

## LATTICE BOLTZMANN SIMULATION OF HIDRODYNAMICAL SPINODAL DECOMPOSITION

**Antônio Vinicius Gomes Teixeira, [vinicius@lmpt.ufsc.br](mailto:vinicius@lmpt.ufsc.br)**

**Rodrigo Surmas, [surmas@lmpt.ufsc.br](mailto:surmas@lmpt.ufsc.br)**

**Luiz Adolfo Hegele Junior, [hegele@lmpt.ufsc.br](mailto:hegele@lmpt.ufsc.br)**

**Luís Orlando Emerich dos Santos, [emerich@lmpt.ufsc.br](mailto:emerich@lmpt.ufsc.br)**

**Paulo César Philippi, [philippi@lmpt.ufsc.br](mailto:philippi@lmpt.ufsc.br)**

LMPT, Departamento de Engenharia Mecânica, UFSC

Trindade, Florianópolis, Santa Catarina

CEP 88040-900, Caixa Postal 476

**Abstract.** Binary mixtures separate into two immiscible fluids when quenched below a critical temperature. Once the process starts, the two fluid domains grow and the interfacial area decreases as a power law with time. This process, known as spinodal decomposition, is important in the metallurgical, oil and food industries. In this work, a lattice Boltzmann method (LBM), based on a discretization of the continuous Boltzmann equation using a BGK collision operator, is used to study the spinodal decomposition. Because of its mesoscopic character, the LBM is suitable for the macroscopic description of microscopic interactions, as interface dynamics and capillary phenomena. We investigate the effect of domain size, the viscosities of the fluids and the interfacial tension in two dimensional simulations. The results obtained show a very good agreement with experimental results and other works. The viability of using the present model to simulate two-phase two-component flow is evaluated.

**Keywords:** lattice Boltzmann method, spinodal decomposition, immiscible fluids

### 1. INTRODUCTION

When a mixture of two immiscible fluids is quenched below a critical temperature, known as the spinodal temperature, it segregates into two phases with different compositions. This phenomenon is called spinodal decomposition and it is a process of significant intellectual and industrial relevance. For 50:50 mixtures, also called critical or symmetric mixtures, the phases form interconnected domains, which at late times produce a bicontinuous structure with sharp, well developed interfaces. Once integral domains have formed, experimental and theoretical evidences show that the system evolves with time  $t$  in a way that is scale invariant. Hence lengths such as the domain size  $R(t)$  grows according to a power law  $R(t) \sim t^\alpha$  and the interfacial area  $A$  decreases with time as  $A(t) \sim t^\beta$ ,  $\beta < 0$ . The exponents  $\alpha$  and  $\beta$  are believed to be universal (González-Segredo *et al.*, 2003), depending only on the growth mechanism and not on the details of the particular system.

Spinodal decomposition has been studied by experimental, analytical and numerical approaches. The fact that it involves a lot of mechanisms that can act concurrently and at different time and length scales, has made it an important test for complex fluid simulation methods.

The lattice Boltzmann method is a mesoscopic approach to simulate fluid flows, based on Kinetic Theory. In this method, the Boltzmann transport equation is solved with a simplified collision model, the BGK (Bhatnagar *et al.*, 1954). The lattice Boltzmann model is an efficient way to simulate hydrodynamics, coupling easy implementation and algorithm efficiency due to the simplicity of the Boltzmann-BGK collision operator.

We study the growth of the domains and the decrease of interfacial area with time. Results show very good agreement with other works and with theoretical prediction.

### 2. LATTICE BOLTZMANN METHOD

The lattice Boltzmann method can be interpreted as a finite difference solver for the Bhatnagar-Gross-Krook (BGK) approximation to the Boltzmann transport equation. This method appeared in the end of the 80's as an extension of the lattice gas model (Lattice Gas Automata). In the lattice gas, particles in the nodes of a discrete system have a discrete velocity. After a time interval, the particles move to neighbor sites, according to their velocity. This phase is known as propagation. Then the particles collide and change their velocity, at the collision phase. After that, the simulation proceeds in an alternation between collisions and propagations.

The major inconvenience in lattice gas simulations is the presence of noise. To avoid this noise, is necessary to do averages over a very large domain and over a long time. The lattice Boltzmann method solves this problem by pre-averaging the number of particles in a lattice gas site. Instead of one particle at each direction, in the lattice Boltzmann method a distribution of particles exists at each node, at each direction.

The general form of the discrete Boltzmann equation is shown at Eq. 1, where  $f$  represents the distribution function, which is the concentration of particles that travel with velocity  $\mathbf{c}_i$ , and  $\Omega_i$  is the collision operator.

$$f_i(\mathbf{X} + c_i \Delta T, T + \Delta T) - f_i(\mathbf{X}, T) = \Omega_i \quad (1)$$

The local density  $\rho$  and velocity  $\mathbf{u}$  are the first and second order moments of the particle distribution  $f$ ,

$$\rho(\mathbf{X}, T) = \sum_i f_i \quad (2)$$

$$\mathbf{u}(\mathbf{X}, T) = \frac{\sum_i f_i \mathbf{c}_i}{\rho(\mathbf{X}, T)} \quad (3)$$

In order to simulate the behaviour of a immiscible fluid, one particle distribution function is related to each fluid. The two distributions interact with each other by a potencial, generated by field mediators, Santos *et al.* (2003). These mediators are particles with no mass that are emanated from the each site of the domain and whose only effect is to invert the momentum of particles, simulating the long-range field. Four distribution functions will be used, each one representing the two types of particles and their respective mediators,  $N_i^\psi(\vec{X}, T)$  and  $M_i^\psi(\vec{X}, T)$ , where  $\psi = r, b$  represents the type of fluid. Mediator dynamics can be described by equation

$$M_i^\psi(\vec{X} + \vec{c}_i, T + 1) = \frac{\rho^\psi(\vec{X}, T)}{\rho^r(\vec{X}, T) + \rho^b(\vec{X}, T)} \quad (4)$$

The velocity of mediators  $\vec{u}^m$  is defined as

$$\vec{u}^m(\vec{X}, T) = \sum_i M_i^r(\vec{X}, T) - M_i^b(\vec{X}, T) \quad (5)$$

Remembering the long-range interactions are expressed by changes in particle velocities, *modified velocities* are defined by the mediator action.

$$\vec{v}^r = \vec{u}^r - A \frac{\vec{u}^m}{|\vec{u}^m|} \quad (6)$$

$$\vec{v}^b = \vec{u}^b - A \frac{\vec{u}^m}{|\vec{u}^m|} \quad (7)$$

where the parameter A is related to the interaction intensity and, consequently, to the interfacial tension.

The interaction between fluid particles is modeled by a split collision operator, representing the collision between particles of the same type and of different types. Considering a single-phase flow, the main collision effect is to relax the  $N_i$  distribution towards a prescribed equilibrium distribution  $N_i^{eq}$ , which can be described by macroscopic parameters as density and velocity, using a BGK operator

$$\Omega_i^{\alpha\beta} = \frac{N_i^{eq} - N_i}{\tau^{\alpha\beta}} \quad (8)$$

with the relaxation time represented by  $\tau^{\alpha\beta}$ .

Then, the particle dynamics can be stated in the form

$$N_i^\psi(\vec{X} + \vec{c}_i, T + 1) = N_i^\psi(\vec{X}, T) + \left( \frac{\rho^\psi}{\rho^r + \rho^b} \right) \Omega_i^{\psi\psi}(\vec{X}, T) + \left( \frac{\rho^\psi}{\rho^r + \rho^b} \right) \Omega_i^{\psi\bar{\psi}}(\vec{X}, T) \quad (9)$$

where the single-phase operator  $\Omega_i^{\psi\psi}$  is reproduced by Eq. (8) ( $\psi = r$  or  $b$ ). Although, the two-phase operator  $\Omega_i^{\psi\bar{\psi}}$  also can be written in Eq. (8) form ( $\psi = r$  or  $b$ ,  $\bar{\psi} \neq \psi$ ), the equilibrium distribution has to be calculated with modified velocities according to Eqs. (6) and (7). The relaxation time  $\tau^r$  refers to the interactions between particles in the wetting fluid,  $\tau^{bb}$  in non-wetting fluid and  $\tau^b$  in the interface. After a Chapman-Enskog analysis, Santos *et al.* (2003), these three

relaxation times can be related to the viscosities of the pure phases and to the diffusivity. The macroscopic equations obeyed by the fluids in the limit of small Knudsen numbers are obtained using a perturbation method. The state equation retrieved by this analysis for the pure fluids is that of a ideal gas and large density gradients are not allowed, limiting the simulations to fluids with almost the same density. The gravity plays no role in the simulations, which is equivalent to say that the simulations were done in a horizontal plane.

### 3. SPINODAL DECOMPOSITION

When a mixture of two immiscible fluids is quenched below a critical temperature, known as the spinodal temperature, it segregates into two phases with different compositions. After the domain boundaries have achieved their thinnest configuration via diffusion, the binary structure that is formed presents similarity over time. In this work, the *dynamical scaling hypothesis* was adopted, which states that at late times, when diffusion is no longer important, there is a unique characteristic length scale which grows with time, so that the geometrical structure is independent of time when its lengths are scaled with it. The parameters that influence the characteristic length are the fluids viscosity, interfacial tension and density provided that no mechanisms are involved in their late stage growth other than viscous dissipation, fluid inertia and capillary forces.

Simulations were done to determine the effects of these parameters and to determine the growth of the characteristic length with time. Interfacial area decrease is also simulated and results are explained in the next sections. Since the main objective of this work is to determine the later-time growth exponents, we simulate generic fluids. In this manner, all units that are expressed here are dimensionless.

#### 3.1 Domain Growth

In order to evaluate the characteristic length  $R(t)$ , we define the order parameter  $\psi$  as the difference between the local densities of the fluids.

$$\psi(\mathbf{X}, T) = \rho^r(\mathbf{X}, T) - \rho^b(\mathbf{X}, T) \quad (10)$$

So the domain size  $R(t)$  will be the first zero of the order parameter correlation function, defined in Eq. 11, according to (Bray, 1994). Averages are taken over shells of radius  $r$ .

$$G(r, T) = \langle \psi(r) \psi(0) \rangle - \langle \psi \rangle^2 \quad (11)$$

Figure 1 shows  $R(t)$  for a two dimensional model. The parameters used in the simulation were  $\tau^r = 1.0$ ,  $\tau^{bb} = 1.0$ ,  $\tau^{rb} = 1.0$  and  $A = 0.4$ , size of  $512^2$  nodes and random initial distribution of  $\rho^r$  and  $\rho^b$ . The exponent found shows very good agreement with theoretical prediction (Furukawa, 1985) and other works (Chin and Coveney, 2002), (Alexander *et al.*, 1993) and (González-Segredo *et al.*, 2003) of  $t^{2/3}$ . Figure 2 depicts a sequence of snapshots of the density distribution at various times.

To guarantee that the exponent  $\alpha$  is well defined and do not depend on particular arrangement of the initial system, we ran the simulation with the same parameters as the first one shown, but with different initial displacement. The results found were the same.

Computational resources limited the simulations to  $512 \times 512$  nodes. It was observed that, at later times, when the fluid structures formed had a magnitude equivalent to the domain size, the deviances from the theoretical prediction were very large.

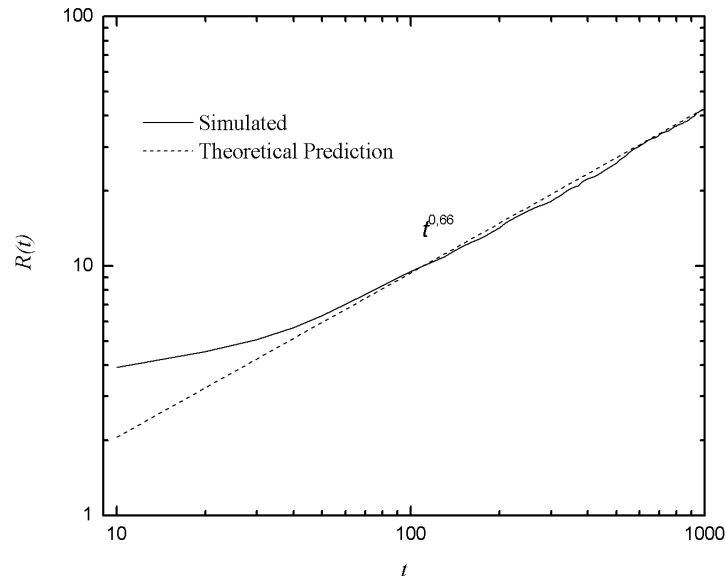


Figure 1 – Evolution of the characteristic size  $R(t)$ .

The deviation in the beginning of the graph reflects the early-time diffusive stage, when the interfaces are still under formation through diffusion. This process is very fast because the initial condition is quite unstable, i.e., a mixture of fluids that are, in normal conditions, immiscible and that have the diffusivity set to zero. When the first bubbles are formed, the system evolves following a power law scale, as already discussed. Although the behaviour of the fluid in the early-stages of the spinodal decomposition seems to follow a power law scale too, Fig.1., the determination of the exponent of this power law was not done in this work and stay as a open issue for future studies.

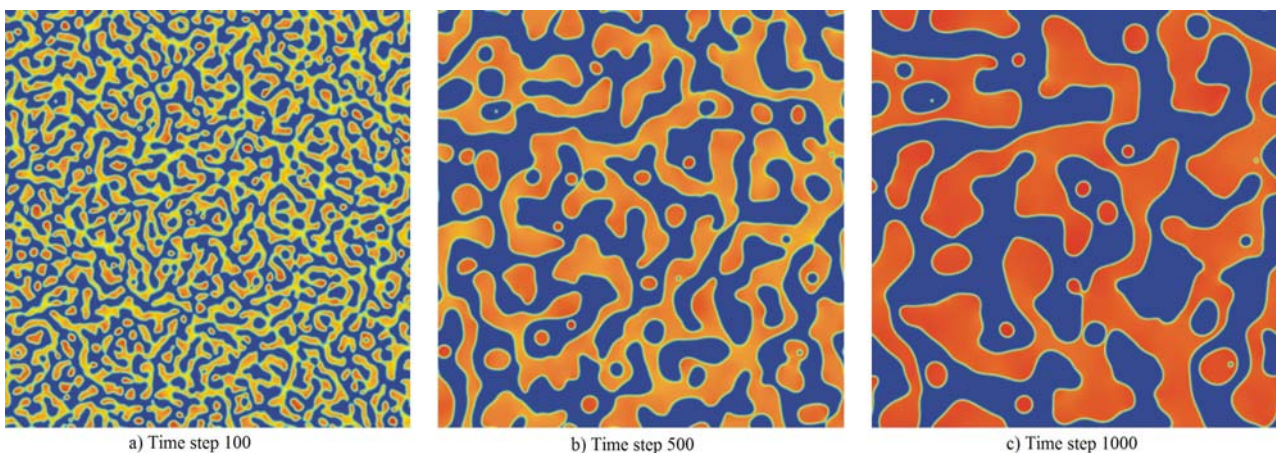


Figure 2 – Snapshots of the simulation at various steps, in a  $512^2$  domain.  
 The color gradient in the red fluid represents small fluctuations of the local density.

To appraise the influence of the parameters, several simulations were done. Figure 3 shows that *red* fluid viscosity, obtained when the parameter  $\tau^r$  was changed, does not affect substantially the growth exponent. Data are shown for  $\tau^r$  of 0.6, 0.75, 1.0 and 5.0, which corresponds to a viscosity relation  $\eta^r/\eta^b$  of 0.2, 0.5, 1.0 and 9.0.

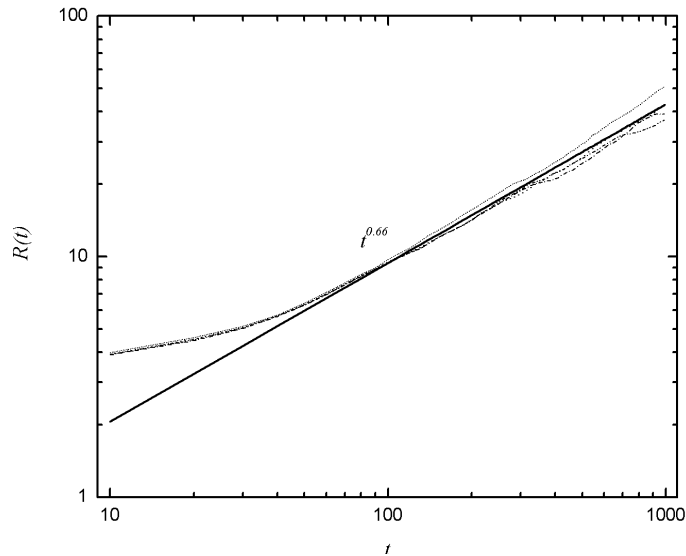


Figure 3 – Influence of the red viscosity in the evolution of the characteristic size  $R(t)$ .

### 3.2 Decrease of interfacial area

When the fluid domains grow, the interfacial area (the total area between the two phases) decreases. As the domain grows obeying a power law with time, it is expected that the interfacial area decreases as a power law with time as well.

Flow of immiscible fluids is classically treated considering that the transition layer has a null thickness and performing a momentum balance around this layer. But, the existence of a transition layer where the two fluids coexist is inherent to lattice Boltzmann methods, so it is necessary to define a critical concentration that will define the interface. The concentration of fluid  $r$  is defined as  $\rho^r/(\rho^r + \rho^b)$ , so a fluid node will be considered as being an interfacial node if its concentration is between two critical values, e.g., 0.1 and 0.9. The sum of the interfacial nodes will give the total interfacial area.

The definition of the interface should not alter in any way the exponent found for the power law, because, if it did so, we should talk in some kind of ideal definition of interface and the results would not be consistent. We simulated the process with different critical concentration values and no variation was found on the exponent. The only modification was the reduction of the zero-decrease initial phase, a consequence expected because of the diffusive process occurring in the beginning of the simulation. Results are illustrated in Fig. 4.

To our knowledge, no work has been done to calculate the area decrease, but there is a lot of works about the fluid domain growth. We observed that the interfacial area is very much easier to measure, requiring significantly less computational effort. In fact, domain growth simulations could not be performed with  $1024^2$  nodes due to the huge time involved.

The later times deviation on the power decrease is a consequence of the size of the computational domain. In Fig. 5 we show the normalized graphic for different computational domain sizes. As the domain grows, the deviation of the power law scale is postponed to later times. This is expected to occur because larger domains can accommodate larger structures. When the length of these structures reaches the length of the computational domain, the scale is broken. Simulations were run for mesh sizes up to  $1024^2$ , but that demanded very high computational power and time so the majority of the simulations were run for  $512^2$  meshes.

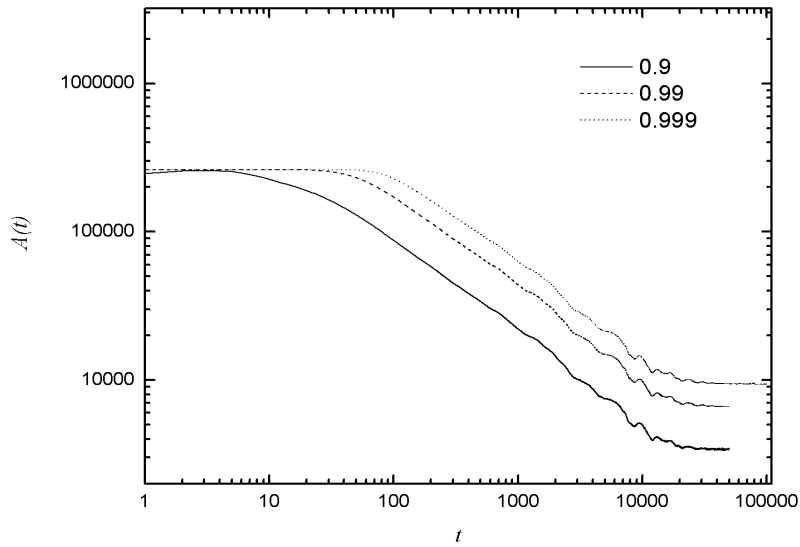


Figure 4 – Comparison between the interface definitions. No variation on the exponent  $\beta$  was observed.

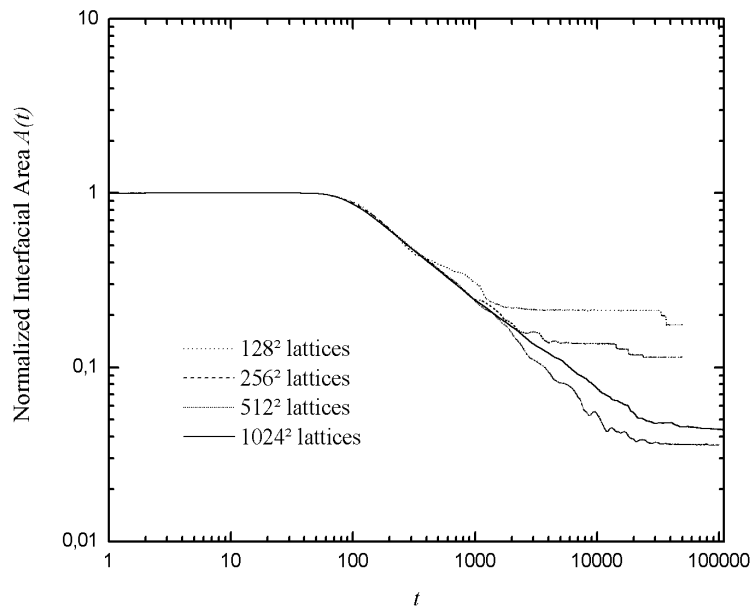


Figure 5 – Computational domain size effect. Deviations of the power law occur when the fluid structures formed are of the same size of the computational domain.

In Fig. 6 we show the evolution of  $A(t)$  with time. The critical values are 0.001 and 0.999 and the parameters used in the simulation were  $\tau^r = 1.0$ ,  $\tau^{bb} = 1.0$ ,  $\tau^b = 1.0$  and  $A = 0.4$ . A  $512^2$  mesh and a random initial distribution of  $\rho^r$  and  $\rho^b$  were used. The initial zero-decrease line represents the interface formation via diffusion, when the interface is still forming.

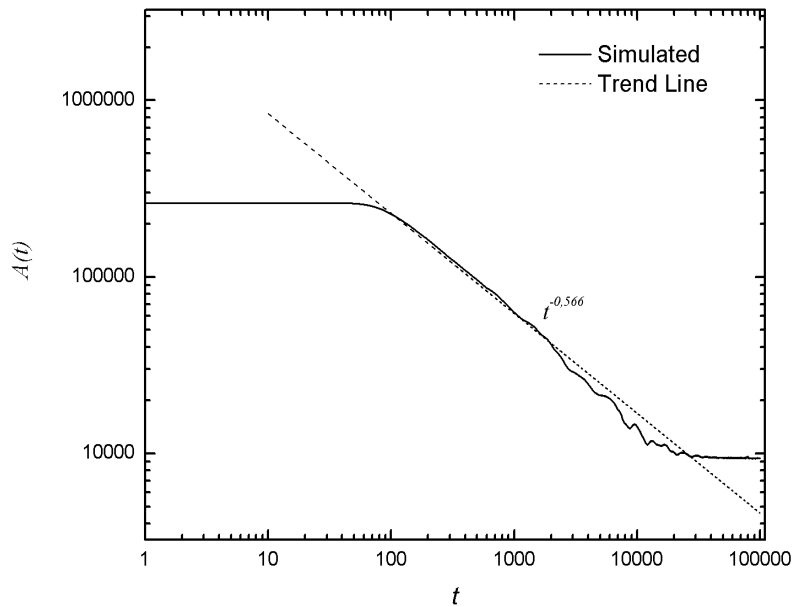


Figure 6 – Evolution of the interfacial area for a  $1024^2$  mesh.

There is, in both graphs presented for the interfacial area decrease, a tail on the right that does not obey the power law. This indicates the end of the spinodal decomposition process, when the fluid domains have achieved their largest size and are no longer growing, so the interfacial area does not decrease anymore.

Varying the viscosity of the red fluid did not cause appreciable changes on the growth exponent, so it is expected that it does not influence the interfacial area decrease as well. We simulated  $\tau'$  equals 0.6, 0.75, 1.0 and 5.0. The results are depicted in Fig. 7. Divergence is only seen at later times, when the domain size effects diminish the accuracy of results.

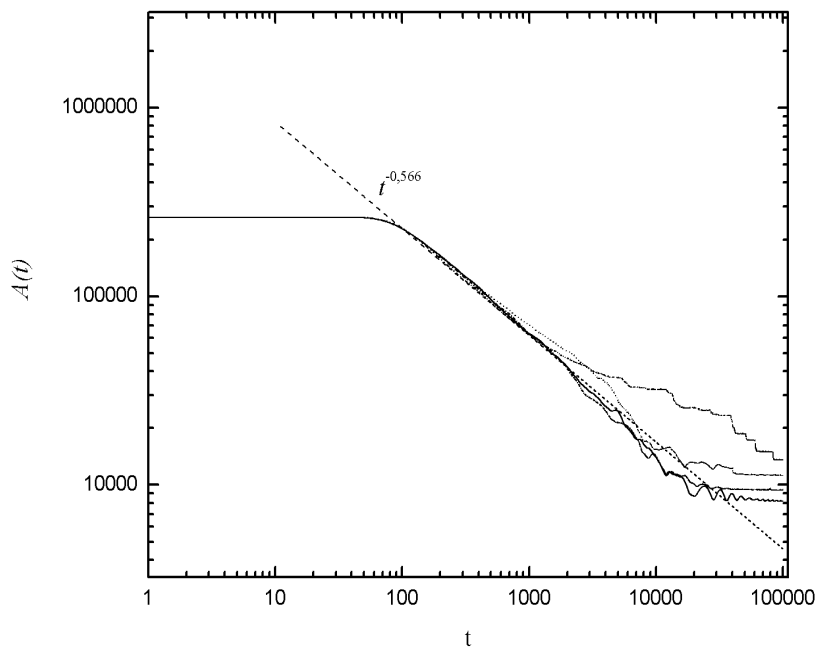


Figure 7 – Effect of the fluid viscosity on the area decrease. On the right side, bottom-up, the red relaxation time is 0.6, 1.0, 0.75 and 5.0.

#### 4. CONCLUSIONS

A lattice Boltzmann method has been proposed to simulate immiscible fluids, in a process of spinodal decomposition. We studied both the growth of fluid domains and the decrease of the interfacial area. Results for fluid domain growth were in a very good agreement with other works and theoretical prediction. To our knowledge, there is

no work concerning the interfacial area decrease, but the results we found couples with the domain growth rate, as shown before.

Numerical effects, such as the mesh size and the definition of the interface, were evaluated. We found no influence of viscosity over the exponents. Further work is necessary to estimate the effects of interfacial tension on this process.

## 5. ACKNOWLEDGEMENTS

We acknowledge the support by CNPq, Finep and Petrobras for the opportunity to participate and to collaborate in the development of this project.

## 6. REFERENCES

- Alexander, F.J., Chen, S. and Grunau, D. W.,1993, "Hydrodynamic spinodal decomposition: Growth kinetic and scaling functions.", *Phys. Rev. B* **48**, 634.
- Bray, A.J.,1994, "Theory of phase-ordering kinetics", *Adv. Phys.*, Vol **43**, No 3, pp 357-459.
- Bhatnagar, P., Gross, E. P. and Krook, M. "A model for collision processes in gases. I. Small amplitude processes in charged and neutral one-component systems". *Physical Review*, v. 94, p 511-525, 1954.
- Chin, J. and Coveney, P. V., 2002, "Lattice Boltzmann study of spinodal decomposition in two dimensions", *Phys. Rev. E* **66**, 016303.
- Furukawa, H.,1985, "A dynamic scaling assumption for phase-separation", *Adv. Phys.* **34** 703.
- González-Segredo, N., Nevokee, M. and Coveney, P. V.,2003, "Three-dimensional lattice-Boltzmann simulations of critical spinodal decomposition in binary immiscible fluids", *Phys. Rev. E* **67**, 046304.
- Santos, L. O. E., Facin, P. C. and Philippi, P. C.,2003, "Lattice-Boltzmann model based on field mediators for immiscible fluids.", *Phys. Rev. E* **68**, 056302.

## 7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.