Another way to determine the nature of a phase transition is to use the Binder cumulant method. The cumulant is defined by

$$U_L \equiv 1 - \frac{\langle E^4 \rangle}{3 \langle E^2 \rangle^2}. \tag{15.60}$$

It can be shown that the minimum value of U_L is

$$U_{L,\min} = \frac{2}{3} - \frac{1}{3} \left(\frac{E_+^2 - E_-^2}{2E_+ E_-} \right)^2 + O(L^{-d}), \tag{15.61}$$

where E_+ and E_- are the energies of the two phases in a first-order transition. These results are derived by considering the distribution of energy values to be a sum of Gaussians about each phase at the transition, which become sharper and sharper as $L \to \infty$. If $U_{L,\min} = 2/3$ in the infinite size limit, then the transition is continuous.

Problem 15.29 The Binder cumulant and the nature of the transition

(a) Suppose that the energy in a system is given by a Gaussian distribution with a zero mean. What is the corresponding value of U_L?

(b) Consider the two-dimensional Ising model in the absence of a magnetic field and consider the cumulant

$$V_L \equiv 1 - \frac{\langle M^4 \rangle}{3 \langle M^2 \rangle^2}. \tag{15.62}$$

Compute V_L for a temperature much higher than T_c. What is the value of V_L? What is the value of V_L at $T = 0$?

(c) Compute V_L for values of T in the range $2.20 \le T \le 2.35$ for $L = 10$, 20, and 40. Plot V_L as a function of T for these three values of L. Note that the three curves for V_L cross at a value of T that is approximately T_c. What is the approximate value of V_L at this crossing? Can you conclude that the transition is continuous?

(d) Repeat Problem 15.28 using the Binder cumulant method and determine the nature of the transition. ∎

*15.12 ∎ OTHER ENSEMBLES

So far, we have considered the microcanonical ensemble (fixed N, V, and E) and the canonical ensemble (fixed N, V, and T). Monte Carlo methods are very flexible and can be adapted to the calculation of averages in any ensemble. Two other ensembles of particular importance are the constant pressure and the grand canonical ensembles. The main difference in the Monte Carlo method is that there are additional moves corresponding to changing the volume or changing the number of particles. The constant pressure ensemble is particularly important for studying first-order phase transitions because the phase transition occurs at a fixed pressure, unlike a constant volume simulation where the system passes through a two-phase coexistence region before changing phase completely as the volume is changed.

In the NPT ensemble, the probability of a microstate is proportional to $e^{-\beta(E+PV)}$. For a classical system, the mean value of a physical quantity A that depends on the positions of the particles can be expressed as

$$\langle A \rangle_{NPT} = \frac{\int_0^\infty dV \, e^{-\beta PV} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N A(\{\mathbf{r}\}) \, e^{-\beta U(\{\mathbf{r}\})}}{\int_0^\infty dV \, e^{-\beta PV} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N \, e^{-\beta U(\{\mathbf{r}\})}}. \tag{15.63}$$

The potential energy $U(\{\mathbf{r}\})$ depends on the set of particle coordinates $(\{\mathbf{r}\})$. To simulate the NPT ensemble, we need to sample the coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ of the particles and the volume V of the system. For simplicity, we assume that the central cell is a square or a cube so that $V = L^d$. It is convenient to use the set of scaled coordinates $\{\mathbf{s}\}$, where $\mathbf{s}_i$ is defined as

$$\mathbf{s}_i = \frac{\mathbf{r}_i}{L}. \tag{15.64}$$

If we substitute (15.64) into (15.63), we can write $\langle A \rangle_{NPT}$ as

$$\langle A \rangle_{NPT} = \frac{\int_0^\infty dV \, e^{-\beta PV} V^N \int d\mathbf{s}_1 \, d\mathbf{s}_2 \cdots d\mathbf{s}_N A(\{\mathbf{s}\}) \, e^{-\beta U(\{\mathbf{s}\})}}{\int_0^\infty dV \, e^{-\beta PV} V^N \int d\mathbf{s}_1 \, d\mathbf{s}_2 \cdots d\mathbf{s}_N \, e^{-\beta U(\{\mathbf{s}\})}}, \tag{15.65}$$

where the integral over $\{\mathbf{s}\}$ is over the unit square (cube). The factor of V^N arises from the change of variables $\mathbf{r} \to \mathbf{s}$. If we let $V^N = e^{\ln V^N} = e^{N \ln V}$, we see that the quantity that is analogous to the Boltzmann factor can be written as

$$e^{-W} = e^{-\beta PV - \beta U(\{\mathbf{s}\}) + N \ln V}. \tag{15.66}$$

Because the pressure is fixed, a trial configuration is generated from the current configuration by either randomly displacing a particle or making a random change in the volume, for example, $V \to V + \delta(2r - 1)$, where r is a uniform random number in the unit interval and δ is the maximum change in volume. The trial configuration is accepted if the change $\Delta W \le 0$ and with probability $e^{-\Delta W}$ if $\Delta W > 0$. It is not necessary or efficient to change the volume after every Monte Carlo step per particle.

In the grand canonical or μVT ensemble, the chemical potential μ is fixed and the number of particles fluctuates. The average of any function of the particle positions can be written (in three dimensions) as

$$\langle A \rangle_{\mu VT} = \frac{\sum_{N=0}^\infty (1/N!) \, \lambda^{-3N} e^{\beta \mu N} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N A(\{\mathbf{r}\}) \, e^{-\beta U_N(\{\mathbf{r}\})}}{\sum_{N=0}^\infty (1/N!) \, \lambda^{-3N} e^{\beta \mu N} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N \, e^{-\beta U_N(\{\mathbf{r}\})}}, \tag{15.67}$$

where $\lambda = (h^2 / 2\pi mkT)^{1/2}$. We have made the N-dependence of the potential energy U explicit. If we write $1/N! = e^{-\ln N!}$ and $\lambda^{-3N} = e^{-N \ln \lambda^3}$, we can write the quantity that is analogous to the Boltzmann factor as

$$e^{-W} = e^{\beta \mu N - N \ln \lambda^3 - \ln N! + N \ln V - \beta U_N}. \tag{15.68}$$

If we write the chemical potential as

$$\mu = \mu^* + kT \ln(\lambda^3 / V), \tag{15.69}$$