Monte Carlo methods for the study of phase transitions and phase equilibria

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Abstract. Monte Carlo methods can predict macroscopic properties of N-body systems from the (classical) Hamiltonian describing the interactions between the particles and hence can serve as a basic tool of equilibrium statistical mechanics, avoiding uncontrolled approximations. However, a necessary ingredient is the control of finite size effects. For this purpose, the finite size scaling analysis of suitable distribution functions is a powerful tool. The basic ideas of this approach will be discussed, including extensions to critical phenomena where the hyperscaling relation between critical exponents is violated (colloid-polymer mixtures in random media as a realization of the random field Ising model, phase transitions caused by competition of interfacial and surface effects, etc.) Finite size effects on two-phase coexistence cause the existence of a van-der-Waals-like loop, but it has a completely different origin, the “spinodal” reflecting the “droplet evaporation/condensation” transition. Also the possibility to extract interface free energies is discussed.

PACS. 02.70.Uu Applications of Monte Carlo methods – 05.10.Ln Monte Carlo methods – 05.70.Jk Critical point phenomena

1 Introduction: why equilibrium statistical mechanics needs Monte Carlo simulation

The statistical mechanics of classical systems in thermal equilibrium starts with Ludwig Boltzmann: The statistical definition of the entropy, \( S = k \ln W \), a formula engraved on his tomb, provides a connection between the microscopic atomic description of a many-body system with macroscopic thermodynamics. Here \( W \) is the number of “microstates” of the system belonging to a thermodynamic state characterized by macroscopic thermodynamic variables (energy \( E \), volume \( V \), and particle number \( N \)). In a closed, thermally isolated system \( S \) takes a maximum, the corresponding statistical distribution then being the microcanonical ensemble [1]. As is well-known, in the thermodynamic limit \( N \to \infty \) an equivalent description results when we put the system in a heat bath, specifying the temperature \( T \). Thermal equilibrium then is characterized by the minimum of the free energy \( F \), that is then linked to the microstates via the partition function \( Z \), Boltzmann’s constant now being denoted as \( k_B \).

\[
F = -k_B T \ln Z = \int dX \exp[-\mathcal{H}(X)/k_B T]
\]  

where \( X \) denotes a point in phase space, and \( \mathcal{H}(X) \) the (classical) Hamiltonian of the system. Equation (1) also includes cases where the integration of the Boltzmann factor \( \exp(-\mathcal{H}/k_B T) \) over all phase space rather is a summation, such as in the case of the Ising model

\[
\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j, \quad S_i = \pm 1.
\]  

Here the sum is extended once over all nearest-neighbor pairs of sites \( \{i,j\} \) on the lattice, and \( X \) is a discrete set of \( 2^N \) states \( \{S_i = \pm 1, i = 1, \ldots, N\} \). The associated probability distribution \( P_{\text{eq}}(X) \) that a state \( X \) occurs defines the well-known canonic ensemble, from which averages of any observables \( A(X) \) can be calculated,

\[
\langle A \rangle = \int dX P_{\text{eq}}(X) A(X),
\]

\[
P_{\text{eq}}(X) = \left(1/Z\right)\exp[-\mathcal{H}(X)/k_B T].
\]  

This theoretical framework is perfectly well-defined; however, the task is difficult since apart from non-interacting systems such as the ideal gas, ideal paramagnet etc. Equation (3) can be worked out exactly only for very few exactly soluble models [2]. Although these exact solutions provide very valuable guidance, there is nevertheless the need to find a way to deal with equation (3) in the general case where no exact solution is available.

One then often postulates the existence of a coarse-grained description: e.g., in the case of the Ising model,
one sums over all the spins inside a coarse-graining cell of volume \( L^d_{cg} \) (in \( d \) dimensions) to obtain an order parameter field in the continuum, \( \phi(x) = L^d_{cg} \sum S_i \); here \( x \) is the center of mass of this coarse-graining cell. The free energy then is written as a path integral [3–5],

\[
F = -k_B T \ln \int D\phi(x) \exp[-\mathcal{F}\{\phi(x)\}/k_BT]; \quad (4)
\]

the Boltzmann factor now contains a free energy functional \( \mathcal{F}\{\phi(x)\} \) rather than the microscopic Hamiltonian.

Although this formulation is very valuable, as a starting point for the insightful renormalization group theory [3–5] of critical phenomena, it must be stressed that it is a major unsolved problem to carry out the step from \( \mathcal{H} \) to \( \mathcal{F} \) explicitly in a quantitative way. So \( \mathcal{F} \) is rather phenomenologically assumed than calculated. Equation (4) also is the starting point of the Landau theory [1] of phase transitions, where one ignores fluctuations, putting \( \phi(x) = m \), average value of the order parameter (e.g. magnetization of a ferromagnet).

Then

\[
F = -k_B T \ln \int dm Z(m) = -k_B T \ln \int dm \exp[-L^d f(m)/k_BT] \quad (5)
\]

with

\[
f(m) = \frac{1}{2} r'(T/T_c - 1)m^2 + \frac{1}{4} am^4, \quad (6)
\]

where \( T_c \) is the critical temperature of the second order phase transition, and \( r', a \) are positive constants.

As will be emphasized below, Monte Carlo simulations allow to compute the constrained partition function

\[
Z(m) = \sum_{\{S_i=\pm 1\}} \delta(m - \sum_i S_i/L^d) \exp[-\mathcal{H}\{S_i\}/k_BT] \quad (7)
\]

or the related order parameter distribution function

\[
P(m) = Z(m)/Z \quad (8)
\]

directly from the Hamiltonian, avoiding any approximations. It will be shown that analysis of such distributions is very useful and rewarding.

As it is well known Landau theory can not provide an accurate description of phase transitions, of course. One finds power laws for the spontaneous magnetization \( m_c \) and susceptibility \( \chi \) with exponents \( \beta = 1/2, \gamma = 1, \) \( \chi \propto (1 - T/T_c)^{\gamma} \), \( (dm/d\mathcal{H})_T \propto [1 - T/T_c]^{-\beta} \), \( H \) being the field conjugate to the order parameter. A related finding holds for the correlation length \( \xi, \xi \propto [1 - T/T_c]^{-\nu}, \nu = 1/2 \). Moreover a plot of \( m \) vs. \( H \) exhibits a spurious loop (with \( \chi < 0 \) in the region in between the spinodals \( \pm m_{sp}, -m_{sp} < m < m_{sp} \), rather than exhibiting the jump from \( -m_{sp} \) to \( +m_{sp} \) at \( H = 0 \).

Similar problems occur with approximate theories of other first or second order phase transitions. For instance, as a description of the evaporation/condensation transition of fluids, one teaches the van der Waals equation to the students in the statistical mechanics courses. Again it predicts wrongly the singularities near the critical point, and phase coexistence needs to be put in “by hand” with the ad hoc Maxwell construction. The predicted spinodal curve is a mean-field artefact, it has nothing to do with the actual limit of metastability, which requires to consider nucleation [6]: the actual limit of metastability occurs if the nucleation free energy barrier is (at least) \( \Delta F^* / k_BT \approx 10 \). For systems with short range forces, this occurs rather close to the coexistence curve [6,7]. The spinodal (where \( \Delta F^* = 0 \)) is ill-defined, apart from systems with long range forces [6–9].

These phase transitions of the Ising magnet or of a simple fluid are just two examples out of many phenomena one likes to explain, on the basis of the underlying Hamiltonian, using statistical mechanics. This task can be solved by the importance sampling Monte Carlo Method [10–14]. This algorithm replaces the exact average of an observable \( A(X) \)

\[
\langle A(X) \rangle = \int dX P_{eq}(X) A(X),
\]

\[
P_{eq}(X) = (1/Z) \exp[-\mathcal{H}(X)/k_BT] \quad (9)
\]

by the arithmetic average over \( M \) points \( X_\nu \) sampled from phase space

\[
\bar{A} = (1/M) \sum_{\nu=1}^M A(X_\nu), \quad (10)
\]

since the points \( X_\nu \) are chosen with a probability proportional to \( P_{eq}(X_\nu) \) for large enough \( M \) [10–14]. Thus, Monte Carlo sampling provides the tool by which the connection between macroscopic thermodynamic properties of a system and its atomistic description in terms of the Hamiltonian can be established in practice.

### 2 A major stumbling block: finite size effects

However, it is important to recognize that Monte Carlo computer simulations may suffer from various sources of error, such as correlations between the used pseudorandom numbers, correlations between the subsequently generated microstates \( X_\nu \) of the system, possible lack of ergodicity of the algorithm since the states generated via the Markov chain may sample only a pocket of phase space rather than the full space, etc. Although the statement attributed to J.v. Neumann “Anyone using Monte Carlo is in a state of sin!” can be refuted, it is necessary to carefully pay attention to the limitations of the method [11–14]. In the context of the study of phase transitions and phase equilibria, a particular fundamental problem concerns the finite size of the simulated system, since one knows [1] that phase transitions in a strict sense can occur only in the thermodynamic limit, \( N \to \infty \). While this caveat in principle applies also to experiment, there \( N \approx 10^{22} \) is so large