Polymers in Fluid Dynamics Problems
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Citation for published version (APA):

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In polymer processing, melting is always considered a crucial step. Blending of different polymers, which offers the potential of producing a great variety of products, is preceded by melting. The devices in which melting takes place usually are extruders or kneaders. Modelling all the phenomena occurring during melting is known to be a difficult problem. First of all, the geometry of these machines is complex and non-stationary. Even the problem of rigorously calculating the one-phase flow pattern in intermeshing twin-screw extruders is as yet unsolved. In addition, phase changes taking place inside the melting equipment are difficult to grasp with a physical model. Hence, generally speaking, the flow of a material changing from a powder to a highly viscous liquid is still far from being understood completely.

In this thesis we will therefore focus on a small part of the melting process. We will try to gain some fundamental understanding of the specific nature of the melting of polymers when subjected to shear flow. In order to examine the impact of the chain character of polymers on melting we chose a mesoscopic modelling technique. In this thesis the focus will be on a particle-based method: Dissipative Particle Dynamics.
1.1 Dissipative Particle Dynamics

Solving the Navier-Stokes equations is impossible using Molecular Dynamics. The steep potentials used in this simulation method demand small time steps, and would require extremely long computation times before flow phenomena are observed. However, when performing flow simulations using Computational Fluid Dynamics, all molecular detail is lost.

A third possibility, that has gained much attention lately, is the mesoscopic approach. The length scales to which this class of simulation methods apply lie in between the two techniques mentioned before. For the modelling of large molecular structures, like polymers, this offers the possibility to retain their chain-like nature, while small molecules or atoms are lumped together in larger imaginary particles. The resulting interaction between coarse grained polymers and monomers is much softer than the one used in MD, allowing larger time steps and giving access to the time scales of macroscopic flow.

Dissipative Particle Dynamics is one of these methods. Hoogerbrugge and Koelman [1] introduced the method, and proved, both by simulation and theoretical derivation, that it obeys the Navier-Stokes equations. The theoretical foundations of DPD have been discussed in more detail by Español [2] and Español and Warren[3], which led to a slight modification of the original algorithm to ensure a proper thermodynamic equilibrium.

One attractive aspect of this method is the easy implementation of multiple phases, as opposed to conventional CFD. In DPD only a single parameter has to be changed to achieve this, being the interaction potential between similar and different species. This makes DPD capable of dynamically simulating the phase separation of binary immiscible fluids [4, 5] or, for instance, the microphase separation of diblock copolymers [6]. While these two cases focussed on the dynamics of the separation, we noticed that to predict thermodynamic properties of DPD a more efficient sampling scheme could be used [7]. In fact, an advanced Monte Carlo technique under the name of Gibbs ensemble was combined with the DPD potentials. In Figure 1.1 the phase diagram as calculated with standard DPD and using the Gibbs ensemble is shown. Good agreement between the two is observed, al-
though computationally the Gibbs ensemble is preferable, due to the small number of particles used. In addition to these flow simulations incorporating thermodynamics, other kinds of multiphase simulations can be performed as well. Koelman en Hoogerbrugge [8] simulated hard sphere suspensions under steady shear, and found excellent agreement between calculated viscosities and experiments. Clark et al. [9] successfully performed simulations of liquid drops in gravitational and shear fields.

Since the incorporation of different phases has turned out to be straightforward with DPD, the method has attracted the attention of researchers in the field of polymers. It was discovered that the DPD particles, connected by springs, could easily represent polymers. In a first attempt, this approach was tested on the behaviour of an isolated chain in a solvent. Both the variation of the radius of gyration with the number of beads in the polymer and relaxation time were found to be consistent with Rouse-Zimm behaviour [10]. By adjusting the DPD parameters, the quality of

Figure 1.1: Phase diagram as calculated with DPD and Gibbs ensemble. $\rho_1$ is the concentration of one fluid in the two phases.
The solvent can also be changed, again showing consistency with well-established theory [11]. Solubility is usually expressed in terms of the $\chi$-parameter in Flory-Huggins theory. Groot and Warren [12] established a mapping of the DPD parameters onto this $\chi$-parameter. Finally, the non-Newtonian behaviour as predicted by DPD was investigated [13], and a study of confining effects on polymer behaviour was carried out [14].

These promising results for the simulation of polymers using the DPD method were the incentive to our investigations using this method. A first check was to determine whether agreement with theory could be found in the case of a polymer melt as well. A polymer in a solvent shows a self avoiding walk, but in the case of a polymer melt the great number of polymers together yield a random walk again [15]. In Figure 1.2 the scaling of the distance between the endpoints of the polymer (directly related to the radius of gyration) is plotted for the case of a polymer in a solvent or in the melt. It can be seen that for the case of a polymer melt, the polymer shows the correct scaling exponent. A value of 0.49 (theoretically 0.50) is found for the melt, as compared to 0.57 (in theory 0.588) for the case of a polymer in solution.

**Figure 1.2:** Scaling of the mean square endpoint distance of the polymer with the polymer length. Both the case of a polymer in solution and a polymer in the melt are given. The number in the legends shows the scaling exponent for these cases.
Hence it is concluded that the polymer scaling is correct for a polymer melt as well. As a next check we examined whether the viscosity of the polymer melt also shows non-Newtonian behaviour, as is the case for the polymer in solution. Figure 1.3 shows that this behaviour is found indeed; at high shear rate the viscosity decreases, so shear thinning behaviour is observed in the case of a polymer melt. The simulation reveals the cause of this shear thinning behaviour: at high shear rates the polymers tend to stretch out completely, which facilitates flow and leads to decreasing viscosity. These results have strengthened our confidence that DPD is indeed suitable for describing the flow of a polymer melt correctly.

Since energy is not a conserved quantity in the original DPD scheme, it is impossible to perform thermal simulations. It was only after the introduction of an energy conserving form of the DPD scheme by both Español [16] and Avalos et al. [17], that this class of problems could be solved. In this thesis the energy conserving form of DPD is extended to incorporate a melting model. In the next section the history of melting modelling is discussed.
1.2 Melting

Melting of a substance seems to be a phenomenon that can easily be described. Nobody even thinks about melting behaviour when looking at the ice cubes in their soda, or when eating ice cream in the hot sun. However, melting is a difficult problem in many industrial applications, like metal processing, thermal energy storage or the topic of this thesis - polymer processing. Due to increasing environmental concern, also the melting of the polar caps is a phase change phenomenon that is being studied by many researchers.

1.2.1 Analytical methods

The polar cap melting problem led to the first investigation into modelling of a melting process, as Stefan [18] did around 1890. He was the first to analytically describe the movement of a melting front in time. A whole class of problems, called 'moving boundary problems', still bears his name. Stefan describes the movement of a melting front in a semi-infinite region that is initially at the melting temperature of the substance being heated on one side. Since a temperature profile will only exist in the melt region, this problem is called a 'one-phase' melting problem. Neumann [19] extended this problem to a 'two-phase' problem by lowering the initial temperature below the melting temperature. In both solutions only heat conduction is assumed.

1.2.2 Numerical methods

With the advent of computers a few decades ago, a numerical solution was also attempted, by discretising the differential equations through finite differences or finite element methods. Initially, in these cases convection was neglected as well. Several approaches exist to the solution. The first class is the strong solution class. Here, the position of the melting front is explicitly solved in time, and treated as a boundary condition. The movement of this boundary complicates the problem. When using a fixed grid, both in space and time, the front is not likely to coincide
with the grid points. Nonetheless, it is possible to interpolate the position between
the grid points, see Crank [20]. A different approach is to use a variable grid. Gupta
and Kumar [21] change the time step in such a way that the moving front always
coincides with the spatial grid. Although this approach works in one dimension,
it is difficult to extend this to more dimensions. This only becomes possible with
an adaptive meshing technique introduced by Brackbill and Saltzman [22]. Here,
a new mesh is created every time step to follow the changing shape of the solid.
Although the mesh generation is very time consuming, with ever increasing com­
puter power, it may become feasible in due time.

The difficulty with the methods described so far stems from the fact that the moving
front position is explicitly solved. Another approach is to reformulate the problem
in such a way that the entire region is solved by a single equation. These solutions
are called weak solutions, of which the enthalpy method is one. It was first pro­
posed in 1947 by Eyres et al. [23] and later on improved by Voller and Cross [24]. In
this method rather than calculating the temperature with the energy equation, the
enthalpy is solved. A specific relation has to be provided to link the enthalpy to the
temperature, which will involve the latent heat. Since this enthalpy formulation
is very close to the original implementation of the energy conserving DPD model,
this is a natural choice for the melting model to be used.

1.3 Outline

The remainder of this thesis is organised as follows:

- In Chapter 2 the implementation of the enthalpy method into the Dissipative
  Particle Dynamics framework is described. The method is tested against
  an analytical solution, and a method to overcome an incorrect boundary
  condition is presented.

- In Chapter 3 the boundary condition problems for non-thermal DPD are
  investigated. The new approach to implementing boundary conditions in
  DPD is extended for the case of a no-slip boundary condition. The method is
tested on both steady-state and instationary calculations.

- In Chapter 4 examples are given of the strength of DPD when simulating flows containing polymers. A detailed study on the phenomena of hydrodynamic chromatography is presented together with some preliminary results of melting a solid object in shear flow.

- In Chapter 5 a method to investigate the accuracy of the DPD method is given. When simulating polymers in DPD, several spring force descriptions can be used. A method is provided to select from the alternatives. An elaborate study of the melting of a polymeric solid object in shear flow is described. The description of the polymer is changed to incorporate the thermodynamic behaviour of such a polymer, which is found to influence the melting rate.

- In Chapter 6 the main conclusions of the thesis are given, along with a short outlook into the future.

The chapters in this thesis have been written in a form suitable for publication. Consequently, some overlap exists between the chapters, particularly in the introductions and the sections describing the DPD model.