

PROJECT REPORT

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Phase Transition in Multiphase Systems

Submitted by

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ABSTRACT

Lattice Boltzmann Method is used to study a nonideal fluid in a periodic box. Below the critical temperature (T_c), phase separation occurs which results in two separate liquid and gaseous phase. Three different discretisation schemes, using two different equations of state are compared for accuracy by comparing the final phase densities (ρ_L, ρ_G) at different temperature (T) values with their corresponding Maxwell construction.

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1 Theoretical Background

An equation of state relates the pressure P , volume V and temperature T of a physically homogeneous system in the state of thermodynamic equilibrium. The ideal gas equation of state is the most simple thermodynamic representation of a fluid. When trying to model real fluid the ideal gas equation of state faces limitations as it assumes point particles without any attractive or repulsive forces between them. A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 [3] to consider molecular size and molecular interaction forces. Van der waal's EOS (Equation of State) is one of the two EOS considered for this project. Equation of state is given by,

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2} \quad (1)$$

$$= \frac{\rho k_B T}{1 - \rho b} - a\rho^2, \quad (2)$$

where, N is total number of particles, k is Boltzmann constant, and ρ is density.

The constants a and b have positive values and are characteristic of the individual gas. The constant a provides correction for the intermolecular forces. b is the volume excluded by a mole of molecules as molecules are considered to have finite size. At small values of pressure and volume constants a and b approaches zero as gases tend to behave ideally. Critical temperature(T_c), Critical Volume(V_c) and Critical Pressure(P_c) in terms of a and b are given by,

$$T_c = \frac{8a}{27Rb}, \quad P_c = \frac{a}{27b^2}, \quad V_c = 3b.$$

The Van der Waal's EOS using dimensionless quantities is

$$\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3 - \tilde{\rho}} - 3\tilde{\rho}^2,$$

where

$$\tilde{P} = P/P_c, \quad \tilde{\rho} = \rho/\rho_c, \quad \tilde{T} = T/T_c.$$

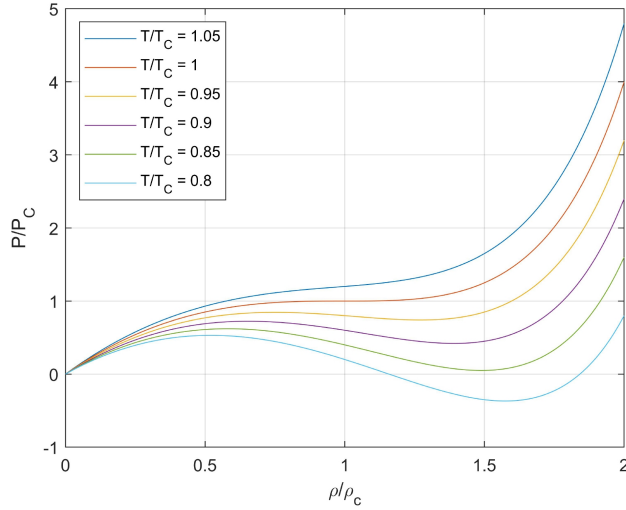


Figure 1: Van der Waal's Isotherms

Fig.1 represents the variation of reduced pressure values (P/P_c) with reduced density values (ρ/ρ_c) for various reduced temperature values (T/T_c).

The Carnahan-Starling equation of state is an approximate equation of state for the hard sphere model of the fluid, where molecules are considered to have finite volume and exhibit attractive and repulsive forces. It is given by

$$P = \rho k_B T \left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - a\rho^2,$$

where $\eta = \rho b/4$. Carnahan-Starling EOS provides larger density ratios at temperatures below Critical Temperature as compared to Van der Waal EOS.

1.1 Numerical Stability

The numerical solutions to differential equations may exhibit unstable behaviour. That is, the computational results may include exponentially growing and sometimes oscillating features that bear no relation to the solution of the original differential equation. This type of behaviour is referred to as a computational instability or numerical instability.

If the error on the data during various time steps does not get amplified, the algorithm is said to have numerical stability for those certain set of input parameters. In general, it would be desirable to have a means of predicting when computational as opposed to physical instabilities can occur. Unfortunately, no general method has yet been devised.

1.2 Discretisation

In the real world, the physical phenomena are macroscopically continuous in nature that is, for example, transition from one phase of matter to another phase takes place in continuous manner. When physical phenomena are simulated in computational environment then those physical phenomena are treated in discrete manner instead of continuous. Computational simulation is done numerically that is computer deals with numerical data and that data collectively simulates the whole physical process. This is known as discretisation.

During discretisation, as the macroscopic continuous process is simulated using discrete numerical data, approximation is inherited in the process, which in turn gives rise to errors. When actual physical phenomena are simulated in computational environment various techniques and expressions are used for the discretisation. These techniques and expressions are called as discretisation schemes. Different discretisation schemes are used to reduce the errors as much as possible when compared with its theoretical values.

2 Problem Statement

We intend to model a fluid having initial temperature (T) below its Critical Temperature (T_C) to obtain following:

- Final density in given domain after a specified time period during which system evolves from its initial state.
- Comparison of the results with theoretical Maxwell Construction[2] to determine accuracy of discretisation schemes.

3 Solution Methodology

3.1 Lattice Boltzmann Method

Lattice Boltzmann method (LBM) is a methodology based on the microscopic particle models and mesoscopic kinetic equations. Its strength lies in the ability to easily represent multiphase flows [4]. The origin of this method is in the molecular description of a fluid and it can directly incorporate physical terms stemming from a knowledge of the interaction between molecules [1].

Generalised Algorithm:

1. Selection of Site
2. Advectioint of incoming particles from direct neighbourhood
3. Collision of new set of particles that have just been advected
4. Post collision rearrangement
5. Next sight selection

3.2 Discretisation Schemes

We know,

$$P = -\frac{\partial F}{\partial V},$$

where F = Helmholtz free energy, V = Volume. For N number of particles, let

$$\frac{F/V}{N/V} = \frac{f}{\rho},$$

from where one obtains,

$$P = -\frac{\partial(f/g)}{\partial \rho} \left(\frac{\partial \rho}{\partial V} \right) \tag{3}$$

$$= \rho^2 \left(\frac{\partial f}{\partial \rho} \frac{1}{\rho} - \frac{f}{\rho^2} \right) \tag{4}$$

$$= \rho \mu - f, \tag{5}$$

where μ = Chemical potential.

Hence, we get

$$\nabla P = \rho \nabla \mu + \mu \nabla \rho - \nabla f \tag{6}$$

We test three differnt discretisation schemes for equation (6). Those are as follows,

1. Scheme 1:

$$\nabla P = \left[\rho_i \frac{\hat{\nabla} \mu}{2} + \frac{\rho_{i+1} + \rho_{i-1}}{2} \frac{\hat{\nabla} \mu}{2} \right] + \left[\mu_i \frac{\hat{\nabla} \rho}{2} + \frac{\mu_{i+1} + \mu_{i-1}}{2} \frac{\hat{\nabla} \rho}{2} \right] - \hat{\nabla} f$$

2. Scheme 2:

$$\nabla P = \rho \hat{\nabla} \mu + \mu \hat{\nabla} \rho - \hat{\nabla} f$$

3. Scheme 3:

$$\nabla P = \frac{\rho_{i+1} + \rho_{i-1}}{2} \hat{\nabla} \mu + \frac{\mu_{i+1} + \mu_{i-1}}{2} \hat{\nabla} \rho - \hat{\nabla} f$$

3.3 Periodic Boundary Condition (PBC)

Periodic Boundary Conditions are used to model infinitely large systems. This is equivalent to considering an infinite, space-filling array of identical copies of the simulation region. The central idea is to predict the properties of a bulk material by simulating a small (finite) system. We assume that, infinite number of such small system (viz. simulation box) exist everywhere. All the molecular features are identical in each of the boxes.

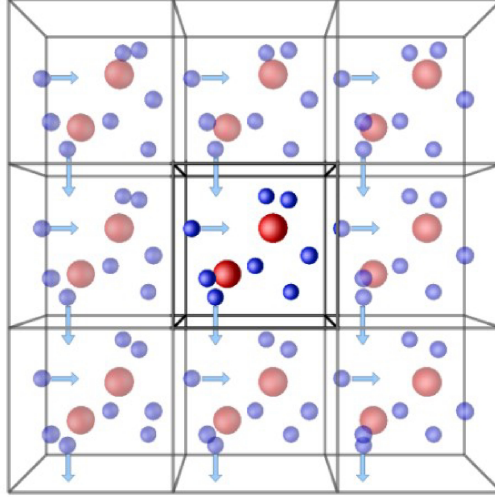


Figure 2: Schematic for Periodic Boundary Condition
Source: <http://isaacs.sourceforge.net/phys/pbc.html>

Here we have central box with certain arrangement of particles. According to PBC, the same arrangement is present in all the boxes surrounding it. Any change takes place within this control box, will replicate in all the boxes. If a particle leaves the central box along any direction, its image particle will enter the box from opposite direction.

4 Result

We worked with dimensionless quantities in which we scaled down Temperature T and Density ρ to T/T_C and ρ/ρ_C respectively. Input parameters for the code are β , T/T_C , ρ/ρ_C . Where β is defined as,

$$\beta = \frac{dt}{2\frac{V_k}{\theta_0} + dt},$$

where $\theta_0 = \rho K_B T$ and $V_k =$ Kinematic Viscosity.

- Van der Waal's Equation of State

1. Scheme 1 (Fig.3 and Fig.4):

- When compared for T/T_C values below 0.85, increasing β value decreases the accuracy and increases the stability for lower values of T/T_C .
- Decreasing β generates numerical instability for lower initial values of ρ/ρ_C .
- Decreasing ρ/ρ_C increases the accuracy.

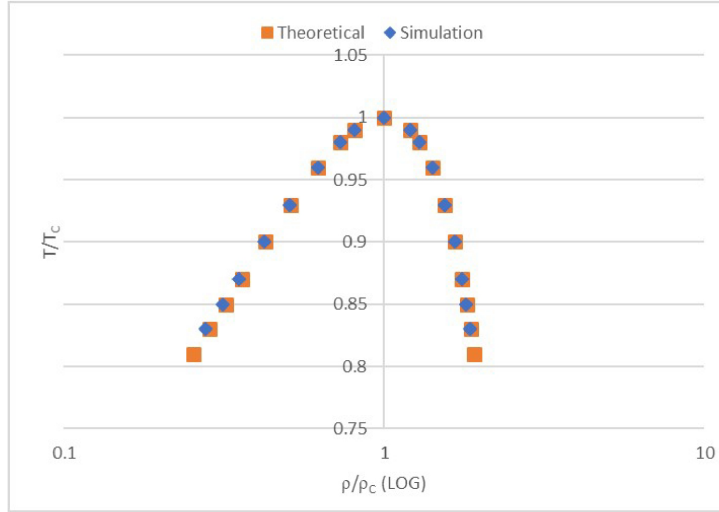


Figure 3: Scheme 1, $\beta = 0.7$

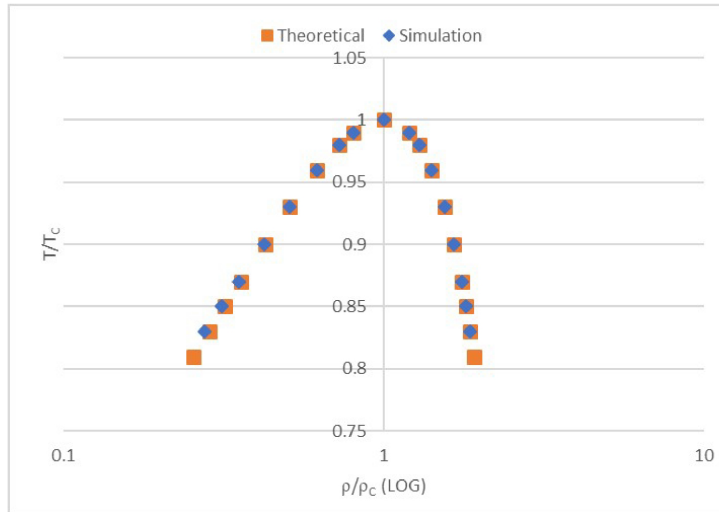


Figure 4: Scheme 1, $\beta = 0.9$

2. Scheme 2 (Fig.5):

- Decreasing ρ/ρ_c decreases the accuracy.
- Keeping ρ/ρ_c constant while decreasing β doesn't affect in making lower T/T_c values numerically stable.
- For beta above 0.7, increasing β decreases the stability.

3. Scheme 3 (Fig.6):

- This scheme is stable only for T/T_c values greater than 0.88. Hence, effect of β on the accuracy cannot be determined as $T/T_c < 0.85$ is not possible.
- Decreasing initial ρ/ρ_c has no effect on final accuracy.

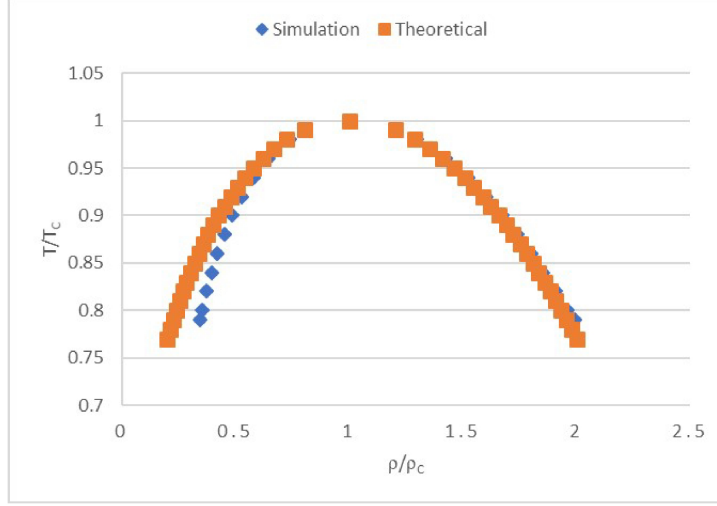


Figure 5: Scheme 2, $\beta = 0.9$

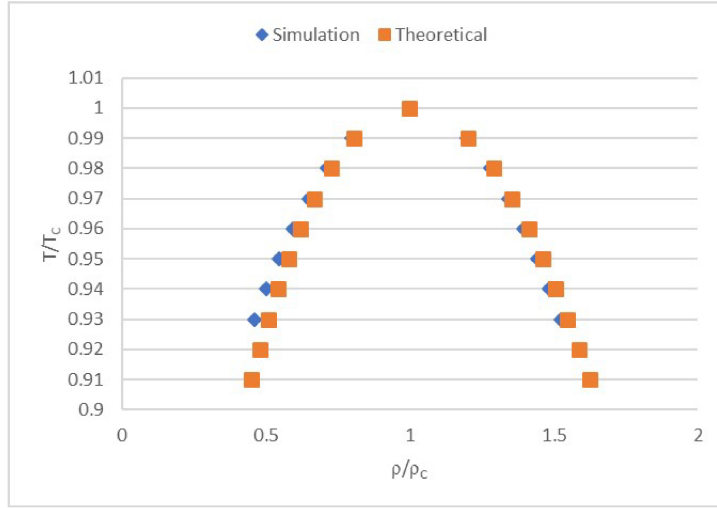


Figure 6: Scheme 3, $\beta = 0.9$

- Carnahan-Starling Equation of State

1. Scheme 1 (Fig.7):

- Beta is having negligible effect on accuracy.
- Increasing beta decreases the stability for lower values of T/T_c . Decreasing ρ/ρ_c increases the accuracy.

2. Scheme 2 (Fig.8):

- Decreasing initial value of ρ/ρ_c increases the accuracy.
- Decreasing β makes lower values of ρ/ρ_c numerically stable.
- Keeping β constant while decreasing ρ/ρ_c makes lower values of T/T_c numerically stable up to a certain limit.

3. Scheme 3:

This scheme gives highly unstable results, irrespective of values of input parameter. Hence, no analysis of this scheme for Carnahan-Starling Equation of State could be done.

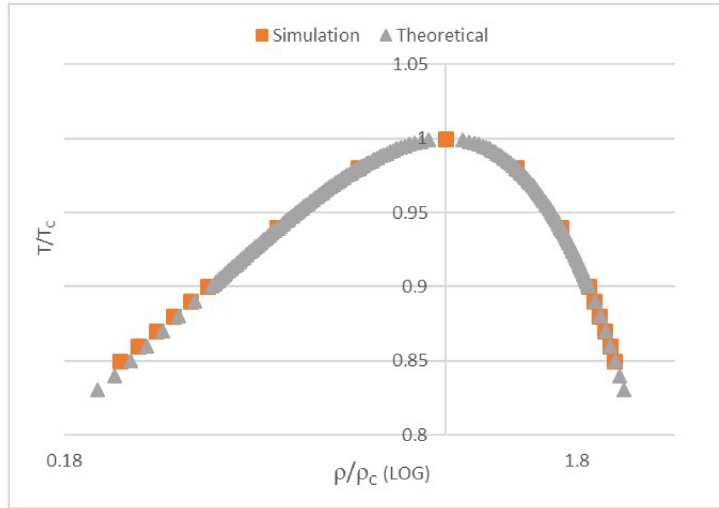


Figure 7: Scheme 1, $\beta = 0.7$

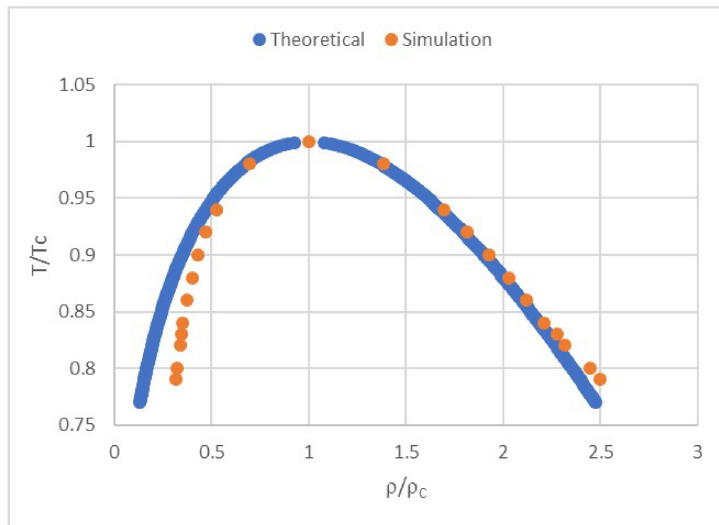


Figure 8: Scheme 2, $\beta = 0.7$

5 Conclusion

When simulation output is compared with theoretical data, it is concluded that scheme 1 is the most accurate of all the three schemes for both equations of state. When there is requirement of ρ/ρ_c values at T/T_c values less than 0.84, scheme 2 is preferred as scheme 1 is numerically unstable in this range.

References

- [1] Lattice boltzmann method - overview.
<http://www.palabos.org/software/lattice-boltzmann-method>. Accessed on 31-05-2019.
- [2] Harvey Gould and Jan Tobochnik. Chapter 7: The chemical potential and phase equilibria. pages 357–388, July 2009.
- [3] Shpilrain. Van der waals equation of state. <http://www.thermopedia.com/content/1232/>, February 2011. Accessed on 31-05-2019.
- [4] Saikishan Suryanarayanan, Shiwani Singh, and Santosh Ansumali. Extended BGK boltzmann for dense gases. *Communications in Computational Physics*, 13(3):629–648, March 2013.