

Chapter 6

Direct Free Energy Calculations in the Continuous Fractional Component Gibbs Ensemble

1 Introduction

Simulations in the Gibbs Ensemble (GE) are frequently used to study Vapor-Liquid Equilibria (VLE) of pure components and mixtures [1, 2, 3]. Similar to simulations in the grand-canonical ensemble, GE simulations rely on sufficiently large acceptance probabilities for particle exchanges between the simulation boxes. However, the acceptance probability for particle exchange can be very low when molecules are large or when the densities are high. When the acceptance probability for insertion/deletion is low, it is not straightforward to verify if the two phases have reached chemical equilibrium, and that the chemical potentials of a certain component are equal in the simulation boxes. To overcome this problem, one possible solution is the so-called expanded ensemble methods [4, 5, 6]. The Continuous Fractional Component Monte Carlo (CFCMC), recently introduced by Shi and Maginn [7], is one of the most commonly used expanded ensemble approaches. In the CFCMC GE There are fractional particles with reduced interactions with the surrounding molecules (instead of inserting whole molecules at once). The strength of this interaction is controlled by a coupling parameter lambda (λ) over which we integrate in the partition function, hence the name: expanded ensemble. Poursaiedesfahani et al have introduced a more efficient formulation of GE combined with the CFCMC technique [8]. In this formulation, there is only a single fractional component per molecule which can be in either one of the boxes. This increases the acceptance ratio for particle insertion/deletion. The advantage of the CFCMC method lies within the fact that it does not depend on the occurrence of spontaneous cavities in the system (as in CBMC). The molecules are inserted gradually in the system instead of a single trial move. In the new formulation of the CFCMC GE, the chemical potential can be computed directly without any extra calculations.

2 Methodology

In the new formulation of the CFCMC GE, there is only a single fractional molecule per component which is distinguishable from whole molecules. In case of LJ pair interactions, the LJ interactions of the fractional molecule are scaled according to:

$$u_{\text{LJ}}(r, \lambda) = \lambda 4\epsilon \left(\frac{1}{\left[\frac{1}{2}(1 - \lambda)^2 + \left(\frac{r}{\sigma}\right)^6 \right]^2} - \frac{1}{\left[\frac{1}{2}(1 - \lambda)^2 + \left(\frac{r}{\sigma}\right)^6 \right]} \right) \quad (1)$$

Where λ is the scaling parameter with $\lambda \in [0, 1]$. The partition function of this system is given by

$$\begin{aligned}
Q_{\text{CFCMC}} = & \frac{1}{\Lambda^{3(N_T+1)} (N_T)!} \sum_{i=1}^2 \sum_{N_1=0}^{N_T} \int_0^1 d\lambda \int_0^{V_T} dV_1 V_1^{N_1+\delta_{i,1}} (V_T - V_1)^{N_T-N_1+\delta_{i,2}} \frac{(N_T)!}{(N_1)! (N_T - N_1)!} \\
& \times \int ds^{N_1} \exp[-\beta U_{\text{int},1}(s^{N_1}, V_1)] \int ds^{N_T-N_1} \exp[-\beta U_{\text{int},2}(s^{N_T-N_1}, V_T - V_1)] \\
& \times \left(\begin{aligned} & \delta_{i,1} \int ds_{\text{frac}}^1 \exp[-\beta U_{\text{frac},1}(s_{\text{frac}}^1, s^{N_1}, \lambda, V_1)] \\ & + \delta_{i,2} \int ds_{\text{frac}}^2 \exp[-\beta U_{\text{frac},2}(s_{\text{frac}}^2, s^{N_T-N_1}, \lambda, V_T - V_1)] \end{aligned} \right) \quad (2)
\end{aligned}$$

where $\beta = 1/(k_B T)$ and Λ is the thermal wavelength. The fractional molecule can be transferred between the boxes and i indicates the box where fractional molecule is in. $U_{\text{int},i}$ and $U_{\text{frac},i}$ are the total internal energy of the whole molecules and the internal energy of the fractional molecule in box i , respectively. V_T is the total volume and V_1 is the volume of box 1. $\delta_{i,j}$ equals 1 when $i = j$ and zero otherwise. Except for the trial moves used for the thermalization of the system and volume changes, three other trial moves are used to facilitate particle exchanges between the simulation boxes:

- Changing the scaling parameter λ with $\lambda \in \langle 0, 1 \rangle$. λ is changed by adding a uniformly distributed random value from the interval $[-\Delta\lambda, \Delta\lambda]$ while the fractional molecule stays in the same simulation box at the same position. It is important to note that the maximum change in λ (denoted by $\Delta\lambda$) can be much larger in the gas phase than in the liquid phase.

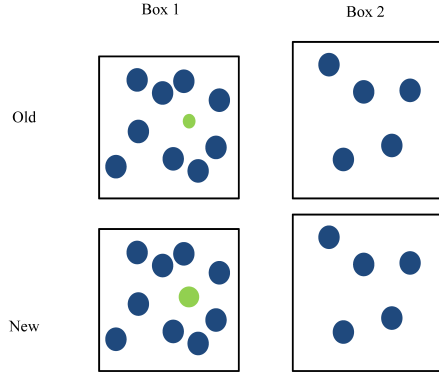


Figure 1: Schematic representation of the trial move attempting to change the coupling parameter λ while the fractional molecule stays in the same simulation box. The green sphere is the fractional molecule.

- Swapping the fractional molecule between the boxes, while keeping the value of λ fixed. The rest of the system is unchanged in this trial move.

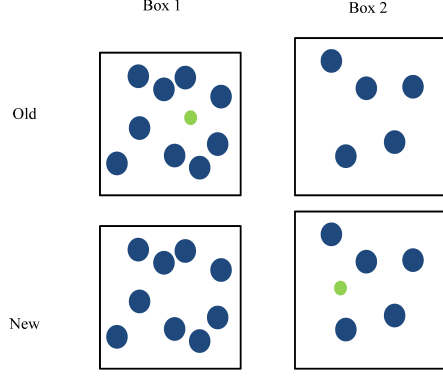


Figure 2: Schematic representation of the trial move attempting to swap the fractional molecule between the simulation boxes. The green sphere is the fractional molecule.

- Changing the fractional molecule into a whole molecule while keeping its position fixed and, simultaneously, changing a randomly selected whole molecule in the other simulation box into a fractional molecule, while not changing the value of λ .

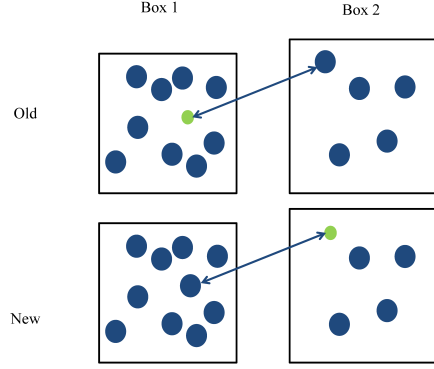


Figure 3: Schematic representation of the trial move attempting to change the fractional molecule into a whole molecule while keeping its position fixed, and simultaneously, change a randomly selected whole molecule in the other simulation box into a fractional molecule while not changing the value of λ .

Chemical Potential: The chemical potential in the CFCMC GE simulations follows directly from the probabilities that λ approaches zero or one. $p_i(\lambda)$ is a two-dimensional probability distribution which shows the probability of finding a certain λ in box i . The chemical potential in the new formulation of the CFCMC GE is identical to that in the conventional Gibbs Ensemble [8]. For sufficiently large systems, the chemical potential in the CFCMC GE becomes

$$\mu_{\text{CFCMC},1} = -k_B T \ln \left\langle \frac{V_1/\Lambda^3}{N_1 + 1} \right\rangle - k_B T \ln \left\langle \frac{p_1(\lambda \uparrow 1)}{p_1(\lambda \downarrow 0)} \right\rangle \quad (3)$$

Where 1 indicates box 1. $p_1(\lambda \uparrow 1)$ is probability of λ approaching 1 in box 1, and $p_1(\lambda \downarrow 0)$ is the probability of λ approaching 0 in box 1. The same expression holds for box 2. At the end of the simulation, chemical potentials of both boxes should be equal if the two boxes are in equilibrium.

3 Biasing:

At high densities, the probability distribution of λ deviates from a flat distribution especially in the liquid box. When the fractional component is in the liquid box, pair interactions between the fractional particle and the whole particles for certain values of λ are energetically more favourable. Therefore, λ becomes stuck at certain values during the simulation, and this reduces the rate of particle exchange. Therefore it takes longer to achieve chemical equilibrium. By applying biasing to each simulation box independently, we can make the probability distribution of λ in such a way that the sampled probability distributions $p_i(\lambda)$ are flat and that the fractional molecule is equally likely to be in box 1 and box 2 (in principle by changing the applied bias one could tune this ratio to any desired value). This will increase the particle exchange rate between the boxes considerably at high densities. In practice, this is realized by multiplying the statistical weight of each system state by a factor $\exp[W(\lambda, i)]$ (i being the box in which the fractional molecule is located). It is important to note that because the fractional molecule can be located in two boxes, the weight function $W(\lambda, i)$ is a two-dimensional function that depends both on λ and the box the fractional molecule is located in (i). To obtain the correct Boltzmann averages, the ensemble average of an observable X should be computed using

$$\langle X \rangle_{\text{Boltzmann}} = \frac{\langle X \exp[-W(\lambda, i)] \rangle_{\text{modified}}}{\langle \exp[-W(\lambda, i)] \rangle_{\text{modified}}} \quad (4)$$

In principle it is possible to run the simulations without a biasing function. The particle exchange however in dense systems will become far less efficient as the λ space is not flat anymore. This will increase the length of the simulation to reach chemical equilibrium.

The Wang-Landau algorithm: In order to make a flat λ space, Wang-Landau algorithm can be used [9]. This algorithm performs a random walk in λ space. Initially a two-dimensional histogram $H(\lambda, i)$ and a two-dimensional weight function $W(\lambda, i)$ are set to zero. Every time a certain system state is visited, based on location and value of λ , the following rules are applied to update $H(\lambda, i)$ and $W(\lambda, i)$

$$H(\lambda, i) \rightarrow H(\lambda, i) + 1 \quad (5)$$

$$W(\lambda, i) \rightarrow W(\lambda, i) - F \quad (6)$$

Where F is the modification factor which is subtracted from the weight function every time a certain system state is visited (as a penalty of visiting that state). The random walk continues until the λ histogram becomes flat. F is then reduced and the whole algorithm is repeated until the optimal weight function is achieved. The accuracy of the scheme is proportional to F . Note that the weight function is changing during the simulation, this means that during the random walk in λ space, the detailed balance condition is not met. The detailed balance is used as a test of the validity of the Monte Carlo scheme [10]. Therefore it is important NOT to take any ensemble averages while the Wang-Landau algorithm is being used.

Questions

Before starting with the simulations, pay attention to the following points.

- File "run" in the Run folder contains the simulation input. There are 4 logical variables in "run" Linit, Lweight, LWL and LIT which can be either true or false. Set the Linit to true in order to use the coordinates from the equilibrated system coordinates provided, named "Coordold". Otherwise the simulation will generate new coordinates in the beginning of the simulation.
 - Set Lweight to true in order to use the optimal weight function, named "Weigthold". Remember that the Wang-Landau scheme (LWL) should be set to false, so the weight function does not change during the simulation.
 - If Wang-landau scheme is running (LWL is true), the simulation will immediately finish after the optimal weight function is calculated. Rename the weight function to "Weightold" and run the simulation again with the logical variable Lweight set to true in order to calculate the ensemble averages using the new weight function.
1. Run the CFCMC GE simulation for a Lennard-Jones fluid at low temperature (reduced) $T = 0.6$ for two cases. First, with the provided optimal weight function named "Weightold" in the Run folder. Second, run a separate simulation with the exact same simulation input except without a weight function (without the optimal weight function). Answer the following questions for each case
 - What is the difference between the acceptance ratios for the swap and change moves?
 - In which case has the system reached chemical equilibrium?
 - What is the value of the chemical potential for the gas and the liquid phase in each case?
 2. Repeat question 1 for a Lennard-Jones fluid with reduced temperature of $T = 0.95$ (close to critical temperature). Use the optimal weight function provided for $T = 0.95$.
 - Does increase in temperature affect the acceptance ratio for swap and change moves? Explain this for both cases with and without the optimal weight functions.
 3. Plot the weight functions for both reduced temperatures $T = 0.6$ and $T = 0.95$. What causes one to be more flat than the other?
 4. Run the Wang-Landau scheme to calculate the weight function for $T = 0.6$ and $T = 0.95$.
 - Are the new weight functions in agreement with the optimal weight functions? Use gnuplot or similar programs for visualisation.
 - Run the simulations again with the new weight functions for $T = 0.6$ and $T = 0.9$ and compare the acceptance ratios with the ones from questions 1 and 2.
 5. Is it possible to obtain a perfectly flat weight function using the Wang-Landau scheme? Why?

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