In many respects, computer simulations resemble experiments. Yet, in the study of first-order phase transitions, there seems to be a difference. In experiments, a first-order phase transition is easy to locate: at the right density and temperature, we will observe that an initially homogeneous system will separate into two distinct phases, divided by an interface. Measurement of the properties of the coexisting phases is then quite straightforward. In contrast, in a simulation we often locate a first-order phase transition by computing the thermodynamic properties of the individual phases, then finding the point where the temperature, pressure, and chemical potential(s) of the two bulk phases are equal.

The reason we are usually forced to follow this more indirect route in a simulation is related to the small size of the system studied. If two phases coexist in such systems, a relatively large fraction of all particles resides in or near the interface dividing the phases. To estimate this effect, consider the idealized case that we have a cubic domain of one phase, surrounded by the other. We assume that the outermost particles in the cube belong to the interface and that the rest is bulk-like. The fraction of particles in the interface depends on the system size. As can be seen in Table 8.1, systems with fewer than 1000 particles are interface dominated. And, even for quite large systems, the fraction of particles in the interface is nonnegligible. It is essential therefore to use relatively large systems to calculate reliable coexistence properties. Unfortunately, for large systems long equilibration times are needed, not only because the systems contain many particles, but also because equilibration times in two-phase systems tend to be longer than those in homogeneous systems.
Chapter 8. The Gibbs Ensemble

<table>
<thead>
<tr>
<th>N</th>
<th>125</th>
<th>1,000</th>
<th>64,000</th>
<th>1,000,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{int}}$</td>
<td>78%</td>
<td>49%</td>
<td>14%</td>
<td>6%</td>
</tr>
</tbody>
</table>

**Table 8.1:** Percentage of particles ($P_{\text{int}}$) in the interface of a cubic domain containing $N$ particles. Only the outermost particles are assumed to belong to the interface.

Direct simulations of first-order phase coexistence therefore often are computationally rather expensive.\(^1\) However, in the mid-1980s, Panagiotopoulos [94] devised a new computational scheme for studying first-order phase transitions. This scheme has many of the advantages of a direct simulation of coexistence yet few of its disadvantages. Where applicable, this scheme (usually referred to as the *Gibbs ensemble method*) results in a very significant reduction of the computer time required for phase equilibrium calculations. With this method, phase equilibria can be studied in a single simulation. At present, the Gibbs ensemble method has become the technique par excellence to study vapor-liquid and liquid-liquid equilibria. However, like simulations in the grand-canonical ensemble, the method does rely on a reasonable number of successful particle insertions to achieve compositional equilibrium. As a consequence, the Gibbs ensemble method is not very efficient for studying equilibria involving very dense phases. However, there is a technique that greatly facilitates the numerical study of phase equilibria of dense phases. This is the so-called *semigrand ensemble method* of Kofke and Glandt [198], which is discussed in Chapter 9.

The success of the Gibbs ensemble method relies on the possibility of exchanging particles between the two coexisting phases. If one of the coexisting phases is a crystal, one would need to find a vacancy in order to insert a particle. However, the equilibrium concentration of such defects is usually so low that the conventional Gibbs ensemble method becomes impractical. Tilwani and Wu [199] suggested an alternative approach in which an atom is added to the unit box of the solid and this new unit box is used to fill up (tile) space. In this way particles can be added or removed from the system, while the crystal structure is maintained. Tilwani and Wu showed that for the two-dimensional square-well fluid, their method agrees well with the results from free energy calculations [200].

---

\(^1\)It should be pointed out, though, that, as computers become more powerful, the direct method becomes increasingly attractive because of its simplicity.
The condition for coexistence of two or more phases I, II, ... is that the pressure of all coexisting phases must be equal (\(P_1 = P_{II} = \cdots = P\)), as must be the temperature (\(T_1 = T_{II} = \cdots = T\)) and the chemical potentials of all species (\(\mu_1 = \mu_{II} = \cdots = \mu\)). Hence, one might be inclined to think that the best ensemble for studying would be the "constant-\(\mu\)PT ensemble". The quotation marks around the name of this "ensemble" are intentional, because, strictly speaking, no such ensemble exists. The reason is simple: if we specify only intensive parameters, such as \(P\), \(T\), and \(\mu\), the extensive variables (such as \(V\)) are unbounded. Another way to say the same thing is that the set \(P, T, \mu\) is linearly dependent. To get a decent ensemble, we must fix at least one extensive variable. In the case of constant-pressure Monte Carlo simulations this variable is the number of particles \(N\), while in grand-canonical Monte Carlo the volume \(V\) of the system is fixed.

After this introduction, it may come as a surprise that the Gibbs ensemble method of Panagiotopoulos [94, 147] comes very close to achieving the impossible: simulating phase equilibria under conditions where the pressure, temperature, and chemical potential(s) of the coexisting phases are equal. The reason this method can work is that, although the difference between chemical potentials in different phases is fixed (namely, at \(\Delta \mu = 0\)), the absolute values are still undetermined. Here, we show how the Gibbs ensemble method can be derived, following the approach developed in the previous chapters.

At this stage, we focus on the version of the Gibbs ensemble where the total number of particles and the total volume of the two boxes remain constant; that is, the total system is at \(N, V, T\) conditions. The description of the \(N, P, T\) version can be found in [147]. This constant-\(P\) method can be applied only to systems containing two or more components because in a one-component system, the two-phase region is a line in the \(P-T\) plane. Hence, the probability that any specific choice of \(P\) and \(T\) will actually be at the phase transition is vanishingly small. In contrast, for two-component systems, the two-phase region corresponds to a finite area in the \(P-T\) plane.

Note that in either formulation of the Gibbs method, the total number of particles is fixed. The method can be extended to study inhomogeneous systems [146] and is particularly suited to study phase equilibria in multicomponent mixtures [147]. A review of applications of the Gibbs ensemble technique is given in [201]. The great advantage of the Gibbs method over the conventional techniques for studying phase coexistence is that, in the Gibbs method, the system spontaneously "finds" the densities and compositions of the coexisting phases. Hence, there is no need to compute the relevant chemical potentials as a function of pressure at a number of different
compositions and then construct the coexistence line.

8.2 The Partition Function

In his original article [94], Panagiotopoulos introduced the Gibbs ensemble as a combination of the N, V, T ensemble, N, P, T ensemble, and μ, V, T ensemble. In the previous section we stated that the Gibbs ensemble is not a "constant-μ, P, T ensemble", but we did not say what ensemble it actually corresponds to. This point is considered in detail in Appendix H, where we demonstrate that, in the thermodynamic limit, the (constant-V) Gibbs ensemble is rigorously equivalent to the canonical ensemble.

We start our discussion with the expression for the partition function for a system of N particles distributed over two volumes V1 and V2 = V - V1, where the particles interact with each other in volume 1 but behave like an ideal gas in volume 2 (see equation (5.6.1)):

\[ Q(N, V_1, V_2, T) = \sum_{n_1=0}^{N} \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{\Lambda^{3N}n_1!(N-n_1)!} \int ds_2^{N-n_1} \int ds_1^{n_1} \exp[-\beta U(s_1^{n_1})]. \]

To derive the partition function of the grand-canonical ensemble (section 5.6), we assumed that the particles in volume V2 behaved as ideal gas molecules. Now we consider the case that the particles in both volumes are subject to the same intermolecular interactions and that the volumes V1 and V2 can change in such a way that the total volume V = V1 + V2 remains constant (see Figure 8.1). In this case, we have to integrate over the volume V1, which gives, for the partition function [201–203],

\[ Q_G(N, V, T) = \sum_{n_1=0}^{N} \frac{1}{V^{3N}n_1!(N-n_1)!} \int_0^V dV_1 V_1^{n_1}(V - V_1)^{N-n_1} \int ds_1^{n_1} \exp[-\beta U(s_1^{n_1})] \int ds_2^{N-n_1} \exp[-\beta U(s_2^{N-n_1})]. \]

(8.2.1)

From the preceding expressions, it follows that the probability of finding a configuration with n1 particles in box 1 with a volume V1 and positions s_1^{n_1} and s_2^{N-n_1} is given by

\[ \mathcal{N}(n_1, V_1, s_1^{n_1}, s_2^{N-n_1}) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp \left\{ -\beta [U(s_1^{n_1}) + U(s_2^{N-n_1})] \right\}. \]

(8.2.2)

We shall use equation (8.2.2) to derive the acceptance rules for trial moves in Gibbs ensemble simulations.
8.3 Monte Carlo Simulations

Equation (8.2.2) suggests the following Monte Carlo scheme for sampling all possible configurations of two systems that can exchange particles and volume. In this scheme, we consider the following trial moves (see Figure 8.2):

1. Displacement of a randomly selected particle.
2. Change of the volume in such a way that the total volume remains constant.
3. Transfer of a randomly selected particle from one box to the other.

The acceptance rules for these steps in the Gibbs ensemble can be derived from the condition of detailed balance

\[ K(o \to n) = K(n \to o), \]

where \( K(o \to n) \) is the flow of configuration \( o \) to \( n \), which is equal to the product of the probability of being in configuration \( o \), the probability of generating configuration \( n \), and the probability of accepting this move:

\[ K(o \to n) = \mathcal{N}(o) \times \alpha(o \to n) \times \text{acc}(o \to n). \]

8.3.1 Particle Displacement

We assume that state \( n \) is obtained from state \( o \) via the displacement of a randomly selected particle in box 1. The ratio of the statistical weights of
these two configurations is given by

\[
\frac{N(n)}{N(o)} = \frac{\exp[-\beta U(s_{n}^{o})]}{\exp[-\beta U(s_{o}^{n})]}.
\]

Substitution of this ratio into the condition of detailed balance (5.1.1) gives, as an acceptance rule,

\[
\text{acc}(o \rightarrow n) = \min \{1, \exp\{\beta [U(s_{n}^{o}) - U(s_{o}^{n})]\}\}.
\]

(8.3.1)

This acceptance rule is identical to that used in a conventional N,V,T ensemble simulation (see section 5.2).

### 8.3.2 Volume Change

For a change of the volume of box 1 by an amount \(\Delta V\), \(V_1^o = V_1^o + \Delta V\), the ratio of the statistical weights of the configurations after and before the move
is given by

\[ \frac{\mathcal{N}(n)}{\mathcal{N}(0)} = \frac{(V_1^n)^{n_1} (V - V_1^n)^{N-n_1}}{(V_0^n)^{n_1} (V - V_0^n)^{N-n_1}} \exp[-\beta U(s_n^N)] \]

Imposing the condition of detailed balance gives, as an acceptance rule for this volume change,

\[ \text{acc}(o \rightarrow n) = \min \left\{ 1, \frac{(V_1^n)^{n_1} (V - V_1^n)^{N-n_1}}{(V_0^n)^{n_1} (V - V_0^n)^{N-n_1}} \exp\{-\beta [U(s_n^N) - U(s_o^N)]\} \right\} \]

(8.3.2)

This way of changing the volume was originally proposed by Panagiotopoulos et al. [94,147]. A more natural choice for generating a new configuration in the volume change step is to make a random walk in \( \ln[V_1/(V - V_1)] \) instead of \( V_1 \) (see also Chapter 5 for the N, P, T ensemble). This has the advantage that the domain of this random walk coincides with all possible values of \( V_1 \). Furthermore, the average step size turns out to be less sensitive to the density. To adopt this method to the Gibbs ensemble, the acceptance rule for the volume has to be modified.

If we perform a random walk in \( \ln[V_1/(V - V_1)] \), it is natural to rewrite equation (8.2.1) as

\[ Q_{N,V,T} = \frac{1}{\Lambda^3 N!} \sum_{n_1=0}^{N} \binom{N}{n_1} \int_{-\infty}^{\infty} d\ln \left( \frac{V_1}{V - V_1} \right) \frac{V_1(V - V_1)}{V} V_1^{n_1}(V - V_1)^{N-n_1} \]

\[ \times \int d s_1^{n_1} \exp\{-\beta U(s_1^{n_1})\} \int d s_2^{N-n_1} \exp\{-\beta U(s_2^{N-n_1})\} \]

The statistical weight of a configuration \( n \) with volume \( V_1 \) is proportional to

\[ \mathcal{N}(n) \propto \frac{(V_1^n)^{n_1+1}(V - V_1^n)^{N-n_1+1}}{V_1!(N-n_1)!} \exp[-\beta U(s_n^N)]. \]

Imposing detailed balance for this move leads to the acceptance rule

\[ \text{acc}(o \rightarrow n) = \min \left\{ 1, \left( \frac{V_1^n}{V_0^n} \right)^{n_1+1} \left( \frac{V - V_0^n}{V - V_1^n} \right)^{N-n_1+1} \right\} \times \exp\{-\beta [U(s_n^N) - U(s_o^N)]\} \]

(8.3.3)

Note that this modification does not affect the acceptance rules for the particle displacement or particle exchange.
8.3.3 Particle Exchange

Let us assume that we generate configuration \( \mathbf{r} \) from configuration \( \mathbf{o} \) (\( n_1 \) particles in box 1) by removing a particle from box 1 and inserting this particle in box 2. The ratio of statistical weights of the configurations is given by

\[
\frac{\mathcal{N}(\mathbf{n})}{\mathcal{N}(\mathbf{o})} = \frac{n_1!(N-n_1)!(V-V_1)^{N-(n_1-1)}V_1^{n_1-1}}{(n_1-1)!(N-(n_1-1))!V_1^{n_1}(V-V_1)^{N-n_1}} \exp\{-\beta[U(s^N_n)-U(s^N_o)]\}.
\]

Imposing detailed balance for this move leads to the following acceptance rule:

\[
\text{acc}(\mathbf{o} \rightarrow \mathbf{n}) = \min\left\{1, \frac{n_1(V-V_1)}{(N-n_1+1)V_1} \exp\{-\beta[U(s^N_n)-U(s^N_o)]\}\right\}.
\] (8.3.4)

8.3.4 Implementation

A convenient method for generating trial configurations is to perform a simulation in cycles. One cycle consists of (on average) \( N_{\text{part}} \) attempts to displace a (randomly selected) particle in one of the (randomly chosen) boxes, \( N_{\text{vol}} \) attempts to change the volume of the subsystems, and \( N_{\text{swap}} \) attempts to exchange particles between the boxes. It is important to ensure that at each step of the simulation the condition of microscopic reversibility is fulfilled. Possible Gibbs ensemble algorithms are shown in Algorithms 17–19.

In the original implementation of a Gibbs ensemble simulation the calculations were performed slightly differently [94]; instead of making a random choice of the type of trial move (particle displacement, volume change, or particle exchange) at every Monte Carlo step, the different trial moves were carried out in a fixed order. First, \( N \) attempts were made to move every particle in succession (the \( N, V, T \) part), then one attempt was made to change the volume (the \( N, P, T \) part), and finally \( N_{\text{try}} \) attempts were made to exchange particles (the \( \mu, V, T \) part). However, if in a simulation it is possible to choose from a repertoire of trial moves, random selection of the type of trial move is recommended, because this way microscopic reversibility is guaranteed. An additional disadvantage of performing trial moves in a fixed order is that it may make a difference at what point in the program the measurement of the physical properties is performed (e.g., after the \( N, V, T \) part, the \( N, P, T \) part, or the \( \mu, V, T \) part). If trial moves are selected at random, all trial moves are on average equivalent and one can simply perform measurements after a predetermined number of MC cycles.
Algorithm 17 (Basic Gibbs Ensemble Simulation)

PROGRAM mc_Gibbs

do icycl=l,ncycl
    ran=ranf()*(npart+nvol+nswap)
    if (ran.le.npart) then
        call mcmove
    else if (ran.le.(npart+nvol))
        call mcvol
    else
        call mcswap
    endif
    call sample
endo
end

Comments on this algorithm:

1. This algorithm ensures that, in each Monte Carlo step, detailed balance is obeyed. On average, we perform per cycle npart attempts to displace particles, nvol attempts to change the volume, and nswap attempts to swap particles between the two boxes.

2. Subroutine mcmove attempts to displace a randomly selected particle; this algorithm is very similar to Algorithm 2 (but remember that particles are in two different boxes). The subroutine mcvol attempts to change the volume of the two boxes (see Algorithm 18), the subroutine mcswap attempts to swap a particle between the two boxes (see Algorithm 19), and subroutine sample samples the ensemble averages.

The implementation of trial moves for particle displacement and volume change in Gibbs ensemble simulations is very similar to that of the corresponding trial moves in a normal N, V, T or N, P, T simulation. However, the attempts to exchange particles require some care. To ensure that detailed balance is obeyed, it is important to first select at random from which box a particle will be removed and subsequently select a particle at random in this box. An alternative would be to first select one particle at random (from all N particles) and then try to move this particle to the other simulation box. However, in that case, acceptance rule (8.3.4) has to be replaced by a slightly different one [125].

The number of attempts to exchange a particle will depend on the condi-
Algorithm 18 (Attempt to Change the Volume in the Gibbs Ensemble)

SUBROUTINE mcvol

    call toterg(box1,en1o)
call toterg(box2,en2o)
vol=box1**3
vo2 =v-vol
lnvn=log(vol/vol2)+
+ (ranf() - 0.5) *vmax
vln=v*exp(lnvn)/(1+exp(lnvn))
v2n=v-vln
boxln=vln**(1/3)
box2n=v2n**(1/3)
do i=1,npart
    if (ibox(i).eq.1) then
        fact=boxln/boxlo
    else
        fact=box2n/box2o
    endif
    x(i)=x(i)*fact
enddo
    call toterg(boxln,enln)
call toterg(box2n,en2n)
argl=-beta*((enln-en1o) +
+ (npbox(1)+1) *log(vln/vlo)/beta)
arg2=-beta*((en2n-en2o)+
+ (npbox(2)+1) *log(v2n/v2o)/beta)
if (ranf().gt.exp(arg1+arg2)) then
    do i=1,npart
        if (ibox(i).eq.) then
            fact=boxlo/boxln
        else
            fact=box2o/box2n
        endif
        x(i)=x(i)*fact
    enddo
endif
return
end

attempt to change
the volume
energy old conf. box 1
and 2 (box1: box length)
old volume box 1 and 2
random walk in ln V1/V2
new volume box 1 and 2
new box length box 1
new box length box 2
determine which box
rescale positions
total energy box 1
total energy box 2
appropriate weight function
acceptance rule (8.3.3)
REJECTED
determine which box
restore old configuration
Comments to this algorithm:

1. The term $i_{\text{box}}(i) = 1$ indicates that particle $i$ is in box 1; $n_{\text{part}} = n_{\text{pbox}}(1) + n_{\text{pbox}}(2)$ where $n_{\text{pbox}}(i)$ gives the number of particles in box $i$.

2. In this algorithm we perform a random walk in $\ln V$ and we use acceptance rule (8.3.3).

3. The subroutine $\text{toterg}$ calculates the total energy of one of the two boxes. In most cases the energy of the old configuration is known, and therefore it is not necessary to determine this energy at the beginning of the volume step.

In some cases of the system. For example, it can be expected that close to the critical temperature, the percentage of accepted exchanges will be higher than close to the triple point. As a possible check whether the number of attempts is sufficient, calculate the chemical potential. Since the calculated energy of a particle that is to be inserted corresponds to just the test particle energy, the chemical potential can be calculated without additional costs. Appendix H shows that, in the Gibbs ensemble, the chemical potential can be obtained from

$$\mu_1 = -k_B T \ln \frac{1}{\Lambda^3} \left\langle \frac{V_1}{n_1 + 1} \exp \left[ -\beta \Delta U_1^+ \right] \right\rangle_{\text{Gibbs, box 1}}, \quad (8.3.5)$$

where $\Delta U_1^+$ is the energy of a (ghost) particle in box 1 and $\langle \cdots \rangle_{\text{Gibbs, box i}}$ denotes an ensemble average in the Gibbs ensemble restricted to box $i$. It is important to note that this ensemble average is valid only if the boxes do not change identity during a simulation.

Inspection of the partition function (8.2.1) shows that one must allow for $n_1 = 0$ (box 1 empty) and $n_1 = N$ (box 2 empty) to calculate ensemble averages correctly. It is important therefore to ensure that the program can handle the case that one of the boxes is empty. As is clear from equation (8.3.4), the acceptance rule is constructed such that it indeed rejects trial moves that would attempt to remove particles from a box already empty. However, if one also calculates the chemical potential during the exchange step one should be careful. To calculate the chemical potential correctly (see Appendix H) one should continue to add test particles when one of the boxes is full.

Case Study 16 (Phase Equilibria of the Lennard-Jones Fluid)

To illustrate the use of the Gibbs ensemble technique, we determine the vapor-liquid curve of the Lennard-Jones fluid. In Case Studies 1, 7, and 9 we already determined parts of the equation of state of this fluid and in
Algorithm 19 (Attempt to Swap a Particle between the Two Boxes)

```fortran
SUBROUTINE mcswap
  if (ranf().lt.0.5) then
    in=1
    out=2
  else
    in=2
    out=1
  endif
  xn=ranf()*box(in)
  call ener(xn,enn,in)
  w(in)=w(in)+vol(in)*
    exp(-beta*enn)/(npbox(in)+1)
  if (npbox(out).eq.0) return
  ido=0
  do while (ido.ne.out)
    o=int(npart*ranf())+1
    ido=ibox(o)
  enddo
  call ener(x(o),eno,out)
  arg=exp(-beta*(enn-eno +
    log(vol(out)*(npbox(in)+1)/
    (vol(in)*npbox(out)))/beta))
  if (ranf().lt.arg) then
    x(o)=xn
    ibox(o)=in
    nbox(out)=npbox(out)-1
    nbox(in)=npbox(in)+1
  endif
  return
end
```

**Comments to this algorithm:**

1. The acceptance rule (8.3.4) is used in this algorithm.
2. The subroutine `ener` calculates the energy of a particle at the given position and box.
3. At the end of the simulation, the chemical potential can be calculated from $w(\text{box})$ using $\mu_{\text{box}} = -\ln \langle w_{\text{box}} \rangle / \beta$. 
In Figure 8.3, the density of the fluid in the two boxes is plotted as a function of the number of Monte Carlo cycles (as defined in Algorithm 17). The simulation was started with equal density in both boxes. During the first 1000 Monte Carlo cycles, the system has not yet "decided" which box would evolve to a liquid density and which box to a gas density. After 5000 Monte Carlo cycles, the system already has reached equilibrium and the coexistence properties can be determined.

Figure 8.3: Density of the two boxes of the Gibbs ensemble as a function of the number of Monte Carlo cycles for a system of Lennard-Jones particles; the number of particles was $N = 256$ and temperature $T = 1.2$.

In Figure 8.4, the phase diagram of the Lennard-Jones as obtained from Gibbs ensemble simulations is compared with the phase diagram obtained from the equation of state of Nicolas et al. [61]. The Gibbs ensemble data are in very good agreement with the equation of state of Nicolas et al. Close to the critical point the results deviate because Nicolas et al. fitted the equation of state in such a way that the critical point coincides well with the estimate of Verlet [13]: $T_c = 1.35$ and $\rho_c = 0.35$. The Gibbs ensemble simulations [53] give as the estimate for the critical point $T_c = 1.316 \pm 0.006$ $\rho_c = 0.304 \pm 0.006$. Lofti et al. [204] used a combination of $N,P,T$-simulations and test particle insertion to determine the coexistence curve. The estimate of the critical point of Lofti et al. ($T_c = 1.310$ and $\rho_c = 0.314$) is in good agreement with the estimate obtained from the Gibbs ensemble. The Gibbs ensemble simulations and the simulation of Lofti et al. indicate that the estimate of the critical temperature of Verlet is too high. Johnson et al. [62] used this new estimate of the critical point together with additional equation-of-state data.
Figure 8.4: Phase diagram of the Lennard-Jones fluid as calculated with the Gibbs ensemble technique (squares) and equation of state of Nicolas et al. (solid lines). The solid circle gives the estimate of the critical point.

to improve the equation of state of Nicolas et al.

8.3.5 Analyzing the Results

Assuming that we have a working algorithm to perform a simulation in the Gibbs ensemble, we must now address the question whether the numbers generated in a simulation are reliable. First of all, the equilibrium conditions should be fulfilled:

- The pressure in both subsystems must be equal.
- The chemical potential must be equal in both phases.

Unfortunately, both the chemical potential and the pressure of the liquid phase are subject to relatively large fluctuations. Hence, the observation that the equilibrium conditions have been fulfilled within the statistical error is not always sufficient. It is convenient therefore to use additional methods to analyze the data and judge whether a simulation has been successful.

Graphical Analysis of Simulation Results

In Appendix H, we describe a graphical technique for analyzing the results of a Gibbs ensemble simulation. In this scheme, the fraction of all particles \((n_i/N)\) in box \(i\) is plotted versus the fraction of the total volume \((V_i/V)\) taken up by this box. In the \(x-y\) plane, where \(x = n_i/N\) and \(y = V_i/V\), every dot represents a point sampled in the simulation.
Figure 8.5: probability plot in the x – y plane of a successful simulation of a Lennard-Jones fluid well below the critical temperature (T = 1.15 and N = 500).

In the thermodynamic limit, only two points in the x-y plane are sampled; namely, those that correspond to the coexisting liquid and gas density (see Appendix H). For a finite system, we expect to observe fluctuations around these points. Figure 8.5 shows an x-y plot for a simulation of two-phase coexistence well below the critical temperature. The fact that the simulation results cluster around the two points that correspond to the coexisting liquid and vapor indicates that the system was well equilibrated. If a simulation in the Gibbs ensemble is performed far below the critical temperature, it is in general no problem to analyze the results. After the equilibration, it becomes clear which of the boxes contains the vapor phase and which the liquid phase. The densities of the coexisting phases can simply be obtained by sampling the densities at regular intervals. When estimating the accuracy of the simulation one should be careful since the “measured” densities are not sampled independently: in estimating the standard deviations of the results one should take this into account (this aspect is discussed in more detail in Appendix A of [205]).

Close to the critical point, however, it is possible that the boxes continuously change “identity” during a simulation. In Figure 8.6 the evolution of the density in such a simulation close to the critical point is shown. In such a system, the average density in any one of the two boxes will tend to the overall density (N/V). In those circumstances, it is more convenient to construct a histogram of the probability density $P(\rho)$ to observe a density $\rho$ in either box. Even when the boxes change identity during the simulation, the maxima of $P(\rho)$ are still well defined. And, as shown in Appendix H,
Figure 8.6: Density in the two boxes in a Gibbs ensemble simulation close to the critical temperature. The left figure shows the evolution of the density of the two boxes during a simulation. The right figure gives the corresponding probability density. The simulations were performed on a Lennard-Jones fluid with \( N = 256 \) at \( T = 1.30 \).

In the thermodynamic limit, the two maxima of \( P(\rho) \) correspond to coexisting vapor and liquid densities, except precisely at the critical point. (For a discussion of the critical behavior of \( P(\rho) \), see the article by Allen and Tildesley [41].) Because \( P(\rho) \) is obtained by sampling the density in both boxes, the results are not influenced when the boxes change identity. In Figure 8.6 an example of such a density distribution is shown. In this particular example, the simulation was carried out rather close to the critical point. Under those conditions, the interpretation of the density histogram is complicated because interfaces may form in both boxes. As a consequence, three peaks are observed; the two outside peaks correspond to the coexisting liquid and gas phase. A simple model that accounts for the existence of the middle peak is discussed in [148].

Determining the Critical Point

Close to the critical point, the free energy associated with the formation of the liquid-vapor interface becomes very small. As a consequence, the penalty on the creation of an interface in either box becomes small, while the formation of such interfaces is entropically favorable. For this reason, just below the critical point, vapor-liquid coexistence can no longer be observed in a Gibbs ensemble simulation [148]. Therefore, the highest temperature at which the coexistence can be observed is not a proper estimate of the critical temperature of the system. To estimate the critical temperature, the results
can be fitted to the law of rectilinear diameters [206]:

\[
\frac{\rho_l + \rho_g}{2} = \rho_c + A(T - T_c),
\]

(8.3.6)

where \(\rho_l(\rho_g)\) is the density of the liquid (gas) phase, \(\rho_c\) the critical density, and \(T_c\) the critical temperature. Furthermore, the temperature dependence of the density difference of the coexisting phases is fitted to a scaling law [207]

\[
\rho_l - \rho_g = B(T - T_c)^\beta,
\]

(8.3.7)

where \(\beta\) is the critical exponent\(^2\) (for three-dimensional systems \(\beta \approx 0.32\) and for two-dimensional systems \(\beta = 0.125\) [207]). \(A\) and \(B\) depend on the system and are obtained from the fit.

These equations should be used with care. Strictly speaking, they cannot be used for a simulation of a finite system. The reason is that, at the critical point, the correlation length that measures the spatial extent of spontaneous density fluctuations diverges. In a finite system, however, these fluctuations are constrained by the size of the simulation box. If we suppress long-range fluctuations, we in fact are modeling a classical system, which has mean field critical exponents. We therefore can expect to observe a crossover temperature; below this temperature we sample all relevant fluctuations and we expect to observe nonclassical behavior. Above this temperature we expect classical behavior. The crossover temperature will depend on the kind of ensemble used in the simulation.

For the Lennard-Jones fluid in three and two dimensions the finite-size effects for the Gibbs ensemble have been analyzed by Panagiotopoulos [208] (see Example 4). The results of this study indicate that for off-lattice systems this crossover temperature is very close to the critical temperature. This suggests that, for applications in which we want to obtain an estimate of the critical temperature, it is safe to use equations (8.3.6) and (8.3.7). In cases where finite-size effects are nevertheless thought to be significant, it is always possible to perform some simulations using different system sizes (although it seems natural to perform such additional simulations on larger systems, an estimate of the importance of finite-size effects can usually be obtained with much less effort from simulations on smaller systems). Of course, if one is interested specifically in finite-size effects or in the accurate determination of critical exponents then one has to be more careful and a proper finite-size scaling analysis should be performed (see, for example, the work of Rovere et al. [99, 101, 209] and Wilding and Bruce [100]). For such calculations, the Gibbs ensemble technique is not particularly well suited.

\(^2\)Strictly speaking, the use of a scaling law with nonclassical critical exponents is not consistent with the use of law of rectilinear diameters. However, within the accuracy of the simulations, deviations from the law of rectilinear diameters will be difficult to observe.
Example 4 (Finite-Size Effects in the Gibbs Ensemble)

Most Gibbs ensemble simulations are performed on relatively small systems \((64 \leq N \leq 500)\). One therefore would expect to see significant finite-size effects, in particular, close to the critical point. Indeed, in simulations of a system of 100 Ising spins on a lattice,\(^3\) phase coexistence is observed at temperatures as much as 25\% above the critical temperature of the infinite system. In contrast to what is found in lattice gases, the first Gibbs ensemble studies of the phase diagram of the Lennard-Jones fluid (in two and three dimensions) [52, 94, 147, 148] did not show significant finite-size effects. This striking difference with the lattice models motivated Mon and Binder [210] to investigate the finite-size effects in the Gibbs ensemble for the two-dimensional Ising model in detail. For the two-dimensional Ising model the critical exponents and critical temperature are known exactly. Mon and Binder determined for various system sizes \(L\) the order parameter \(M_L(T)\) (see equation (8.3.7)):

\[
M_L(T) = \frac{\rho_L(T) - \rho_c}{\rho_c} = \left(1 - \frac{T}{T_c}\right)^\beta,
\]

where \(\rho_L(T)\) is the density of the liquid phase, \(\rho_c\) and \(T_c\) are the critical density and temperature, respectively, and \(\beta\) is the critical exponent.

The results of the simulations of Mon and Binder are shown in Figure 8.7, in which the order parameter \(M_L(T)\) is plotted as \(M_L^{1/\beta}(T)\) versus \(T/T_c\). Such a plot of the order parameter allows us to determine the effective critical exponent of the system. If the system behaves classically, the critical exponent has the mean field value \(\beta = 1/2\) and we would expect a linear behavior of \(M_L^{1/\beta}(T)\). On the other hand, if the system shows nonclassical behavior, with exponent \(\beta = 1/8\), we would expect a straight line for \(M_L^{8/3}(T)\). Figure 8.7 shows that, away from the critical point, the temperature dependence of the order parameter is best described with an exponent \(\beta = 1/8\). Closer to the critical point, the mean field exponent \(\beta = 1/2\) fits the data better. This behavior is as expected. Away from the critical point the system can accommodate all relevant fluctuations and exhibits nonclassical behavior. But close to the critical point the system is too small to accommodate all fluctuations and, as a consequence, mean field behavior is observed. In addition, Figure 8.7 shows that we still can observe vapor-liquid coexistence at temperatures 20\% above the critical temperature of the infinite system, which implies significant finite-size effects. The study of Mon and Binder shows that, in a lattice model of a fluid, finite-size effects on the liquid-vapor coexistence curve are very pronounced. It is important to note that, in this lattice version of the Gibbs ensemble, we do not change the volume and therefore fewer fluctuations are possible than in the off-lattice version.

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\(^3\)The Ising model is equivalent to a lattice-gas model of a fluid. The latter model is the simplest that exhibits a liquid-vapor transition.
Figure 8.7: Finite-size effects in a Gibbs ensemble simulation of the two-dimensional Ising model. Order parameter $M_L^{1/β}(T)$ for $L = 10$ (i.e., $L \times L = 100$ spins) versus $T/T_c$, where $T_c$ is the exact critical temperature for the infinite system. The lines are fitted through the points. The simulation data are taken from [210].

The striking differences between the findings of Mon and Binder and the results of the early simulations of the Lennard-Jones fluid motivated Panagiotopoulos to reinvestigate in some detail the finite-size effects of Gibbs ensemble simulations of the two- and three-dimensional Lennard-Jones fluid [208]. The results of the simulations of Panagiotopoulos are shown in Figure 8.8. For the Lennard-Jones fluid, the order parameter is defined as

$$M_L(T) = \rho_l - \rho_g.$$ 

The results for the two-dimensional Lennard-Jones fluid are qualitatively similar to the results of Mon and Binder. At low temperatures, Ising-like behavior is observed and close to the critical point mean-field-like behavior. An important difference is the magnitude of the finite-size effects. Figure 8.8 shows that, for the two system sizes, the results are very similar; the finite size effects are at most 5%. In addition, Figure 8.8 also indicates why the initial Gibbs ensemble studies on the Lennard-Jones fluids did not show significant finite-size effects. All these studies used equations (8.3.6) and (8.3.7) to determine the critical point. If we use these equations we implicitly assume nonclassical behavior up to the critical point. In Figure 8.8, this corresponds to extrapolating the lines, fitted to the data point, for $β = 1/8$. Extrapolation of these lines to $M_L^β(T) = 0$ gives a critical point that is not only independent of this system size but also very close to the true critical point of the infinite system.
Figure 8.8: Finite-size effects in the liquid-vapor coexistence curve of the two-dimensional Lennard-Jones fluid (truncated potential \( r_c = 5.0\sigma \)) studied by Gibbs ensemble simulation. The order parameter \( M \) corresponds to the density difference between the coexisting liquid and vapor phases. The figure shows \( M^{1/\beta}_L(T) \) versus \( T/T_c \) for various system sizes \( L \). \( T_c \) is the estimated critical temperature for the infinite system (\( T_c = 0.497 \pm 0.003 \)). The simulation data are taken from [208].

For the three-dimensional Lennard-Jones fluid Panagiotopoulos did not observe a crossover from Ising-like to mean field behavior in the temperature regime that could be studied conveniently in the Gibbs ensemble (\( T < 0.98T_c \)). Also for liquid-liquid equilibria for the square well fluid, Recht and Panagiotopoulos [211] and de Miguel et al. [212] did not observe such a crossover. Moreover, for the three-dimensional Lennard-Jones fluid, the finite-size effects were negligible away from \( T_c \) and very small close to \( T_c \).

8.4 Applications

The Gibbs ensemble technique has been used to study the phase behavior of a variety of systems. The results of these simulations are reviewed in [201,213,214]. Here we discuss a few applications of the Gibbs ensemble for which the algorithm differs significantly from the one described in section 8.3.4.

Example 5 (Dense Liquids)
At high densities, the number of exchange steps can become very large and the simulation requires a significant amount of CPU time. This problem occurs also in conventional grand-canonical Monte Carlo simulations. Various
methods, which are used to extend simulations in the grand-canonical ensemble to higher densities, can also be used in the Gibbs ensemble. An example of such a technique is the so-called excluded volume map sampling. This technique, based on the ideas of Deitrick et al. [215] and Mezei [111], has been applied to the Gibbs ensemble by Stapleton and Panagiotopoulos [216]. Before calculating the energy of the particle that has to be inserted, a map is made of the receiving subsystem, by dividing this subsystem into small boxes that can contain at most one particle. Each box carries a label that indicates whether it is empty or contains a particle. This map can then be used as a lookup table to check whether there is “space” for the particle to be inserted. If such a space is not available, the trial configuration can be rejected immediately. When using the excluded-volume map, some additional bookkeeping is needed to guarantee detailed balance (see [111] for further details).

Example 6 (Polar and Ionic Fluids)
Because of the long range of the dipolar and Coulombic interactions, the dipolar and Coulombic potential cannot simply be truncated. Special techniques, such as the Ewald summation or reaction field (see Chapter 12.1), have been developed to take into account the long-range nature of the potential in a simulation. A simple truncation of long-range intermolecular interactions at half the box diameter can lead to an incorrect estimate of the phase coexistence curve. In addition to the truncation of dipolar or Coulomb interactions never being admissible, there is a problem if the potential is truncated at half the diameter of the periodic box. As the size of the simulation box fluctuates during the simulation, the effective potential is also changing. As a consequence, a particle in a large simulation box feels a very different interaction potential than a particle in a small box. The result is that a Gibbs ensemble simulation with simulation boxes of different sizes may find apparent phase coexistence between two systems that are described by different potentials. In fact, this problem is not limited to Coulomb or dipolar interactions. Even for the relatively short-range Lennard-Jones potential, the phase diagram is very sensitive to the details of the truncation of the potential (see section 3.2.2). An example of an application of the Gibbs ensemble technique to a fluid with Coulomb interactions is the study by Panagiotopoulos [217] of a simple model for an ionic solution, namely, the restricted primitive model. The estimate of the location of the critical point that follows from this simulation differed appreciably from an earlier estimate [188,218] obtained by truncating the Coulomb potential at half the box diameter.

When the Ewald summation method is used to account for Coulomb or dipolar interactions, then the system size dependence of the results of a Gibbs ensemble simulation is usually quite small. Such weak system size

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4 The restricted primitive model is a hard-core potential with a point charge.
dependence, for instance, was found in a Gibbs ensemble simulation of the liquid-vapor transition in a Stockmayer fluid\(^5\) [219, 220].

In the case of a closely related system, the dipolar hard-sphere fluid, the Gibbs ensemble simulations have even resulted in new insights into an old problem, namely, the location of the liquid-vapor critical point. At first sight, nothing seems to be special about the liquid-vapor transition in the dipolar hard-sphere fluid. As the orientationally averaged interaction between two dipoles results in a van der Waals-like \(1/T^6\) attraction, de Gennes and PinCUS conjectured that the vapor-liquid coexistence would be similar to that of a conventional van der Waals fluid [221]. Kalikmanov [222] used this conjecture to estimate the critical point. More sophisticated liquid-state theories [223] gave qualitatively similar (though quantitatively different) results. And, indeed, early constant \(N, V, T\) Monte Carlo simulations of Ng et al. [224] found evidence for such liquid-vapor coexistence, supporting the theoretical predictions of the existence of liquid-vapor coexistence in a dipolar hard-sphere fluid.

However, more recent simulations found no evidence for a liquid-vapor transition [225, 226]. To be more precise, these simulations found no evidence for liquid-vapor coexistence in the temperature range predicted by the different theories. Even at the lowest temperatures that could be studied, liquid-vapor coexistence was not observed. Rather, it was found that at low temperatures the dipoles align nose to tail and form chains [226, 227]. These chains make it very difficult to equilibrate the system. Hence, it becomes difficult to distinguish between two possibilities: either the system is in a thermodynamically stable, homogeneous phase or the system would like to phase separate into a liquid phase and a vapor phase, but this phase separation is kinetically inhibited. In either case, the simulations show that the theoretical description of the liquid-vapor transition in a dipolar hard-sphere fluid needs to be revised. Camp et al. [228] have performed extensive (NPT and NVT) Monte Carlo simulations to determine the equation-of-state of the dipolar hard-sphere fluid. These simulations suggest that, in the dipolar hard-sphere system, there is a phase transition between a dilute and a more concentrated isotropic fluid phase. Both phases appear to consist of a network of chains of dipolar molecules. A possible explanation for the occurrence of this phase transition, in terms of a defect-induced critical phase separation, was suggested by Tlusty and Safran [229]. A normal liquid-gas transition is driven by the isotropic aggregation of particles. This conventional mechanism is absent in dipolar hard spheres because it is preempted by chain formation. In the language of ref. [229], the two coexisting phases of the dipolar hard-sphere fluid can be thought of as a dilute gas of chain ends and a high-density liquid of chain branching points. The formation of branching points in the dipolar chains costs entropy but lowers the energy.

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\(^5\)The Stockmayer potential is a Lennard-Jones potential plus a point dipole.
Which of the two factors dominates depends on the density of the fluid. For details, we refer the reader to ref. [229].

**Example 7 (Mixtures)**

An important application of the Gibbs ensemble technique is the simulation of the phase behavior of mixtures (see, e.g., [147,230,231]). One of the main problems in studying liquid-liquid phase coexistence is that both phases are usually quite dense. It is difficult therefore to exchange particles between the two phases. This problem is more serious for the larger of the two species. Fortunately, it is not necessary to carry out such exchanges for all species, to impose equality of the chemical potentials in the coexisting phases. It is sufficient that the chemical potential of only one of the components, label $i$, is equal in both phases. For the other components, $j$, we impose that $\mu_j - \mu_i$ should be equal in the two phases. Of course, this implies that, when $\mu_i$ is the same in both phases, then so are all $\mu_j$. However, the condition that $\mu_j - \mu_i$ is fixed is much easier to impose in a simulation. In practice, this is achieved by performing Monte Carlo trial moves in which change is attempted on the identity of a particle (e.g., from $i$ to $j$). The imposed chemical potential difference determines the acceptance probability of such trial moves. This approach was first applied to Gibbs ensemble simulation of mixtures by Panagiotopoulos [232]. In these simulations, only the smaller particles are swapped between the two simulation boxes, while for the larger particles only identity change moves are attempted.

The situation becomes even simpler when studying symmetric mixtures. In such systems, the densities of the coexisting phases are equal, while the molar compositions in boxes I and II are symmetry related ($x_1 = 1 - x_{11}$). As a result, in Gibbs ensemble simulations of such symmetric systems, it is not necessary to perform volume changes [233,234] or particle exchanges between the boxes [212].

### 8.5 Questions and Exercises

**Question 18 (Gibbs Ensemble)** When one of the boxes in the Gibbs ensemble is infinitely large and the molecules in this box do not have intermolecular interactions, the acceptance/rejection rule for particle swap becomes identical to the acceptance/rejection rule for particle swap in the grand-canonical ensemble. Derive this result.

**Question 19 (Scaling of the Potential)** When an attempt is made to change the volume in the Gibbs ensemble, the energy of the new configuration can be calculated efficiently if scaling properties of the potential can be used. Consider a system of
Lennard-Jones particles. The total energy $U$ of the system is equal to

$$U = \sum_{i<j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]. \quad (8.5.1)$$

Suppose that the box size of the system is changed from $L$ to $L'$ and $s = L'/L$.

1. Why is this scheme so efficient?
2. What is the expression for the total virial of this system?
3. Why does this method only work when the cutoff radius is scaled as well?
4. Derive expressions for the new energy $U'$ and new virial $V'$ as a function of $s$, the old energy ($U$) and virial ($V$).
5. How does the tail corrections scale?

**Exercise 14 (Vapor-Liquid Equilibrium)**

In this exercise, we use Widom’s test particle method (see section 7.2.1) to locate a vapor-liquid equilibrium. The results are compared with a Gibbs ensemble simulation.

1. Modify the Monte Carlo program of Lennard-Jones particles in the NVT ensemble (only in the file `mc_nvt.f`) in such a way that the chemical potential can be calculated using Widom’s test particle method:

$$\mu = \mu_0 - \frac{\ln \left( \rho^{-1} \langle \exp [-\beta A U^+] \rangle \right)}{\beta}, \quad (8.5.2)$$

in which $\rho$ is the number of particles per volume, $U^+$ is the energy of a test particle, and

$$\mu_0 = -\frac{\ln (\Lambda^3)}{\beta}. \quad (8.5.3)$$

- Make a plot of the chemical potential and pressure as a function of the density for $T = 0.8$.
- Why is it more difficult to calculate the chemical potential at high densities than at low densities?
- How can you locate the vapor-liquid coexistence densities?

2. Perform a Gibbs ensemble simulation of the system at $T = 0.8$. In the Gibbs ensemble, the chemical potential of box $i$ is equal to [203]

$$\mu_i = \mu_0 - \frac{\ln \left( \frac{V_i}{n_i+1} \exp [-\beta A U^i_+ \r] \right)}{\beta}, \quad (8.5.4)$$

in which $n_i$ is the number of particles in box $i$ and $V_i$ is the volume of box $i$. Do the vapor-liquid density and chemical potential agree with your previous results?