Abstract

The gas-liquid phase transition of the three dimensional Lennard-Jones fluid is studied using a Gibbs Ensemble Monte Carlo simulation. The densities of both phases are computed for several temperatures in order to build the phase diagram. The critical parameters, as the temperature, density and the exponent of the order parameter $\beta$ are calculated using the scaling law and the law of rectilinear diameter. Results are compared with others available in the literature concluding that this model belongs to the Ising-like universality class.
1 Introduction

The study of phase transitions has a vital importance in material sciences because there exist a wide variety of problems that have a direct mapping to a phase transition at some scale or scales. For instance, turbulence in fluid dynamic is one of the most complex problems since the first attempts of theoretical description and still nowadays is and open question. It is challenging because to understand it, the starting point is the laminar-turbulent transition which involves a cascade of energy transfer from large to small scales making it difficult to study either from a continuum media or a microscopic approach.

Many manufacture problems in a broad number of applications as metal casting and molding, polymer synthesis, metallic glasses among others, involve a deep knowledge of the precise parameters of the phase transitions in order to optimize the processes, so in order to investigate these problems and thanks to the exponential increase of computational power, in the present is common to approach these questions from a numerical point of view which helps to understand how the microscopic interactions, i.e potential, influences the phase transition and the properties of the materials. Bearing this in mind, the present work is a first approximation to the application of these methods, specifically the Monte Carlo scheme, to the study of the phase transition in a off-lattice model problem, the gas-liquid transition in the Lennard-Jones fluid. The study of this simple model will give an overview of the connection between the outcome of these numerical techniques and the theory of phase transitions, leading to have a deeper insight of the physical problem not only from a quantitative point of view but also a quantitative.

2 Models and simulation method

To study computationally the phase coexistence of the Lennard-Jones fluid, in the literature there are mainly two approaches, the first consists in dividing the physical domain into two subsystems, each containing either the gas or liquid phase without any physical contact between them. This scheme was proposed by Panagiotopoulos [3] with the aim of studying first order phase transitions in liquids. Obviously this approach is suitable by definition to be performed on the frame of Monte Carlo simulations due to the impossibility of moving a particle from one system to another by following a physical path, thus commonly this method is known as Gibbs Ensemble Monte Carlo (GEMC). On the other hand, around 25 years later and thanks to the improvement of computational resources, Watanabe et al [10] proposed to simulate the full system including the liquid-gas interphase inside a unique domain, using Molecular Dynamics (MD) with a Lennard-Jones (LJ) truncated and shifted potential. This novel approach leads to study the evolution and critical behavior of new parameters as the surface tension and the thickness of the interphase.

In the present study we are going to follow the former approach, based mainly on the ideas proposed by Frenkel and Smith [2]. Before going into the details of the implementation of the algorithm, it is worth mentioning that this GEMC describes finite systems with periodic boundary conditions, so it is complicated to approach and estimate the critical behavior by definition due to the divergences present, specially with the correlation length that can be studied only under a detailed finite size scaling anal-
ysis, which can be performed easily on a lattice problem but not in off-lattice models, specially using the Gibbs ensemble where the variability in the number of particles and volume make it difficult to implement. Even though, an excellent study of the finite size effects with a more defined GEMC technique was performed by Panagiotopoulos [4] leading to the important conclusion that for Lennard-Jones type potentials in three dimensional problems, these effects are present but they do not influence drastically the results even for relatively short cutoffs. While for low dimensionality, for instance the 2D Lennard-Jones problem, they do play an important role.

Here we use the well known 12-6 LJ potential of the form:

\[ V_{LJ}(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \]  

(1)

where \( \sigma \) is the distance at which the intermolecular potential between the two particles is zero, and \( \epsilon \) is the well depth. It is important to note that all the measurements and quantities reported in this work are in reduced units with respect to the LJ parameters.

Additionally, the pairwise potential is truncated at \( r_c \) for the sake of practicality, so,

\[ V_T(r) = \begin{cases} 
V_{LJ}(r) & : r \leq r_c \\
0 & : r > r_c 
\end{cases} \]

Now, continuing with the description of our algorithm, as it was mentioned previously, we assume two subsystems, two microscopic regions within the bulk phases far away from the interface. Both having the same temperature and being able to exchange volume and particles. Then to satisfy the phase coexistence condition and to check the convergence of the technique it is expected that at the end of the simulation, in addition to the temperature, also the pressure and chemical potentials in both systems will be equal. Thus there are basically three Monte Carlo trial moves available [1]:

1. Displacement of a randomly selected particle within one of the boxes, in order to satisfy internal equilibrium.
2. Change of the volume keeping the total volume of the system constant, to reach equal pressure in both volumes.
3. Exchange of a randomly selected particle between the boxes, to reach equality of chemical potential in both systems.

Each of the movements with a given acceptance rule in the Metropolis scheme.

In order to fulfill detailed balance, in accordance with Smit [8], trials moves are randomly chose to avoid trapping of the system in certain regions of the configuration space. In our case, for every 100 particle displacements, there are 10 particle swapping and just 1 volume change. This with the aim of keeping the efficiency of the algorithm, giving more chances to rather inexpensive trial moves, as particle displacement, than to volume changes. Also it was set during the implementation of the algorithm that after each 10% of the total simulation run, the maximum volume and particle displacement were adjusted in order to get a 50% of acceptance rate.

Simulations were performed for 256 particles, with 10000 Monte Carlo Steps (MCS)
per run, each step consisting on 222 attempts of trial moves. In order to obtain statistically relevant data, sampling of the parameters started after the equilibration of the system. As an example, in Figure 1 it is shown that for the reduced temperature $T^* = 0.8$ a reasonable point to start sampling is after 5000 MCS, when the potential energy for both boxes just oscillates with a small amplitude. It is also important to remark here that in order to process the data obtained from the simulations an autocorrelation analysis has to be performed due to the nature of the Metropolis Monte Carlo scheme.

Moreover, equilibration is required because the initial configuration is set with both boxes having the same volume and containing equal number of particles, so the initial density might be far away from the characteristic densities for both phases at the given temperature. In Figure 2 it is shown how the density of both boxes evolve for $T^* = 0.8$, which is a temperature relatively far from the critical point so a regular behavior is expected after each box has defined its identity, either in the gas or liquid phase. Later on, it is going to be discussed that this does not apply for temperatures close to the critical point.

Figure 1: Equilibration behavior of the potential energy for both boxes at reduced temperature $T^* = 0.8$. 

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Once the computational procedure is stated, then it is important to remark some points about the critical behavior of the Lennard-Jones fluid. It is well known in the literature that the order parameter for the liquid-gas transition is the density difference between both phases $\Delta \rho = \rho_l - \rho_g$, which becomes zero at the critical temperature and the behavior near the criticality is given by the scaling relation:

$$\Delta \rho \sim \left( \frac{|T_c - T|}{T_c} \right)^\beta$$

where $T_c$ is the critical temperature and $\beta$ the critical exponent.

In general, it is difficult to determine both the critical temperature and exponent simultaneously only by using the scaling relations, so usually the Ising universality is assumed on the literature, then it is straightforward to find the critical temperature. Now, after finding the critical temperature the aim is to find the critical density $\rho_c$ to define completely the critical point in the phase diagram. Bearing this in mind, we can use the law of rectilinear diameters [5]:

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

This equation states basically that the average density has a linear dependence on the temperature. This phenomenological law has been extensively studied and can be assumed that it describes with high accuracy the behavior of simple fluids [9].

3 Results and discussion

As it was mentioned before, it is easy to obtain all the relevant physical quantities once the system reaches the equilibrium during the simulation when the temperature
is far from $T_c$. But there is a problem when the system is approaching the critical point because as it happens in the real experience, at a certain point the system can go from gas to liquid phase and vice versa with a rather small perturbation, this is observed on the simulations when the identity of the boxes is no more well defined as before as shown in Figure 3, where this density switching is evidenced, showing that both boxes move from liquid to gas densities and thus the system never reaches a steady state.

![Figure 3: Density switching between the two boxes at $T^* = 1.25$.](image)

Fortunately, one can build a histogram of the probability density $P(\rho)$ to observe a density $\rho$ in either box and as the results are not influenced when the boxes change identities thus the maxima of the probability is well defined. In Figure 4 it is shown how the histogram is built for two different temperatures, $T^* = 0.8$ and $T^* = 1.25$, for the former there is no density switching and there is not even need of building a histogram. On the other hand, for the later, it can be observed that there are three peaks, the two peaks from the extremes corresponding to the gas and liquid densities and the central peak is a result of the evolution during the identity swapping and can be avoided [7].
Figure 4: Probability density $P(\rho)$ to observe a density $\rho$, (a) $T^* = 1.25$ (b) $T^* = 0.8$.

In Figure 5 the phase diagram of the liquid-gas transition is shown, including the estimation of the Law of rectilinear diameters (LRD) given by Equation 3 and the critical point. The critical temperature $T_c$ and exponent $\beta$ were calculated using the scaling relation in Equation 2 together with the Levenberg-Marquardt algorithm which performs a non-linear least squares analysis to fit the function, thus without assuming the Ising universality.
Simulation
LRD
Critical point

Figure 5: Phase diagram of the 3D Lennard-Jones fluid, statistical error are smaller than
the symbol size

Results from the present work and other studies are summarized in Table 1. In
accordance with the results obtained by Watanabe [10] or in the present work, where
the critical exponent was obtained without any initial assumption, it can be observed
that the critical exponent of the order parameter $\beta$ is consistent with the Ising univer-
sality class. On the other hand, there is no consensus with respect to the critical point,
this might be due to three factors: the different techniques used, Molecular Dynamics
or Monte Carlo. The variety of approaches including or not the interphase, different
ensembles, etc. And the last but not the least important, as showed by Smith [8],
the truncation of the potential in bulk properties calculations makes little difference,
however for the liquid-vapor coexistence curves, small changes in truncation procedure
make a very large difference indeed in the obtained results.

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Table 1: Critical properties of 3D Lennard-Jones fluid

4 Conclusions

The Gibbs ensemble approach leads to study the phase coexistence of the Lennard-
Jones fluids avoiding to deal with the interphase problem, making it much easier to
study off lattice problems. This approximation falls between the mean field theory approximation and the real experimental behavior because despite the fact that gives a deeper numerical description than the former, still it is difficult to deal with the finite size effects inherent to the computational approach. After studied this simple model one can add more complexity to study mixtures of different particles to describe colloids and more sophisticated systems. The extension is in principle straightforward once the algorithm is running for the simple case.

Thanks to the theory of phase transition and critical phenomena it is possible to perform calculations on the critical properties based on the numerical estimates on the phase diagram of the liquid gas transition. Thus using the scaling relation for the order parameter one can obtain the critical exponent $\beta$ and the critical temperature. Moreover, assuming the law of rectilinear diameters then the critical density can be obtained to determine completely the critical point in the phase diagram. However, comparing the results with those on the literature it can be inferred that this problem is very sensitive with respect to the models used, the numerical technique implemented and the most important, the truncation of the potential.

Finally, the obtention of the critical exponent of the order parameter without any assumption leads to conclude that problems with Lennard-Jones type potentials might belong to the Ising-like universality class. This fact opens the door for more theoretical studies of this model using this evidence as a starting point.

References