



Algorithms for Phase Coexistence

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Overview

This module comprises material for two lectures. The aim is to examine the prediction of phase behaviour.

The specific learning objectives are:

- (a) To understand the difficulties in simulating phase equilibria;
- (b) To understand the Gibbs Ensemble;
- (c) To implement the Gibbs Ensemble Algorithm in C.



Introduction

- The simulations that we have so far considered have only involved represent the properties of the fluid for a single isolated phase.
- The techniques of molecular simulation can be extended to multiple phases, providing a powerful tool for the investigation of the phase coexistence of both pure fluids and fluid mixtures.
- Historically, the application of molecular simulation to phase equilibria has lagged behind applications to other areas.
- This can be attributed partly to the difficulty in obtaining free energy or chemical potential data required for phase coexistence.



Introduction (Contd)

- Conceptually, the most straight forward method for simulating coexisting phases is to divide the simulation box into distinct regions. For example, vapour-liquid equilibria can be simulated in a box containing three distinct regions which correspond the liquid phase, vapour phase, and an interfacial region, respectively. The simulation is initiated by introducing a slab of previously equilibrated liquid into the centre of the simulation box with a vacuum on either side. If the density of the liquid is close to coexisting density, the liquid will evaporate into the vacuum to form a stable two-phase system. This approach is particular useful for interfacial studies.



Introduction (Contd)

The two-phase method is conceptually appealing because it corresponds directly with experimental observation. However, the disadvantages of the method are numerous. The main problems are:

1. The simulations are slow because a large number of molecules are required and the equilibration of the interfacial region is a slow process.
2. It is difficult to simulate stable phase equilibria between phases of similar densities.
3. Furthermore, the confinement of the fluid between parallel walls can potentially influence both the density and pressure of the coexisting phases resulting in a simulation of the properties of confined fluids rather than a bulk fluid.



Introduction (Contd)

- The limitations of the traditional two-phase method are overcome by using the Gibbs ensemble (Panagiotopoulos, 1987 & 1992a).
- The Gibbs ensemble method is characterised by two homogeneous phases that are in thermodynamic equilibrium but not in physical contact. Unlike the two-phase method, there is no interface thus resulting in much shorter run times.
- The Gibbs ensemble was formulated originally as a Monte Carlo method, however, several promising molecular dynamics implementations of the Gibbs-ensemble have been proposed (Palmer and Lo, 1994; Vega et al., 1994; Kotelyanskii and Hentschke, 1995).



Introduction (Contd)

- Indirect methods provide an alternative to direct methods of simulating phase equilibria. Indirect methods work by calculating the chemical potential for a series of state points. Phase coexistence can be determined by finding points in the state space where two phases have the same chemical potential, pressure, and temperature.
- Conventional molecular simulations do not provide information on thermal properties such as free energies but instead, yield mechanical properties such as the energy and pressure. Consequently, special techniques are required such as test particle methods, umbrella sampling, grand canonical and semigrand ensembles, and thermodynamic integration.
- Comprehensive reviews of these methods are available elsewhere (Gubbins et al., 1983; Gubbins, 1989 & 1994; Frenkel, 1986). Generally, indirect methods are less efficient computationally than direct methods.



Calculating the Chemical Potential

- The criteria for phase equilibria requires the equivalence of temperature (thermal equilibrium), pressure (mechanical equilibrium), and chemical potential (material equilibrium) for every particle in the coexisting phases.
- In a simulation, the temperature and pressure are controlled by molecular displacements and volume changes, respectively.
- In addition, for the simulation phase equilibria, the chemical potential is a very important quantity, particularly for indirect methods which rely on an accurate determination of the chemical potential.
- In other methods such as the Gibbs ensemble which does not rely on knowledge of the chemical potential, calculating the chemical potential can serve as independent verification that equilibrium has been attained.



Calculating the Chemical Potential (Contd)

- The most common approach for calculating the chemical potential is the Widom test particle method (Widom, 1963).
- The Widom method involves inserting a “ghost” particle (i) randomly into the ensemble and calculating the energy of its interaction ($E_{i,\text{test}}$) with the particles of the ensemble. For a canonical ensemble, the residual chemical potential (i.e., the chemical potential minus the contribution from the ideal gas) is obtained subsequently from the following ensemble average.

$$\mu_{ir} = -kT \ln \left\langle \exp(-\beta E_{i,\text{test}}) \right\rangle_N$$



Calculating the Chemical Potential (Contd)

- It should be stressed that because the test particle is a “ghost,” it does not affect the properties of the N real molecules of the ensemble.
- The Widom equation can be applied to every type of molecule and it is completely independent of any assumption concerning pairwise additivity or the nature of intermolecular forces. It can be incorporated easily into a conventional molecular simulation. In principle, it can be used to calculate the chemical potential at any density, however, in practice some difficulties are encountered at high density. At high density, attractive configurations make the dominant contribution to the chemical potential but they are sampled less frequently as the density is increased because of the $\exp(-\beta E_{itest})$ term.



Calculating the Chemical Potential (Contd)

- Strictly the Widom Equation is only valid for the canonical ensemble. In the NPT ensemble, density variations mean that the following should be used:

$$\mu_{ir} = -kT \ln \left[\frac{\langle V \exp(-\beta E_{itest}) \rangle}{\langle V \rangle} \right]$$

In generally, either of these equations yield similar results. However, there are significant differences near the critical region.



Calculating the Chemical Potential (Contd)

- For the Gibbs ensemble, the correct theoretical value of the chemical potential can be calculated from (Smit and Frenkel, 1989):

$$\mu_{ir} = -kT \ln \left\langle \frac{V}{N+1} \exp(-\beta E_{itest}) \right\rangle$$

The calculation of the chemical potential is an area of continuing research interest. Rowley et al. (1994 & 1995) proposed an osmotic molecular dynamics method for calculating the chemical potential. Their method involves establishing an osmotic equilibrium across a semi permeable membrane.



Calculating the Chemical Potential (Contd)

- The chemical potential is calculated using the mechanical properties of the fluid on either side of the membrane. Swope and Andersen (1995) reported calculations of the chemical potential in a “bicanonical ensemble.” The bicanonical ensemble is characterised by a temperature and a volume in which all systems have either N or $N - 1$ particles. The chemical potential is related to the fraction of the systems that have N particles. Sokhan (1997) developed a coupled test particle approach for determining the chemical potential at high liquid densities. Soto-Campos et al. (1998) have discussed the calculation of chemical potentials using a small system grand ensemble method.



Gibbs Ensemble -Theory

In principle, because the grand canonical ensemble allows chemical potential to be specified, it can be used to determine phase coexistence. However, the grand canonical ensemble is not a practical method for calculating phase coexistence because a large number of simulations are required to determine the phase envelope, and the computational cost increases dramatically for two or more components. The chemical potential can also be calculated by using Widom's test particle approach in conjunction with a NVT ensemble simulation. Currently, the most convenient and widely used method for calculating phase coexistence is to use the Gibbs ensemble (Panagiotopoulos, 1987; Panagiotopoulos et al., 1988).



Gibbs Ensemble - Theory (Contd)

Panagiotopoulos (1987) proposed that phase coexistence could be simulated by following the evolution in phase space of a system composed of two distinct regions. Equilibrium between the different region or phases is achieved by performing three distinct Monte Carlo moves as illustrated by Figure 1.

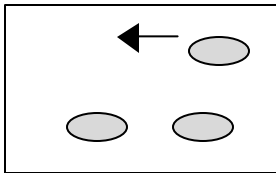
1. Molecular displacements are attempted to obtain internal equilibrium resulting in equivalence of temperatures.
2. Mechanical equilibrium requires that the pressure in the two regions are identical and this is obtained by allowing fluctuations in volume.
3. Attempts are made to exchange particles between the regions to obtain material equilibrium.



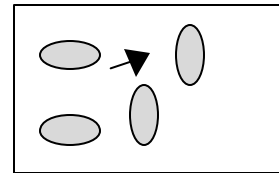
Gibbs Ensemble (Contd) Fig 1.

(1) Attempt molecular displacement

Box 1: N_1, V_1, T

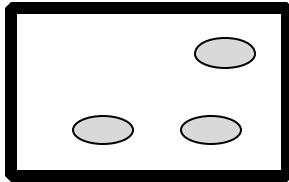


Box 2: N_2, V_2, T

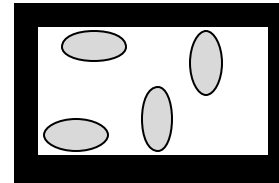


(2) Attempt volume fluctuation

Box 1: $N_1, V_1 + \Delta V, T$

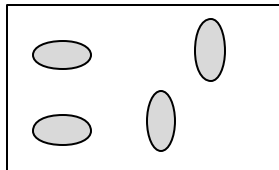


Box 2: $N_2, V_2 - \Delta V, T$

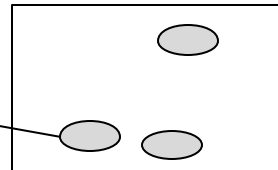


(3) Attempt molecular transfer

Box 1: $N_1 + 1, V_1, T$



Box 2: $N_2 - 1, V_2, T$





Gibbs Ensemble –Theory (Contd)

- The acceptance of the three moves are governed by the normal acceptance criterion for Monte Carlo moves involving the ‘pseudo Boltzmann term’ ($\min[1, \exp(-\beta\Delta Y)]$) discussed in Module 3. In the case of molecular displacement,

$$\Delta Y_{disp} = \Delta E_{\alpha} + \Delta E_{\beta}$$

where the subscripts α and β denote the two different regions or simulation boxes.

- For volume changes, we have:

$$\Delta Y_{volume} = \Delta E_a + \Delta E_b - N_a kT \ln \frac{V_a + \Delta V_a}{V_a} - N_b kT \ln \frac{V_b + \Delta V_b}{V_b} + P(\Delta V_a + \Delta V_b)$$



Gibbs Ensemble –Theory (Contd)

- In the Gibbs ensemble, the total number of particles is conserved. Consequently, a successful particle transfer from box β to box α implies a particle destruction in box β . For particle transfers, we obtain:

$$\Delta Y_{trans} = \Delta E_{\alpha} + \Delta E_{\beta} + kT \ln \frac{V_{\beta} (N_{\alpha} + 1)}{V_{\alpha} N_{\beta}}$$

- A general scheme for a Gibbs ensemble calculation is illustrated by the algorithm below. A feature of this algorithm is that the sequence of moves is determined randomly instead of being predetermined. It is possible to use a predetermined sequence, however, when the probability of particle transfer exceeds 3%, erroneous results may be obtained (Smit, 1992).



Gibbs Ensemble - Algorithm

Part 1

Initialisation:

Specify the number of cycles ($nCycles$), number of particles in the boxes ($nBox1$, $nBox2$), number of volume ($nVol$), transfer attempts ($nTrans$), and the total number of moves ($nTotal = nBox1 + nBox2 + nVol + nTrans$).

Part 2

Generate Markov chain:

loop $i \rightarrow 1 \dots nCycles$

loop $j \rightarrow 1 \dots nTotal$

Part 2.1

if ($\text{rand}() \leq nBox1/nTotal$) //Decide which move to perform

 Displace particle in box 1.

else if ($\text{rand}() \leq (nBox1 + nBox2)/nTotal$)

 Displace particle in box 2.

else if ($\text{rand}() \leq (nBox1 + nBox2 + nVol)/nTotal$)

Part 2.2

 Change volume.

Part 2.3

else if ($\text{rand}() \leq (nBox1 + nBox2 + nVol + 0.5nTrans)/nTotal$)

 Transfer particle from box 1 to box 2.

else

 Transfer particle from box 2 to box 1.

end if

end j loop

end i loop



Gibbs Ensemble –Algorithm (Contd)

In the particle displacement step (Part 2.1), new particles coordinates are chosen randomly whereas in the volume change step (Part 2.2), the length of the simulation box is either decreased or increased by a random amount. Typically, at least a 50% acceptance rate is desirable to achieve equilibrium efficiently, however, this is only a guide and it does not have any theoretical justification. The acceptance rate can be adjusted by altering the values of the maximum possible displacement and maximum change in box length. For many intermolecular potentials, the effect of a change in volume can be calculated simply by scaling the molecular coordinates (see Module 5).



Gibbs Ensemble – Algorithm (Contd)

The particle transfer step (Part 2.3) involves selecting randomly a molecule in one box and attempting to insert it randomly in the other box. It is difficult to prescribe exactly a desirable acceptance rate for particle transfer. In the case of mixtures, it is important that each particle is selected with equal probability to satisfy the requirements of thermodynamic reversibility. Typically, an acceptance rate of a few percent is usually sufficient for material equilibrium. During the particle transfer test, the chemical potential can be easily calculated using Widom's test particle approach. Identical, or at least very similar chemical potentials in the boxes, indicate that the acceptance rate is satisfactory and that material equilibrium has been achieved.



Gibbs Ensemble –Algorithm (Contd)

The acceptance criteria can be used to generate either a *NVT* Gibbs ensemble or an *NPT* ensemble depending on the treatment of volume fluctuations in the volume fluctuation move. For the *NVT* Gibbs ensemble, the total volume of the two boxes is conserved, i.e., $\Delta V_\alpha = -\Delta V_\beta$ whereas for the *NPT* ensemble, the volume fluctuation of the two boxes are independent of each other.



Advantages of the Gibbs Ensemble

- The Gibbs ensemble has been used widely to predict phase coexistence in both one-component fluids and binary mixtures (Panagiotopoulos, 1992a). It has been used in conjunction with several intermolecular potentials including the Lennard-Jones, square-well, Stockmayer, restrictive primitive, Yukawa, and Gay-Berne potentials.
- It can be easily extended for mixtures and systems containing more than two phases. Binary mixtures studied with the Gibbs potential include Lennard-Jones mixtures, hard-sphere/soft-sphere mixtures, hydrocarbon mixtures, and polydisperse fluids.
- The results are remarkably insensitive to the number of molecules used with the possible exception of near-critical equilibria (Valleau, 1998).
- The Gibbs ensemble can also be used in conjunction with a ‘reaction ensemble’ to simulate phase-dependent chemical reactions (Johnson et al., 1994; Smith and Triska, 1994).



Limitations of the Gibbs Ensemble

- The main limitation of the Monte Carlo Gibbs ensemble method is that it is difficult to apply successfully for highly non-spherical, multisegment, or strongly interacting molecules because the particle transfer step has a very low probability of acceptance for these molecules.
- The low particle acceptance probability also means that it cannot be easily applied to fluid-solid equilibria.
- It is inaccurate in the vicinity of the critical point and as such it cannot be used to study critical equilibria in either pure fluids or mixtures.



Alternatives to the Gibbs Ensemble

The simulation of phase equilibria of of continuing research interest. Several alternative algorithms have been proposed:

1. Gibbs–Duhem Integration (Kofke, 1993a & b)
2. Thermodynamic Scaling (Kiyohara et al., 1996)
3. Histogram Re-weighting (Panagiotopoulos et al., 1998)

In addition, molecular dynamics adaptations have been proposed. These alternative approaches are discussed elsewhere (Sadus, 1999).



Project 2 – Implementation of the Gibbs Ensemble

Instead of problems, it is fitting to conclude this introductory course in Monte Carlo methods with a major project, namely to implement the NVT-Gibbs ensemble algorithm in C for the Lennard-Jones fluid. This project builds on Project 1. The main complicating factors are that you must now consider two simulation boxes and a scheme for interchanging particles between the boxes. Accumulate averages of density, energy and pressure. Run the program for several temperatures, and determining the density-temperature phase diagram for the Lennard-Jones fluid. You will probably need to consider at least 500 particles. Use an equilibration of 10,000 cycles and a further 10,000 cycles to accumulate averages. Each cycle should be composed of 500 attempted displacements, 1 volume fluctuation and 500 particle interchanges. Compare your results to those of Panagiotopoulos (1987).



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Widom, B. (1963). Some topics in the theory of fluids. *J. Chem. Phys.* **39**, 2808-2812.



General Reading Material

The material covered in this module is discussed in greater detail in the following books:

M.P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, OUP, Oxford, 1987.

D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, San Diego, 1996, pages.

Stone, A. J., *The Theory of Intermolecular Forces*, Clarendon Press, Oxford, 1996.

R.J. Sadus, *Molecular Simulation of Fluids: Theory, Algorithm and Object-Oriented*, Elsevier, Amsterdam, 1999.