermally connected to a *finite* heat bath with specific properties. Treating the size of the heat bath as a parameter, we show that static properties of finite samples are ensemble dependent. Monte Carlo simulations of phase transitions in Potts models confirm the analysis and demonstrate significant reductions in computer time (sometimes by a factor of 100) compared to canonical-ensemble simulations. For finite samples, second-order transitions are sharpened and are clearly distinguished from first-order transitions as the heat bath becomes smaller.

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Computer simulations of model Hamiltonians involve closed systems consisting of a sample, whose properties we are seeking, in contact with a heat bath. If N and N' are the number of particles in the sample and heat bath, respectively, there are two broad classes of ensembles: those where N' is infinite (such as the canonical ensemble) and that where $N'=0$ (microcanonical ensemble). Well known examples are the Monte Carlo method of Metropolis *et al.*[1] using the canonical ensemble and the molecular-dynamics method of Alder and Wainwright[2] involving the microcanonical one.

Systematic differences can arise between results using different ensembles purely because of finite N. The most dramatic of these occur at first-order transitions when we examine, for example, the temperature $(1/\beta)$ versus energy (E) curves. An isolated (i.e., microcanoncial) system can go through a first-order phase transition by means of a succession of intermediate coexistence states. If the system is finite, it will exhibit a negative specific heat due to interfacial tension, and van der Waals loops would show up if $\beta(E)$ is evaluated in the microcanonical ensemble. It is known that such loops sometimes occur in molecular-dynamics simulations.[3,4] The coexistence states, however, have very low probability in the canonical ensemble so that energy distributions are double peaked and $\beta(E)$ simply possesses an inflection point[5] like at a continuous transition.

The major objective of this paper is to interpret the Gaussian ensemble introduced recently by one of us (J.H.H.)[6] as an interpolating ensemble and thereby account for ensemble-dependent effects in finite systems for the first time. van der Waals loops at first-order transitions are shown to be a small-N' effect, and, by applying the technique to second-order transitions, we demonstrate that the method is a valuable tool for diagnosing the order of a transition.

Let S and E be the entropy and energy of the sample and let primes denote the corresponding quantities of the "thermometer" (a small heat bath). All quantities are extensive unless otherwise stated. We adopt the view that the static properties of the sample are described uniquely by its density of states, $\rho(E)=\exp[S(E)]$, and that the thermometer is a tool for probing the derivatives of $S(E)$ by measurement of the moments $\langle E\rangle$, $\langle E^2\rangle$, etc.

The total energy of the closed system is $E_t = E + E'$, the total entropy is $S_t(E) = S + S'$, and the distribution is $P(E) \propto \exp[S_t(E)]$. The Gaussian ensemble is obtained[6] by the specification $S' = -aE'^2 = -a(E_t - E)^2$. a (>0) is the constant curvature of S' and is obviously of order $1/N'$. We shall henceforth refer to a instead of N' as a parameter. The method is readily implemented as a Monte Carlo process since the probability of a configuration of energy E_μ is $P(E_\mu) \propto \exp[-a(E_\mu - E_t)^2]$.

For a given set of input parameters $\{a, E_t, N\}$ let the most probable energy for the sample be $\tilde{E}$. Expanding $S_t(E)$ about $\tilde{E}$ we obtain, up to second order in small fluctuations of energy,

$$S_t(E) = S_t(\tilde{E}) + \left\{ \frac{\partial S}{\partial E} + \frac{\partial S'}{\partial E} \right\}_{\tilde{E}} (E - \tilde{E}) + \frac{1}{2} \left\{ \frac{\partial^2 S}{\partial E^2} + \frac{\partial^2 S'}{\partial E^2} \right\}_{\tilde{E}} (E - \tilde{E})^2 + \cdots . \quad (1)$$

Consistent with thermodynamics, we define the inverse temperature, β, and the heat capacity, C, through $\beta = \partial S / \partial E$ and $C = -\beta^2 (\partial^2 S / \partial E^2)^{-1}$. Requiring $S_t(\tilde{E})$ to be a maximum yields $\tilde{\beta} = 2a(\tilde{E} - E_t)$ and

$$(\tilde{\beta}/\tilde{C})^2 + 2a > 0. \quad (2)$$

The tildes indicate that the quantities are the true (microcanonical) values and are to be evaluated at $\tilde{E}$. The expansion (1) implies that $P(E)$ is a Gaussian and we obtain readily $\langle E \rangle = \tilde{E}$, $\langle \beta \rangle = \tilde{\beta} = 2a(\langle E \rangle - E_t)$, and

$$\langle C \rangle = \tilde{C} = \tilde{\beta}^2 G_2 / (1 - 2aG_2), \quad (3)$$

where we have introduced the notation $G_n = \langle (E - \langle E \rangle)^n \rangle$, $n = 2, 3, 4, \ldots$. The limit $a \to 0$, $-2aE_t \to \beta$ yields the canonical ensemble while the $a \to \infty$, $E_t \to E$ limit is the microcanonical case; thus the Gaussian ensemble interpolates smoothly between these extremes. Equation (3) recovers the canonical-ensemble definition of $\langle C \rangle$ in the limit $a \to 0$ and it can be shown that, for a given bath (a fixed), (3) is identical to the definition $\langle C \rangle = -\langle \beta \rangle^2 (\partial \langle E \rangle / \partial \langle \beta \rangle)$. For $a > 0$, it is possible for $\langle C \rangle$ to be negative as long as (2) is obeyed; thus van der Waals loops are permitted for finite N'.

While the above formulas are adequate for the estimation of $\tilde{E}$ and $\tilde{\beta}$ over most of the range of E, a-dependent deviations become significant near phase transitions because of large fluctuations. We approximate the leading-order corrections by accounting for the third-order term in (1) as follows. Let $\tilde{S}_3 = (1/3!)(d^3 S / dE^3)_{\tilde{E}}$ and $z = 3\tilde{S}_3 \tilde{C}^2 / (\tilde{\beta}^2 + 2a\tilde{C})^2$. By approximating $\exp(x^3) = 1 + x^3$, we obtain

$$z^3 + z(G_2/2) - (G_3/4) = 0, \quad (4)$$

$$\frac{\tilde{E}}{N} = \frac{\langle E \rangle}{N} - \frac{z}{N}, \quad (5a)$$

and

$$\tilde{\beta} = \langle \beta \rangle - 2az. \quad (5b)$$

z denotes the deviations of $\langle E \rangle$ and $\langle \beta \rangle$ from $\tilde{E}$ and $\tilde{\beta}$ and can be numerically evaluated since Eq. (4) has only one real root. z is a function of a and, for finite N, the curves $\langle \beta \rangle$ vs $\langle E \rangle$ will in general depend on a through (5). The microcanonical results, $\langle \beta \rangle \to \tilde{\beta}$ and $\langle E \rangle \to \tilde{E}$, are recovered when $a \to \infty$ and the canonical limit yields correctly $\langle \beta \rangle \to \tilde{\beta}$ and corrections of order unity in $\langle E \rangle$. That these ensemble-dependent deviations vanish for macroscopic systems is evident by our taking $N \to \infty$ while retaining $\lambda (\propto aN) = N/N' = \text{const}$; the corrections then vanish independent of the value of λ.

Since $z \propto \partial^2 \beta / \partial E^2$, Eqs. (5) show that inflection points in $\beta(E)$, denoted $\{\beta^*, E^*\}$, are "fixed points" with respect to N' and thus β^* provides an alternative choice for the transition temperature of the sample. Note that far from phase transitions $P(E)$ is a Gaussian ($G_3 = 0$) and thus $\beta = 0$ and ∞ represent trivial fixed points. Though the fixed points are a leading-order effect, we noticed significant a dependences in β^* only at asymmetric first-order transitions; the equal-area construction[6] then provides a better definition for the transition temperature.

In practice, the microcanonical limit is reached when a is of the order of the maximum of $\partial \beta / \partial E$ (0.01–0.1 for Potts models on 8×8 lattices). It is then possible to estimate $\rho(E/N)$ by integration of the $\langle \beta \rangle$ vs $\langle E \rangle$ curve for the largest value of a and thereby obtain $\langle \beta \rangle$ vs $\langle E \rangle$ for all smaller values of a. As will be seen, such calculations agree very well with data from simulations.

We illustrate the validity of the above analysis through simulations of q-state Potts models on $L \times L$

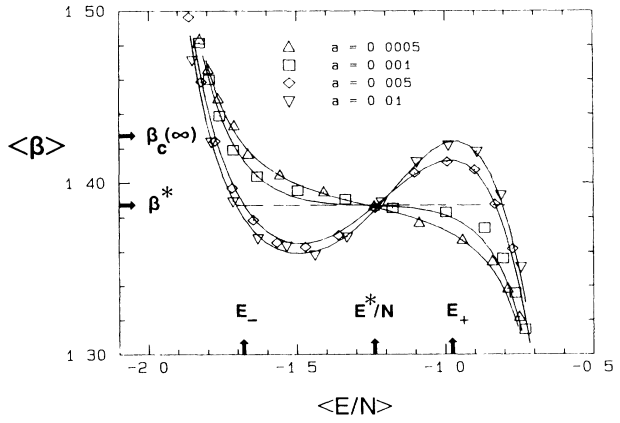

FIG. 1. Typical $\langle \beta \rangle$ vs $\langle E \rangle / N$ curves for various a at a first-order transition. Symbols are data from simulations of the $q = 10$ Potts model on an 8×8 lattice and are averages over 200000 MCS each. Curves are predictions using the data for $a = 0.05$ (not shown) to estimate $\rho(E/N)$. Horizontal dashed line is from the equal-area construction for $a = 0.01$. The notation is explained in the text.

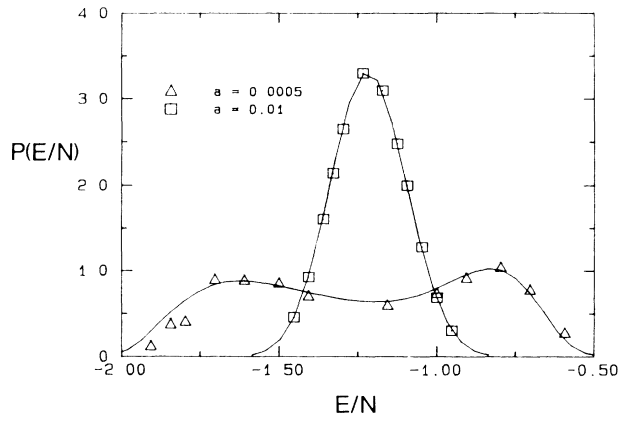

FIG. 2. Energy distributions, $P(E/N)$, in the vicinity of $\{\beta^*, E^*\}$ of Fig. 1 for $a=0.01$ and 0.0005. Symbols represent data and the curves are predictions as explained in Fig. 1 near the fixed point. The probability distribution develops two peaks when the $\beta(E)$ curves do not show a van der Waals loop ($a=0.0005$ and 0.001 in Fig. 1).

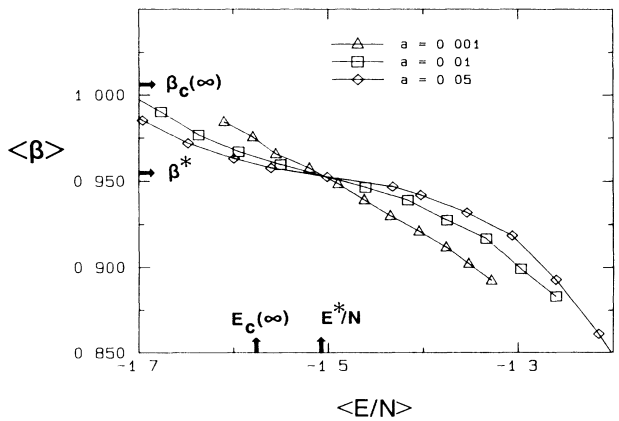

FIG. 3. Typical $\langle\beta\rangle$ vs $\langle E\rangle/N$ curves for various a at a second-order transition. Symbols represent data for the $q=3$ Potts model on an 8×8 lattice. Data in the transition region are averages over 10^6 MCS. Some data have been omitted to preserve the clarity. The curves are straight-line interpolations between data points.

($=N$) lattices. These models are convenient for our purpose since the nature of the transition is q dependent and many of the properties such as the nature of the transition and the transition temperatures are exactly known.[7-9] The following notation is used below. $\beta_c(\infty)$ is the inverse of the infinite-lattice transition temperature. Energies *per site* at the transitions in the infinite lattice are denoted by $E_c(\infty)$ if the transition is second order and by E_- and E_+ at a first-order transition. (These values are given in Refs. 7 and 8.) The notation $\beta^*(L)$ emphasizes the L dependence of β^*. Computing times are in terms of Monte Carlo steps per site (MCS).

Figure 1 shows typical $\langle\beta\rangle$ vs $\langle E\rangle$ plots at the first-order transition in the $q=10$ model. While the β^* values from the fixed-point rule and equal-area construction agree as shown in the figure, such a coincidence does not happen at highly asymmetric transitions. Data for G_3 (not shown) confirm that this quantity vanishes at β^*. The van der Waals loop disappears for small a because it is more favorable for the system to develop a double-peaked distribution where the specific heats corresponding to the two peaks are positive. This is explicitly shown in Fig. 2 where we have plotted the distributions in the vicinity of the transition. As expected from the analysis following Eqs. (5), the N' effects vanish as $N\rightarrow\infty$ and the loops shrink to a horizontal straight line in the limit. Using lattices up to 20×20, we found that $\beta_c(\infty)-\beta^*(L)\propto N^{-1}$ in agreement with earlier work.[5]

Figure 3 shows the behavior of $\beta(E)$ at the second-order transition in the $q=3$ model. The van der Waals loops are conspicuous by their absence (no a dependences were observed for $a>0.05$) and thus the method provides an unambiguous diagnosis of the order of the transition. We have also verified that the method clearly distinguishes the second-order transition for $q=4$ and the weak first-order transition for $q=5$. (Of course, careful extrapolations as $N\rightarrow\infty$ are unavoidable for a conclusive diagnosis.) Using den Nijs's value[10] of $\frac{5}{6}$ for the critical exponent[11] ν for $q=3$, we found that $\beta_c(\infty)-\beta^*(L)\propto L^{-1/\nu}$ in agreement with theoretical conjectures.[12]

The specific-heat data at the above second-order transition are striking. As shown in Fig. 4, we get the distinct impression that a cusp in C is developing for large a. While it is evident from Fig. 4 that a sharp transition in a finite sample would be smeared when the canonical ensemble is used, there is no easy extension to the microcanonical limit since $\rho(E/N)$ is discrete for discrete models (such as Potts models) on a finite sample and the

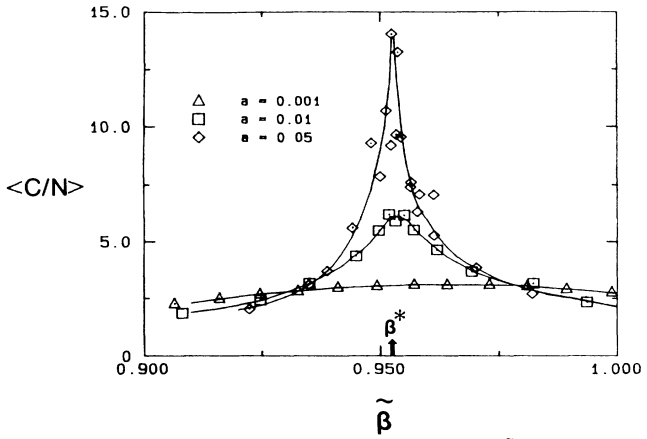

FIG. 4. Specific heat, $\langle C\rangle/N$, as a function of $\tilde{\beta}$ for the data of Fig. 3. $\langle C\rangle$ is obtained through Eq. (3) and $\tilde{\beta}$ from Eq. (5b). The curves are smooth guides to the eye. The second-order transition is remarkably sharpened as one moves away from the canonical ensemble.

derivatives of $\rho(E/N)$ are highly singular. But the finite a in our simulations means that we are sampling a smooth envelope of the singularities. Perhaps we can meaningfully refer to an extrapolation to $a=\infty$ but not the limit itself! Finally, while we find that the maximum in C grows with L, any finite-size analysis of the data is not feasible at present because of the theoretical and numerical difficulties.

In conclusion, we have used the interpolating nature of the Gaussian ensemble to show how static properties of finite systems become ensemble dependent. The successful prediction of the N' effects in Figs. 1 and 2 together with the phenomena of Fig. 4 indicate that the density of states is the key to understanding finite systems. Note that the analysis has been facilitated by the complete specification of S'. Such a treatment should also be possible with Creutz's interpolating ensemble[13] if S' can be determined for his method.

Computationally, the method is advantageous because (1) it involves Monte Carlo sampling and (2) it can approach the microcanonical limit. The first point implies that, unlike molecular dynamics, the technique is applicable even to stochastic models and that ergodicity is less of a problem. Thus the loops are easily reproducible and become better defined as the computation time is increased. (Contrast this with recent molecular-dynamics results of Jellinek, Beck, and Berry[14] where the loops of Ref. 3 disappeared when long-time averages were taken.) The second point significantly reduces the computer time at a first-order transition since, by using a sufficiently large value of a, we can directly sample the two-phase states. This avoids the double-peaked distributions and the resultant hystereses which are characteristic of canonical-ensemble simulations. Since the maxima of $P(E)$ grow with N, this feature becomes particularly attractive when large lattices are involved. For example, we found a van der Waals loop and obtained a good estimate of $\beta_c(\infty)$, E_+, and E_- for the $q=10$ Potts model on a 50×50 lattice with only 5000 MCS; similar results with the canonical ensemble required over 10^6 MCS.[5]

Several new directions of research are available. For instance, we can study nucleation processes at first-order transitions and formulate detailed theories for the van der Waals loops. Second-order transitions in finite systems now deserve a closer look especially since we find that specific-heat data for the Ising model in three dimensions are similar to those of Fig. 4 while no "sharpening" was seen in an Ising paramagnet. We need to see if the cusps exist and if so, whether the critical exponents have their infinite-lattice values. Such a development would yield a deeper understanding of critical phenomena.

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