Lubricants, paints, surfactant-aided oil recovery fluids, liquid crystals, plastics and shampoos are known as complex fluids since they share the property that they present structures at mesoscopic scales (suspended particles, macromolecules, bubbles, droplets, vesicles, micelles, lamellae, ...) despite their continuum appearance at macroscopic scales. By complex, one emphasises the conspicuous coupling of these mesoscopic structures present in a fluid with its macroscopic flow properties. Complex fluids are important to study because of their occurrence in chemical processes such as polymerisation, heterogeneous catalysis, as well as being important in the oil industry, the pharmaceutical industry, the food chemistry, and metallurgy.

Phase separating fluids are a particular instance of complex fluids where the mesoscopic structure is due to the presence of interfaces. Boiling water in a pot, the formation of a cloud, or even the rise of bubbles in a carbonated drink are fascinating everyday experiences that involve liquid-vapour coexistence in non-trivial flow situations. Knowledge of the dynamics of this phenomena is crucial in less pleasant situations like the prediction and control of nuclear accidents and refrigerated nuclear reactors.

1.1 The van der Waals theory

The liquid-vapour transition is perhaps the simplest instance of phase separation in a fluid. One of the first attempts to describe liquid-vapour phase transition at equilibrium was made by J.D. van der Waals who obtained his doctor’s degree in 1873 for a thesis entitled Over the continuïteit van den Gas- en Vloeistooftoestand (On the continuity of the gas and liquid state) [1]. In this outstanding piece of work he put forward an equation of
state embracing both the gaseous and the liquid state. He could demonstrate that these
two states of aggregation not only merge into each other in a continuous manner, but
that they are in fact of the same nature. He simply stated that the interactions of the
atoms (molecules) consist only of a two-particle potential $\phi(r)$, which can be decomposed
into a hardcore part $\hat{\phi}(r) \geq 0$ (gas molecules repel each other at short distances like
impenetrable spheres) and an attractive part $\overline{\phi}(r) \leq 0$. More precisely, the potential of
interaction between molecules of species $\alpha, \beta$ writes:

$$\phi_{i,\alpha,j,\beta} = \hat{\phi}(\mathbf{q}_{i,\alpha} - \mathbf{q}_{j,\beta}) + \overline{\phi}(\mathbf{q}_{i,\alpha} - \mathbf{q}_{j,\beta})$$

where $\mathbf{q}_{i,\alpha}$ is the position of the $i$-th molecule of species $\alpha$. It follows the well-known van
der Waals equation of state \[2\]

$$\left( P + \frac{a}{v^2} \right) (v - b) = k_B T$$

where $P$ is the pressure, $T$ the temperature, $v$ the molecular volume, $k_B$ the Boltzmann
constant, with $a$ and $b$ being the so-called van der Waals parameters.

This equation, in contrast to the ideal gas equation, has the following properties: i) the
attractive interaction causes a reduction in the pressure via the term $-a/v^2$, ii) the
specific volume $v$ has been decreased by $b$ because the molecules are not point-like
but instead occupy their own finite volumes. The constants $a$ and $b$ are also specific to
each gas or liquid in consideration. The combined action of the repulsion and attraction
of the molecules results in typical isotherms shapes for the van der Waals equation of state \[3\][4],
displaying critical temperature, pressure and volume given respectively by
$k_B T_c = 8a/27b$ $P_c = a/27b^2$ and $v_c = 3b$. If one uses the reduced variables $P^* = P/P_c$, $V^* = v/v_c$ and $T^* = T/T_c$ then a dimensionless form of the equation is obtained that
yields a family of curves $T^*/P^*V^* = f(T^*)$. This is known as the law of corresponding
states \[3\][5]. Experiments show that a large variety of liquids lie on a single curve at
constant $T^*$, sometimes even beyond the validity of the van der Waals equation.

The van der Waals theory remains too simplistic but yet yields remarkable results
and a good insight on first-order phase transition from gas state to liquid state. Of
course many others have tried either to modify van der Waals’ theory, or to propose new
equations of state \[6\][7]. We shall however solely consider the original van der Waals
theory in the present work.

Phase separation implies the creation of interfaces. The nature of the interface be-
tween two fluids has been the subject of extensive investigation for over two centuries.
Young, Laplace, and Gauss, in the early part of the 1800s, considered the interface be-
tween two fluids to be represented as a surface of zero thickness endowed with physical
properties such as surface tension. In these investigations, which were based on static
or mechanical equilibrium arguments, it was assumed that physical quantities such as
density were, in general, discontinuous across the interface. Physical processes such as
capillarity occurring at the interface were represented by boundary conditions imposed
terre. While being very appealing, this theory proved very difficult to use in reality and
Poisson, Maxwell, Gibbs soon recognised that the interface actually presented a rapid but smooth transition of physical quantities between the bulk fluid values. The idea that the interface has a non-zero thickness was developed in detail by Lord Rayleigh [8] and by van der Waals [1]. These original ideas have been developed further and refined over the past century [9].

If now one considers not one fluid, but several ones present in one unique system, the problem of writing the equations of state for a fluid mixture needs to be addressed. Not only can each fluid undergo a gas-liquid phase separation, but liquid-liquid phase separation can also occur, therefore dramatically increasing the phase diagram complexity. The simplest case, the binary mixture of two fluids was studied by van der Waals himself [10]. He introduced extra coefficients $a_{ij}$'s and $b_{ij}$'s accounting for the interactions between the different fluids and proposed rules for combining the $a_{ij}$'s and $b_{ij}$'s such that a "classic" van der Waals equation of state can be written for the melange. In other words, it was assumed that there exists a hypothetical equivalent (pure) substance which has the same configurational free energy as the mixture for specified conditions. This idea was widely accepted and used and its theoretical predictions [11] [12] confronted to experiments [13], while the combining rules became a matter of discussion [14]. At the day of today, given the van der Waals parameters for each fluid, the theoretical phase diagram can be analytically obtained [12].

1.2 The hydrodynamics of a phase separating mixture

The van der Waals theory is a theory for fluid systems at equilibrium. Of course the interesting question is how one can extend this theory to non-equilibrium situations.

Although the hydrodynamics equations for the van der Waals fluid were posed as early as 1901 by Korteveg [15] [16], the formulation of the full set of hydrodynamic equations for phase separating fluids is still a subject of present research. Different theoretical approaches have been taken to derive the continuum equations, amongst them are the kinetic theory [17] [18], irreversible thermodynamics [19] [20] [21] [22], diffuse interface models [9], the GENERIC approach [23], and projection operators [24].

In the fifties, Irving, Kirkwood, Bearman, Zwanzig, Green et al published a series of thirteen articles entitled The statistical mechanical theory of transport processes [25], among which the fourth included the equations of hydrodynamics for a single fluid derived by means of classical statistical mechanics. In the eleventh article, published eight years later, these results were extended to multicomponent systems.

In the late sixties, a variant of the Korteveg theory was introduced by Kawasaki [26], following the ideas of van Kampen [27]. It can be shown that the Kawasaki theory is thermodynamically inconsistent. In the Kawasaki theory, the long range attractive mean field potential between molecules acts as an external force in the momentum equation. A gradient approximation of this mean-field potential leads to purely local equations involving third order spatial derivatives of the density field. Such a theory was proposed
by Felderhof who constructed a thermodynamically consistent set of hydrodynamic equations for a van der Waals fluid [28]. However, the Felderhof theory only deals with inviscid fluids and does not include dissipation nor fluctuations. Therefore a generalisation of his theory seems appropriate.

The usual avenue for obtaining hydrodynamic equations for complex fluids is through thermodynamics of irreversible processes. The fundamentals of non-equilibrium thermodynamics were laid through the twentieth century by some of the greatest names of physics: Thomson, Boltzmann, Onsager, Casimir, Meixnert, and Prigogine just to name a few. It provides us with a general framework for the macroscopic description of irreversible processes. As such, it is a branch of macroscopic physics, which has connections with other macroscopic disciplines such as fluid dynamics and electromagnetic theory. Hydrodynamics treats the state variables as field variables, i.e. as continuous functions of space coordinates and time (as opposed to equilibrium thermodynamics where the state variables are usually independent of the space coordinates). Moreover, one likes to formulate the basic equations in such a way that they only contain quantities referring to a single point in space and time, i.e. in the form of local equations.

1.3 From micro to macro

In this thesis we will reconsider the derivation of hydrodynamic equations starting from the molecular level of description. The process of coarse graining allows us to bridge the gap between microscopic and meso/macroscopic descriptions. This process consists of the representation of a system with fewer degrees of freedom than those actually present in the system. By coarse-graining, one eliminates the "uninteresting" fast variables and keeps the coarse-grained variables with time scales much larger than typical molecular scales. Therefore, by coarse-graining we not only gain in terms of a reduction of computational units but also on the possibility of exploring a much larger time span. In the field of complex-fluids, coarse-grained models are usually constructed with a judicious balance of physical intuition, simplicity, respect of symmetries and fundamental laws of physics. The validity of such coarse-grained models is inferred \textit{a posteriori}, by confronting its predictions with experiments (performed in a laboratory or by means of other thoroughly checked models).

The understanding of coarse-graining and its correlated theories such as transport processes and irreversible phenomena was strengthened in the middle of last century by people like Kirkwood [25], Green [29] \cite{Green}, Kubo [31], Zwanzig [32] \cite{Zwanzig} \cite{Zwanzig2} \cite{Zwanzig3}, and many others. In particular, starting from the microscopic equations governing atomic variables, projection operator techniques as wonderfully reviewed by Grabert [35] allowed to derive the equations of motion of the coarse-grained variables that evolve in distinctly slower time scales than the rest of the variables of the system.

Another milestone in the theory of coarse-graining was laid in the mid-nineties by Öttinger and Grmela [36] \cite{Ottinger} \cite{Grmela}. By applying the projection operator method, they
derived the general equation for the non-equilibrium reversible-irreversible coupling, or GENERIC. Provided one has chosen an independent and complete set of relevant variables as well as the appropriate level of coarse-graining to describe the system, the method provides a general framework to handle nonlinear thermodynamics of systems out of equilibrium. This is achieved through a clear separation and treatment of the reversible and irreversible dynamics terms leading to the strict fulfilment of the First and Second Law of thermodynamics. This framework has been successfully used in various domains like polymer/surface interactions[39], polymer blends simulations [40], liquid crystals [41] or even cosmology [42].

As mentioned before GENERIC allows us to build the hydrodynamics equations step by step by making use of coarse-graining tools, in such a way that transport coefficients, cross effects coefficients and viscous terms appear naturally through Green-Kubo expressions, underlying the true microscopic nature of the system in consideration. GENERIC is simply a way of writing the equations in a particularly transparent manner such that the First and Second Law of thermodynamics are captured. It is a very useful tool when one is faced with the development of new dynamics equations of complex fluids. While the hydrodynamic equations of a single fluid have already been derived within this framework [43], we applied the same methodology and derived the hydrodynamic equations of a phase separating fluid mixture.

1.4 Computer simulations

The complex nature of phase separating fluids and the unavoidable highly nonlinear meso/macroscopic coupling defy analytical approaches and computer simulations are therefore required.

Even if during the last fifty years computers have dramatically improved and gained in computational power [44], these resources remain of a finite nature. A good example of today’s computers’ limitations is the Molecular Dynamics (MD) model [45]. It simply aims at resolving Newton’s law equations for every atom or molecule in a system. Molecular dynamics simulations capturing the full molecular detail have been undertaken [46], [47]. However, typical MD simulations can be performed on systems containing thousands, or perhaps millions of atoms, and for a simulation time ranging from a few picoseconds to hundreds of nanoseconds. While these numbers are certainly respectable, and the accuracy of the method not to be questioned, conditions may occur where time and/or size limitations become important. In the case of complex fluids both the size and time limitations pose problems, and there is a need for developing simulation models that allow us to capture the essential features of the materials with minimum computational units and computer time.

However, other methods have also been used to simulate phase separating fluids, the most popular being the lattice Boltzmann equation [48] [49] [50] and, to a lesser extent, the dissipative particle dynamics model (DPD) [51].
A very interesting development within the DPD model has been considered quite recently [52] [53] [54] [55]. The original DPD model displays an equation of state that is quadratic in the density, and can never display a phase separation. Pagonabarraga and Frenkel have proposed a DPD model for non-ideal fluids where a non-trivial free energy is introduced, and this allows for the treatment of fluids that can phase separate [52]. The model has been further studied by simulations [54], and interesting pendant drop simulations have been conducted [55].

The above-mentioned many-body DPD models have several limitations: they are isothermal, the inherent thermal fluctuations of the model are not controllable, and the connection with the macroscopic transport is obscure. These problems have been solved in a new formulation of the DPD equations called Smoothed Dissipative Particle Dynamics, which is thermodynamically consistent and that allows for arbitrary equations of state [56]. The model has a very close connection with Smoothed Particle Hydrodynamics SPH, and the essential idea behind Ref. [56] is that DPD, when properly formulated, is nothing else that SPH plus thermal fluctuations. In the present thesis we introduce the generalisation of Ref. [56] to the multicomponent case.

SPH is a particle model which aims at discretising the Navier-Stokes equations by means of a weight function. This model, used throughout this thesis, is a Lagrangian particle method introduced by Lucy [57] and Monaghan [58] [59] in the seventies in order to solve hydrodynamic problems in astrophysical contexts. Generalisations of SPH in order to include viscosity and thermal conduction and address laboratory scale situations like viscous flow and thermal convection have been presented only quite recently [60] [61] [62] [63] [64] [65].

Phase-separating fluids also present an even more interesting point of interest: the spinodal decomposition they undergo seems to obey a universal growth law, that depends on the nature of the studied order parameter (conserved or not) and on the time scale on which the study is performed (apparition of several growth regimes). These studies have given rise to abundant literature [66] [67] [68] in the second half of the twentieth century mainly due to the increasing number of computer modelling techniques [50] [51] [69] [70] and to the perfecting of measurement devices [71].

1.5 Outlook of the thesis

This thesis is organised as follows: we present in chapter 2 the main features of the GENERIC framework on which the whole thesis is based. Chapter 3 describes how the hydrodynamic equations of a phase-separating fluid mixture are derived from the underlying microscopic dynamics of the system. A projection operator method is used in the GENERIC form and in this way, the thermodynamic consistency of the final equations is apparent. The microscopic potential is separated into short and long range parts, in the spirit of the original work of van der Waals. Explicit expressions for surface tension terms in the hydrodynamic equations are obtained. These terms describe diffuse inter-
faces in the system. Miscible-immiscible and gas-liquid phase transitions are possible, non-isothermal situations can be studied, and explicit account of cross effects is taken. In chapter 4 we introduce a thermodynamically consistent discrete fluid particle model for the simulation of the set of hydrodynamic equations for a phase separating van der Waals fluid mixture obtained in the previous chapter. The model is formulated within the thermodynamically consistent GENERIC framework and we use the discretization procedure given by the smoothed particle hydrodynamics method. Each fluid particle carries information not only of the total mass, momentum and energy, but also of the mass fraction of the different components. The discrete model allows us to simulate non-isothermal dynamic evolution of phase separating fluids with surface tension effects. Chapter 5 is devoted to numerical simulations of the SPH model for phase separating mixtures of chapter 3 in the simplest non-trivial case. Viscous processes are neglected and only mass and energy diffusive processes take place. We restrict ourselves to the case of a binary mixture that can exhibit liquid-liquid phase separation.

The chapters in this thesis have been written in a form suitable for publication. Consequently, some overlap exists between the chapters.


Introduction


[44] The observation made in 1965 by Gordon Moore, co-founder of Intel, that the number of transistors per square inch on integrated circuits had doubled every year since the integrated circuit was invented. Moore predicted that this trend would continue for the foreseeable future. In subsequent years, the pace slowed down a bit, but data density has doubled approximately every 18 months, and this is the current definition of Moore’s Law, which Moore himself has blessed. Most experts, including Moore himself, expect Moore’s Law to hold for at least another two decades.


