Numerical Studies on Spinodal Decomposition of Liquid-Vapor Systems using Smoothed Particle Hydrodynamics

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Martin Pütz

an der

Universität Konstanz

Mathematisch-Naturwissenschaftliche Sektion
Fachbereich Physik

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1. Gutachter: Prof. Dr. Peter Nielaba
2. Gutachter: Prof. Dr. Wolfgang Dieterich
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Speaking about matter in physics, it is always the state of a material that must additionally be considered. Generally, every material has a usual appearance under atmospheric conditions. However, a material can change its state under specific conditions. The classical states appear in our everyday life, such as solids, liquids, gases (or also referred to as vapor), and plasmas\textsuperscript{1}.

Obviously, rheological properties are only meaningful to define for liquids, gases and plasmas. Therefore, matter occurring in one of these states is designated as a so called fluid. The flow behavior of such a fluid can generally be described by the hydrodynamic equations. Surely, the description of a plasma needs to take extra physical quantities into account, such as the Maxwell equations. Therefore, pure liquids and gases that consist of only one component are expected to be easy to describe and referred to as simple fluids \cite{1, 2}. This is indeed true as long as the state of a fluid is stable and in equilibrium, such that it can be described by methods of equilibrium statistical physics.

A system that consists of two or more phases is commonly referred to as a multiphase system. In this definition it is not further distinguished between systems that consist of only one or of multiple components. However, in a one component system the different phases are given by the different states of matter. For example, the boiling or condensation of water is a one component liquid-vapor system, whereas a binary mixture of oil and water is an example for a multicomponent system. However, as long as the system is relaxed and in equilibrium, a multiphase system can also adequately be described with equilibrium statistical physics \cite{3}.

All multiphase systems have in common that they can be homogeneously mixed\textsuperscript{1}.

\textsuperscript{1} Under extreme conditions other states of matter can occur, such as the Bose-Einstein condensate at low temperatures. However, those are not relevant for this work and will not be regarded further on.
to a stable one phase system and vice versa by changing certain environmental conditions \[4\]. The different regions of stability (stable, metastable, and completely unstable) and the different states of a system are recorded in a so called phase diagram, whereby the usual state-defining quantities are an order parameter that depends on the system under consideration (for example the density of the fluid or the concentration in a binary mixture\(^2\)), the pressure, and the temperature \[5\].

Indeed, it is a non-trivial issue to correctly reproduce the interactions and the exchange between the phases and the transport through the interfaces, when investigating the rheology of multiphase systems. Since each phase, taken individually, is subject to hydrodynamics, the interaction between the phases can be modeled by an equation of state (which is needed anyway to close the set of equations of hydrodynamics). The equation of state should be properly chosen to adequately reflect all regions in the phase diagram of the fluid under consideration \[6\]. Moreover, there is also the morphological evolution in each phase that must be considered separately. However, the treatment of a one component fluid turns out to become even more complex, when transitions between the states take place and the separation process must be described. Boiling (or vaporization) and condensation in a liquid-vapor system are classical examples for metastable nucleation phenomena and can be described by the so called van der Waals equation of state. One of the advantages of the van der Waals equation is that it already intrinsically provides surface tension effects \[7\].

A special form of phase transition is the so called spinodal decomposition, where a homogeneous mixed up stable system is rapidly quenched to a completely unstable state \[8\]. In contrast to nucleation, where individual nuclei form at a certain statistically determined nucleation rate \[9\], spinodal decomposition occurs instantaneously throughout the whole volume, by an increase of initially already present density fluctuations. The growth of amplitudes continues until the densities reach stable values of coexistence. Note that the former description is only given for a liquid-vapor system in terms of using the density, although spinodal decomposition is a universal phenomenon that can be observed in numerous other systems such as in binary mixtures. Besides, a theoretical approach for binary mixtures is the widely known Cahn-Hilliard equation (extending the basic assumptions of the van der Waals equation) that adequately describes the phenomenon of spinodal decomposition for a concentration variable. However, all phenomenological approaches have in common that temperature is not taken into account. Thus, the decomposition process is assumed to be isothermal (or at least quasi-isothermal). Although this assumption is rather reasonable in binary mixtures, due to latent heat it is strongly recommended to include temperature effects to liquid-vapor systems \[10\]. It depends on the actual value of the initial quench density (predicting the final ratio of the masses) if the mean temperature increases or decreases during the separation process. This is due to the cooling by rapid expansion of the

\(^2\)From a thermodynamic point of view, it is also the number of particles or the volume that could be changed.
vapor phase and the heating by the compression of the liquid phase. Moreover, including temperature and thermal effects is more realistic from the experimental perspective, because the setup must be coupled to an external heat bath to realize temperature quenches. A theoretical model should further take the strength of this coupling into account that allows us to predict specific quench rates. Thus, the challenge is not only to simultaneously handle the differing densities of liquid and vapor, but also to correctly reproduce the differing strengths of compressibility and thermal conductivities in the two phases.

In this work a method is presented that allows for realistically simulating the dynamics of spinodal decomposition with full respect to hydrodynamics that automatically includes the temporal evolution of temperature. For this purpose, hydrodynamics is combined with the van der Waals equation of state, a thermal conduction modeling heat equation, and several thermostats modeling the different strengths of heat bath coupling. From this perspective, spinodal decomposition can be simply understood as a hydrodynamic instability that leads to structure formation [11].

The basis of the method is the so called smoothed particle hydrodynamics (SPH) method [12]. It is a mesh-free Lagrangian particle based algorithm, where the hydrodynamic equations are solved by weighted kernel interpolations. It is perfectly suited for simulating the high density ratios between liquid and vapor, since the method was originally developed for astrophysical purposes, which includes the handling of large density deviations, such as in the formation of stellar cores out of initial molecular clouds [13], with ratios of up to 10 orders of magnitude. Therewith associated is a density-dependent adaptive resolution, which is one of the main advantages of SPH. Nowadays, only few reliable simulation techniques exist that can intrinsically treat liquid-vapor spinodal decomposition. Therefore, the combination of a van der Waals equation of state and SPH is a promising candidate for future developments and industrial application. Due to its excellent parallelization properties it can easily be applied to three dimensional high resolution systems for more realistic comparison with experimental setups. Possible future applications are real time calculations of condensation and evaporation, for instance in narrow channels. The method is also expected to correctly reproduce the effect of cavitation, which means to correctly reproduce shock driven phase transitions.

The structure of the dissertation is as follows. In chapter 2 the basic physical principles will be presented, including a detailed description of the phenomenon of spinodal decomposition with regard to the van der Waals equation of state and a short presentation of the hydrodynamic equations. In chapter 3 the underlying methods and algorithms, required for this work, will be presented in detail. The basic idea of kernel interpolation is discussed and the governing equations of the SPH method are derived from a Langrangian function. Furthermore, the application of the SPH method to multiphase systems and spinodal decomposition is shown in a separate section, where the necessary modifications and extensions to SPH and analysis methods are presented. The chapter is closed by a brief discus-
sion on the underlying program package GADGET-2 which has been the basis for the programming and a detailed description of the complex procedure of preparing the initial conditions. In chapter 4 simulation results of an investigation on the late stage growth behavior of liquid and vapor domains are presented. Hereby a very strong heat bath coupling at several quench depths is used to explain the growth behavior of pure thermal not-coupled simulations by comparison. Chapter 5 shows simulation results, where the influence of the strength of heat bath coupling is studied by applying a thermostat that allows for relaxation at a specific time scale. The thermostat is then used to show a connection between the forming of diffuse interfaces between the phases and the strength of the heat bath coupling. Chapter 6 sums up the main results of the dissertation and gives an outlook to possible future studies. Finally, the summary is also translated into German, which is given in chapter 7.
This chapter gives an overview of the relevant driving physical processes that are involved in the dynamics in the context of spinodal decomposition. First, the phenomenon of spinodal decomposition is described, with an emphasize from the thermodynamic perspective. Once decomposed, systems undergo a domain coarsening process by theoretically predicted theories, which will also be discussed in this chapter as well as corresponding analysis methods. Since hydrodynamics are expected to play an important role for the dynamics of the, herein considered, phase separating fluidal systems\footnote{Here, the term “fluid” refers to the liquid and vapor phases, neglecting the complexer plasma. It is herein commonly used, where a statement applies to both phases.}, the governing equations of hydrodynamics are described with a particular focus on conservation properties.


2.1 Spinodal decomposition in liquid-vapor systems

The first who named and differentiated spinodal decomposition from ordinary phase transitions and gave a phenomenological description of it were Cahn and Hilliard in 1958. In the first instance, the, so called Cahn-Hilliard-Equation (CH) [14, 15, 16], was a model for binary mixtures. Later on it became a generalized theory to various other fields, such as for thin films and liquid-vapor systems, since it has turned out that spinodal decomposition is a more general phenomenon and independent from the actual type of system.

A general description of the phenomenon in the context of a liquid-vapor system is given as follows. Spinodal decomposition occurs when a nearly equilibrated homogeneous stable system, described by thermodynamic state variables, is quenched to a completely unstable state by a rapid change of one state variable, like pressure or volume. However, the most common use of the term quench means a temperature quench. This, so obtained, unstable one-phase system spontaneously initiates to separate in two phases throughout the whole volume by an arise of initially apparent fluctuations in the density, which can be understood as the first of three consecutive stages of decomposition. This is the initial stage. Since this process occurs very quick, it is hard to observe. However, this arise of fluctuations ends up with reaching a metastable state, where, commonly, nucleation is the dominant phase separating process. The transition line in the phase diagram between unstable and metastable is called spinodal curve. In the second intermediate stage the densities of the separated phases tend to reach stable coexistence density values, but it is also already at a timescale where rheological behavior can not be neglected. The respective coexistence densities vary with temperature, where a line of coexistence, the so called binodal curve, can be drawn in the temperature-density phase diagram. The further temporal evolution of the, so obtained, separated domains is dominated by coarsening and the coalescence of droplets. Several predictions and theoretical descriptions exist for this late stage concerning the hydrodynamics and diffusion, whereas the initial and intermediate stages have received less attention. Furthermore, experimental results are rare, since the experiment requires a setup in microgravity, due to sedimentation processes.

More detailed descriptions of the governing equations are now given in the following subsections. A review on first-order phase transitions in general with special consideration for spinodal decomposition can be found in Ref.[8]. Moreover, an overview of concepts and principles, especially on the liquid-vapor systems is given in Ref.[4]. Both references have mainly been used for the descriptions given in this section.

2.1.1 Quenches

From the thermodynamic point of view a many body system is described by averaged thermodynamic state quantities, such as pressure \( P \), volume \( V \) and tem-
Figure 2.1: Schematic sketch of the temperature-density phase diagram of a one-component liquid-vapor system. The spinodal and binodal curves are plotted by gray lines. The blue arrows indicate the progress of a temperature quench, which is followed by separation of the phases in liquid and vapor phase. The gray and blue ×-marks denote the critical point \((\rho_{\text{crit}}, T_{\text{crit}})\) and initial phase configuration before the quench, respectively.

Temperature \(T\) or the number of particles \(N\), giving the, so called, phase space. The fraction of \(N\) and \(V\) lead to a number density \(n = N/V\), and when the total mass \(M\) is known, one obtains the density \(\rho = M/V\). A change of the state of the system is obtained by a change of, at least, one of the thermodynamic variables. A stable neighborhood in phase space is not affected by the rapidity of that change. It can either be slowly performed such that the system is always in quasi-equilibrium, or by a very rapid change, both yield the same final state. In contrast, in systems where phase transitions occur, forbidden regions in phase space exist. Therefore, the rate of change of a thermodynamic quantity matters, since a rapid change can become too fast for the system to react on the change. For that case the system becomes unstable. Such a rapid change from stable to unstable state, or in reverse direction, is commonly referred to as quench, and means in particular the change in temperature, although the other quantities are sometimes also used.

A schematic picture of a temperature-density phase diagram of a one-component liquid-vapor system is shown in Fig. 2.1. The figure will be frequently referred to in the following subsections. It shows how a system is quenched from the homogeneous one-phase region through the binodal and spinodal curves into the completely unstable state, where it separates into the two phases. The final states of the phases lie on the binodal curve. Note that the figure appears to suggest an isothermal separation process right after the quench. However, it is a highly non-isothermal process, as it will be shown in this thesis.

It is most desirable for spinodal decomposing systems to perform the quench as fast as possible, but the rate of change is restricted by several reasons, why it is
difficult to put an instantaneous quench into experimental practice. The fastest possible quench is instantaneous, which means at infinite quenching rate and this is, indeed, not realizable from an experimental point of view. Restrictions are either given by mechanic limitations such as in volume quenches. For example, a partition must be removed to increase volume. Limitations due to the finite thermal conductivity restrict temperature quenches, where the system is coupled to an external heat bath. However, the latter type of quench is still the most advantageous strategy, because the change in volume is a quasi-irreversible only one-directional process. Note, that a pressure quench is also possible, but with the serious disadvantage of loosing the conservation of mass property.

The process of decomposition initiates instantaneously, once the state gets unstable. Therefore, the finite quench rates lead to the problem, that the system already actually begins to decompose meanwhile the quench is not finished. Moreover, it is hard to compare with predictions from theory, because of the not well defined thermodynamic conditions. However, the descriptions in the following subsections are based on instantaneous quenches, but the difficulty in the experimental realization of such an instantaneous quench should stay in mind for later interpretations of the simulation results.

2.1.2 Van der Waals equation of state

So far, it is not clear how to obtain the spinodal and binodal curves shown in Fig. 2.1, nor what the terms “metastable” and “unstable” actually mean. For this purpose, it needs to be discussed how an appropriate choice of equation of state gives rise to a phase transition and the aforementioned terminology before the stability of states can be discussed.

An equation, that relates the thermodynamic state quantities of a system by a state function $f$ of the form

$$f(P,N,V,T) = 0 \quad (2.1)$$

is called a mechanical equation of state (EOS). Besides, as a consequence, the EOS determines, that a system is isothermal, if $T$ is absent in the equation. However, an alternative common formulation of the equation is given by resolving for an expression of the pressure

$$P(N,V,T). \quad (2.2)$$

Moreover, if $P(N,V,T) = P(N/V,T)$, $N$ and $V$ can be replaced by the mass density $\rho = \mu m_p N/V$, where $\mu$ is the mean molecular weight and $m_p$ the proton mass, such that

$$P(\rho,T). \quad (2.3)$$

A second equation is the caloric EOS, which is required to give a relation between the systems internal energy $U$, temperature $T$ and mass density $\rho$ (or $N$ and $V$ from a thermodynamic point of view). However, in the context of hydrodynamics (see Sec. 2.2), as it is needed for this work, it is more appropriate to use the mass...
specific internal energy per particle \( u = U/(N\mu m_p) \) instead of \( U \) itself. Thus, by combination of both equations, \( P \) can be expressed in terms of \( u \) instead of \( T \) by

\[
P(\rho, u).
\]  

(2.4)

The substitution of the state quantities becomes more clear with view on the standard set of hydrodynamic equations, which will discussed in a later section.

The most common simplest example of an EOS is for the ideal gas, where particles are free to move and interaction between particles is neglected. This is indeed not a realistic approximation, i.e. it fails to adequately reflect the properties of a weakly compressible liquid\(^2\), but for gases at low densities and pressures, it leads to appropriate results. However, if the extent in the phase space is sufficiently small, the ideal gas EOS can even be used for liquids in a first order approximation. The ideal gas EOS in the already combined form according to Eq. (2.4), reads as

\[
P = (\gamma - 1)u \cdot \rho,
\]  

(2.5)

where \( \gamma = (f+2)/f = C_P/C_V \) is the adiabatic index of the actual system, that can either be calculated from the number of degrees of freedom \( f \), or by the fraction of specific heat capacity at constant pressure \( C_P \) and constant volume \( C_V \). In the ideal gas approximation of fluids, the pressure increases linearly with both, \( P \sim \rho \) and \( P \sim u \). However, more complex terms, such as quadratic terms, are possible choices to differentiate between liquid and gas systems. As it will be shown in Sec. 2.2, the negative gradient of pressure is mainly responsible for the forces in fluid flows. Therefore, the actual choice of EOS affects in direct way the dynamic behavior of the fluid. For example, a weak compressibility can be achieved by choosing an EOS with \( P \sim \rho^2 \), such that the repelling forces grow stronger, when the density deviates from the predicted density.

However, it is not only a weaker compressibility, that can be achieved with the proper choice of EOS, since an EOS can be also used to describe the behavior at phase transitions in fluids. An appropriate equation, that adequately describes a phase separation from a one-component fluid to a separated liquid-vapor system is given by the van der Waals equation of state (vdW-EOS). It is named after Johannes van der Waals, who first included molecular aspects to a mean field approach, what an EOS actually is intended to be [7]. The molecular aspects are on the one hand the assumption of volume expansion of the molecules, which manifests then in mean field approximation in a so called, covolume \( b \). On the other hand, cohesive forces are assumed to act between molecules, with the mean field equivalent of a cohesive pressure \( a \). The two new parameters have opposite effects by means the resulting direction of force. Cohesive fores are attractive, whereas the covolume affects a repulsive force component.

\(^2\)Note that a liquid is not strictly incompressible, but must be considered as a weakly compressible fluid, where slight density fluctuations can occur.
Along with these considerations, the mechanical vdw-EOS in terms of classical thermodynamic state variables is given by

\[ P(N, V, T) = \frac{Nk_B T}{(V - Nb)} - \frac{aN^2}{V^2}, \]  

(2.6)

where \( b \) has indeed the dimension of a volume, and \( a \), contrary to the designation, has not the dimension of a pressure but additionally includes a squared volume factor [17]. More appropriate for the context of hydrodynamics is the density dependent representation

\[ P(\rho, T) = \frac{\rho k_B T}{1 - \rho b} - \bar{\sigma} \rho^2, \]  

(2.7)

as it is actually used for the simulations in this work. The mass specific parameters \( \bar{\sigma} = a/(\mu m_p)^2 \) and \( \bar{b} = b/(\mu m_p) \) and \( \bar{k}_B = k_B/(\mu m_p) \) are adapted to fit with the later on discussed hydrodynamic variables, nevertheless, they will be referred to as cohesive pressure, covolume, and Boltzmann constant, respectively. For low density values \( \rho \to 0 \), the squared density terms become negligible and the vdw-EOS becomes linear, like the ideal gas. On the other hand, for higher densities the quadratic terms becomes more dominant, such that the equation describes a weaker compressibility such as given in a liquid. However, density cannot take any arbitrary high value, since it is bounded by \( 1/b \), which is prescribed by the denominator in the first term in Eq. 2.7 for \( \rho \to 1/b \), the \( P \to \infty \). In Fig. 2.2 a visualization of Eq. 2.7 for several isotherms is shown. It can be seen, that the actual shape of the curve is strongly affected by the temperature in the system. For high temperatures the curves strictly increase, whereas at low temperatures an interval appears, where \( \partial P/\partial \rho < 0 \), which is due to the squared density term \(-\bar{\sigma} \rho^2\). This part of the curve is commonly referred to as the vdW-loop. In the following subsections it is shown that the existence of this loop is essential for an EOS providing phase transitions.

One special isotherm, namely that at the temperature \( T_{\text{crit}} \) lies between these two cases, only shows a single inflection point \( P(\rho_{\text{crit}}) = P_{\text{crit}} \), where \( \partial P/\partial \rho = 0 \). This so called critical point can be calculated with the aid of an additional condition, that is \( \partial^2 P/\partial \rho^2 = 0 \). For higher values the equation describes a one-component fluid, whereas a liquid-vapor system is described for values below this critical point. The critical point is defined by the triple \((P_{\text{crit}}, T_{\text{crit}}, \rho_{\text{crit}})\), but all can be expressed in terms of the two parameters \( \bar{\sigma} \) and \( \bar{b} \) [4],

\[ P_{\text{crit}} = \frac{\bar{\sigma}}{27 \bar{b}^2}, \quad T_{\text{crit}} = \frac{8\bar{\sigma}}{k_B 27 \bar{b}}, \quad \rho_{\text{crit}} = \frac{1}{3\bar{b}}. \]  

(2.8)

Thus, a vDW-system is fully described by these two parameters.

Usually, it is only the mechanic vdw-EOS that is meant when one speaks about the vdw-EOS, but the corresponding caloric vdw-EOS is equally important for...
Chapter 2 Basic physical principles

The dynamic evolution of a phase separating system and reads as

\[ u(\rho, T) = \frac{k_B T}{\gamma - 1} - \bar{u}\rho. \]  

(2.9)

In contrast to an ideal gas, there is a density dependence in the equation, which is responsible for heating or cooling when the phases separate. This can be seen by resolving the equation for \( T \). In this formulation, it is obvious, that a density variation directly changes the temperature, where compression increases the temperature and decompression decreases the phase temperature. This is what is commonly referred to as latent heating in separating systems.

In summary, the equations (2.7) and (2.9) can be combined to one single equation, by resolving the latter for \( T \) and inserting in (2.7)

\[ P(\rho, u) = \frac{\rho(\gamma - 1)(u + \bar{u}\rho)}{1 - \rho\bar{b}} - \bar{u}\rho^2. \]  

(2.10)

On basis of this phenomenological vdW-EOS, the following subsections return to the already mentioned terms “unstable” and “metastable” and their actual physical meaning in this context. The terms spinodal and binodal are further specified and it is clarified how to obtain the respective values for a vdW fluid at a given temperature, and how they can be visualized as curves in a phase diagram.

**Spinodal curve**

The isotherms with \( T < T_{\text{crit}} \) all show an interval of decreasing pressure as shown in Fig. 2.2, which means precisely, that there should exist low density regions with higher pressure than in spatially neighbored higher density regions. This is a contrary and unexpected feature, since the vdW-EOS describes a one-component
system and, therefore, the isotherms in the pressure-density diagram should only monotonically increase.

In theory, this inconvenient fact is considered by simply defining it as a prohibited region, where the system is not allowed to pass into. The bounds of these intervals can be calculated by the condition, that the first derivative vanishes \( \frac{\partial P}{\partial \rho} = 0 \) at constant \( T \), which can be expressed in an analytical term for a van der Waals fluid and is given by

\[
\left( \frac{\partial P}{\partial \rho} \right)_T = \frac{k_B T}{(1 - \rho b)^2} - 2\pi \rho. 
\]

(2.11)

Using equations (2.7) and (2.11) leads to two equations [4]. One describes the pressure-density dependency

\[
\frac{P(\rho)}{P_{\text{crit}}} = \left( 3 - 2 \frac{\rho}{\rho_{\text{crit}}} \right) \left( \frac{\rho}{\rho_{\text{crit}}} \right)^2
\]

(2.12)

and the second describes it for the temperature

\[
\frac{T(\rho)}{T_{\text{crit}}} = \frac{1}{4 \rho_{\text{crit}}} \left( 3 - \frac{\rho}{\rho_{\text{crit}}} \right)^2
\]

(2.13)

which are both commonly referred to as the projections of the so called spinodal curve. Equation 2.13 is plotted in Fig. 2.1, where it becomes clear, that below the critical point to each temperature two densities \( \{\rho_{\text{spino}}\}_{L,V} \), liquid and vapor, are assigned. The fact that \( \frac{\partial P}{\partial \rho} < 0 \) for every isotherm in between this interval is not meaningful in classical physics. However, it provides a basis to discuss a completely unstable region below the spinodal curve.

**Binodal curve and Maxwell construction**

Although the criterion of monotonicity is full-filled, it turns out, that the \( \{\rho_{\text{spino}}\}_{L,V} \) are not the true density values of coexistence, which lie actually below and above the respective spinodal values for the vapor and the liquid phase. The spinodal pressure values of the liquid phase become negative for a certain choice of temperature as can be seen from Fig. 2.2. Moreover, the problem of the pressure discrepancy still remains for every density interval, where the pressure value of the lowest density is higher than that for the highest density, even if the spinodal interval in between is excluded.

The actual true density values of coexistence \( \rho_{L,V} \) in thermal equilibrium define the binodal curve, which is also shown in Fig. 2.1. However, it turns out, that the region between spinodal and binodal is not completely unphysical at all, and that such states can be experimentally achieved by supercooling or superheating the fluid. Moreover, from a theoretical point of view, the proper sign of the pressure gradient suggests a physically correct fluid flow. For these reasons, the region between the spinodal and binodal is denoted as metastable region. The densities
of coexistence $\rho_{l,v}$ can be calculated from the EOS. Moreover, it strongly depends on the actual choice of EOS, for where it needs to have the characteristic loop, as described for the vdW-EOS in section 2.1.2. This calculation method is commonly known as the “equal-area rule” or “Maxwell equal-area construction”\(^3\).

The designation “equal-area” already suggests that the values are obtained by an integration, where the desired $\rho_{l,v}$ can be calculated from the limits of the integral. For the purpose of integration, one first needs the vdW-EOS in the volume dependent formulation as shown in Eq.\((2.6)\), which is the thermodynamically consistent basis. Incidentally, the construction method can be understood from the thermodynamic point of view, where it is explained by a continuity condition of the chemical potentials and by the Helmholtz free energy $H$, where pairs of points must be found in the isotherms of the $(H,V)$-diagram, that share the same tangent. Since the gradient of $H$ gives the pressure

$$P = -\left(\frac{\partial H}{\partial V}\right)_{T,N},$$

\(2.14\)

the slope of this tangent gives the requested pressure in the interval between the pair of points. A more detailed description can be found in Ref.\([4]\). Note, that as a consequence of the conditions, the pressure within the coexistence region is constant, such that $P_v = P_l =: P$. Moreover, the actual pressure value must be chosen, carefully by the condition

$$P[V_v - V_l] \overset{!}{=} \int_{V_l}^{V_v} PdV.$$  

\(2.15\)

For an isothermal system, the two volume values directly follow from a given pressure. The left hand of the equation corresponds to a rectangle, whereas the right hand side describes the integral part. Figure 2.3 shows several isotherms for the vdW fluid in the pressure-volume projection. The further interpretation of Eq.\((2.15)\) is then the “equal-area rule”, as shown in the inset box, where the areas $A$ and $B$ must have equal sizes. Finally, the loop becomes replaced by the horizontal line with constant pressure in between the interval $[V_l, V_v]$, visualized in the inset by the gray line. Finally, the density values of coexistence $\rho_{l,v}$ are calculated. Note, that the Maxwell rule is solely a method for the calculation of the coexistence values in thermal equilibrium. However, in the context of hydrodynamics and thermal systems, the states within the loop are explicitly allowed.

**Exceptional regimes in the phase diagram**

The construction and calculation of spinodal and binodal follow a classical approach in the understanding of phase transitions. The spinodal describes the theoretical envelope for a completely unstable region and the binodal gives the strict

\(^3\)The calculation is shown for the vdW-EOS, but the method is generally not only restricted to the vdW-EOS.
transition line from where the stable one-phase region changes to a metastable regime. Metastability intends that the system is mostly stable\(^4\), but undergoes a phase transition when a so called nucleus interrupts the stability. Such a nucleus can emerge from both statistical superposition of internal fluctuations of the fluid or from external intervention \([9]\). The process of nucleation differs significantly from spinodal decomposition. Nucleation is spatially restricted to single points, where an external factor (such as a shock wave) initiates the phase to separate. It statistically occurs at a certain nucleation rate \([18]\). In contrast, in spinodal decomposition static initial density fluctuations are sufficient for isotropic phase separation. This difference eventually manifests in the term “heterophase-fluctuations” as driving process for nucleation in contrast to “homophase-fluctuations” in a spinodal-decomposing system and will be discussed in section 2.1.3.

However, in reality the behavior of a phase separating system is often more complex then the phenomenological approaches appear to suggest. Thus, most of the theoretically predicted strict changes from one to another regime are in fact smooth and continuous. Moreover, the mean-field approach, such as the vdW theory, holds for deep quenches but fails for weak quenches near the critical point, where the system in such a critical state can be described by so called critical point exponents. For example, an exponent \(\lambda\) describes the scaling behavior between the depth of the quench \(\tau = (1 - T/T_c)\) and one system parameter \(X\) by

\[
X \sim \tau^\lambda. \tag{2.16}
\]

By this procedure, systems with identical exponents become universally combined to so called universality classes. Yeomans [3] gives an comprehensive description

\(^4\)In a vapor phase this is mostly also referred to as supersaturation.
of phase transitions from this statistical point of view. The systems that are investigated in this thesis are far from criticality, therefore, this non-mean-field region will not be discussed in more detail here.

The most essential exceptional regimes can adequately be illustrated with the aid of Fig. 2.4, which is adapted from a figure originally printed in Ref. [19] and reviewed in detail in Ref.[8]. A transition line at a certain temperature $T$ from mean-field to non-mean-field critical behavior takes place by

$$h^d (1 - T/T_c)^{2 - d/2} \approx 1,$$  \hspace{1cm} (2.17)

where $h$ is the interaction range in the actual system and $d$ the dimension. Therefore, it is not expected to observe spinodal decomposition for high temperatures near the critical point. The substantiating theory for this is the CH equation [8]. Furthermore, the spinodal is not the real distinction line even if the temperature is below that limit from Eq. (2.17). A transition regime between nucleation and spinodal decomposition exists that lies below the spinodal curve. The metastable regime is subdivided in three subregimes. Near below the binodal curve, occurs what is commonly known as classical nucleation theory [4] and below the metastable regime as already described above, a region appears, where nucleation turns slowly to spinodal decomposition.

### 2.1.3 Stages of the demixing process

Several discrepancies arise by comparing the concepts behind spinodal and binodal with experimental setups. For instance, theory predicts only certain points in
2.1 Spinodal decomposition in liquid-vapor systems

Figure 2.5: Schematic figure of the initial growth of “homophase-fluctuations“ for a certain wavelength at several times with a fixed temperature parameter, where $\rho_0$ is the predefined initial density. The figure is adapted from Ref.[8].

time of the whole process of demixing, whereas it does not describe the temporal evolution of it. The “order” [8] of the herein considered phase transition is also of interest, since a liquid-vapor transition is expected to be of first-order. This means a discontinuous order parameter, which is in fluids the density difference between the two phases. However, first-order is true for deep quenches, whereas, when temperature increases and approaches the critical region, it changes to higher order as the interface between the phases becomes more and more diffuse, as discussed by the exceptional regimes in the previous section. Moreover, the question on how and when diffuse interfaces are formed, is relevant in the context of the morphological evolution, since it turns out that the actual temperature plays an important role, where interfaces can be formed along with the process of separation [10], such as the system heats up due to latent heat. However, it becomes apparent that the theoretical approaches are mostly based on the assumption of an isothermal demixing. The term “spinodal decomposition” comprises the whole dynamics of the demixing process, although the phases pass the spinodal curve only once in a very early stadium of the separation. Three different time regimes can be distinguished in the overall demixing process. These are the early, intermediate, and late stage [20].

Once quenched to the unstable region, the process initiates with an isotropic rise of already initially-present fluctuations in density. A schematic sketch is shown in Fig. 2.5. The amplitudes of those so called “homophase fluctuations” are expected to grow exponentially [8], which can be derived by the linearized CH theory. Moreover, the procedure happens very fast and after a short time period the extreme values of density exceed the spinodal values. In this stage the mean size of the domains $\xi(t)$ and interface width $w(t)$ have roughly the same meaning $\xi(t) \sim w(t)$, since phases a not yet fully formed.
Right after the initial growth of fluctuations first structures of the separated phases begin to form. It depends on the difference between the quenched density and the coexistence density which structure actually forms in this early stage. Incidentally, the density difference predicts the final mass fraction. The types of structure range from individual nuclei of liquid drops or vapor bubbles when near the spinodal curve, to “sponge”-like structures, when the initial quench density is far below the corresponding spinodal density value.

The intermediate stage is a generally underrated in its importance to the demixing process and was paid less attention so far. It is expected to be responsible for the formation of interfaces. The actual behavior in this stage can become any complexity. In a simplified view it could be described as the time regime, where both interface width and average size of the separated domains are evolving. More precisely, the width of the interface $w(t)$ can both further increase or begin to decrease whereas the characteristic domain size $\xi(t)$ strictly increases. It depends on the environmental parameters of the actual system, such as the depth of the quench, the initially predicted density, or if the system behaves isothermal or non-isothermal. For instance, an increase in temperature can cause the formation of more diffuse interfaces, which goes on the expense of domain growth. Fig. 2.6(a) shows a schematic sketch of the phase behavior in this intermediate stage. Note that the intermediate is not connected to reaching the coexistence density, although the sketch shows droplets with binodal density values. It is actually not clearly distinguishable when the stage begins and when it turns over to late stage behavior.

The late stage is probably the best investigated stage, as most studies deal with this stage. A reason for this fact can be found in the better experimental accessibility, whereby the late stage occurs over a long time range. In contrast, the early and intermediate stages, are passed through extremely fast, which has the consequence that experimental analysis methods for these stages are rare. The interfaces are now expected to be already formed and remain stable at a fixed
2.1 Spinodal decomposition in liquid-vapor systems

interface width as shown in Fig. 2.6(b). The scaling hypothesis [21, 20] suggests that the system can now be described by only one characteristic length scale. This is the average domain size $\xi(t)$ that scales with time at a certain growth law. Note that the assumption of a constant interface width in the late stage holds only when the temperature remains constant. If the temperature slightly changes during thermal equilibration, the interface width will of course adjust to the actual temperature. The driving effect is the surface tension that forces the actual structures of the phases to form coarser structures and, if apparent, viscosity also tends to reduce the complexity of a structure.

Three basic time regimes can be observed in a liquid-vapor system. Bray (see Ref. [21]) gives a summary of the expected time regimes with the corresponding growth laws that belong to the scaling hypothesis. Although originally given for binary mixtures it holds also in the case of liquid-vapor systems. The first is the so called Lifshitz-Slyozov (LS) growth law [22], which is based on the assumption of diffusion and predicts a $1/3$ growth rate. The second regime was given by Siggia, who first theoretically predicted a linear viscous hydrodynamic (VH) regime [23]. Note that this regime is only observable if the two separated phases are continuously connected, respectively, since the viscosity forces single droplets to spherical shapes and would not produce a coarser structure. The third regime is based on inertial hydrodynamics IH and was first predicted by Furukawa [24]. In summary the laws are given by

$$\begin{align*}
\xi(t) \sim \begin{cases} 
(\lambda \sigma t)^{1/3}, & \xi \ll (\lambda \eta)^{1/2} \quad \text{(LS)}, \\
(\sigma t/\eta), & (\lambda \eta)^{1/2} \ll \xi \ll \eta^2/\rho \sigma \quad \text{(VH)}, \\
(\sigma \rho t)^{1/3}, & \xi \gg \eta^2/\rho \sigma \quad \text{(IH)},
\end{cases}
\end{align*}$$

(2.18)

where $\sigma$ is the surface tension, $\eta$ is the bulk viscosity coefficient, and $\lambda$ is a transport coefficient, such as thermal conductivity. Eq. (2.18) gives an orientation guide, for which growth rates should be expected. Nevertheless, they should not be mentioned as the “only truth”, which can be seen for some reasons, especially considering liquid-vapor systems. For instance, the surface tension $\sigma := \sigma(T)$ is temperature dependent in a vdW fluid [25]. As a consequence, the limits for the three cases are not totally fixed, which means in effect that crossovers between the regimes are possible and expected to depend on temperature. Another reason is the simplified assumption of the scaling hypothesis, which requires roughly the same averaged domain sizes for both phases. This might be fulfilled for the incompressible binary mixtures, where volume and mass fractions are comparable sizes, but does not hold in liquid-vapor system, where especially the volume fraction is strongly sensitive to the $\rho_0$. Therefore, also the domain sizes of the phases are poorly comparable and might require an isolated consideration of the phases. Moreover, also the growth rates in binary mixtures depend on the initial density $\rho_0$ [26]. Eventually, as a consequence of the effective behavior of viscosity, the VH regime can only occur when the respective phases do not contain single separate droplets or bubbles, but are connected to one single structure [21].
Finally, the system relaxes to an equilibrium state and the characteristic length ceases to grow further. The final shapes of the phases depend on the actual dimension of the system and the mass fraction between the phases that predicts which phase is the minor phase. Therefore, a sphere, but also a cylinder or a plate might be possible final shapes.
2.2 Hydrodynamics

An adequate description of phase transitions, especially that of spinodal decomposition in fluids, must be in consideration with the dynamic evolution of the system. This comprises the rheological, as well as the thermal evolution in time. Both factors give a restriction of the common theories. For its inclusion, the hydrodynamic approach is a promising candidate. The field of hydrodynamics is one of the main fields of application in structure formation, which are usually considered to arise by instabilities [11]. In the first instance, it is a set of coupled partial differential equations (PDE) with certain initial and boundary conditions that is used to describe the motion of a fluid. Due to the complexity of this set of PDE, it exists no general solution method and it can hardly be solved analytically, but only for a few simplified test cases. Promising approaches are given by numerical approximation methods, which provide adequate solutions to the expense of computational effort. However, under certain conditions and numerical approximations the set of PDE can be reduced to a set of ordinary differential equations (ODE), which is quite more comfortable to solve.

The following descriptions in this section are mainly based on the books on hydrodynamics by Landau and Lifshitz [6], Hansen and McDonald [1], Guyon [27] and Bestehorn [11].

The derivation of the equations is based on the continuum approach, where the fluid is described by continuous field quantities. This can be seen from the microscopic structure of a fluid where the interaction has only a short-range order a few molecule diameters. Thus, for longer pairwise distances between particles, the fluid behaves as a continuum. To quantify the hydrodynamic approach, one usually compares scales of length $L$ and time $\Delta t$ of the considered system with mean free path $l$ and mean collision time $\tau$ of a molecule, which yields three regimes (see e.g. [1]). The first is a free-particle regime at $l \gg L$ and $\tau \gg \Delta t$, where the observation times and distances are very short compared the mean free paths and times, respectively. This is followed by the kinetic regime $l \approx L$ and $\tau \approx \Delta t$, where the microscopic structure of molecules affect the dynamics of a system. Finally, the third region is $l \ll L$ and $\tau \ll \Delta t$, which is the hydrodynamic regime. In the continuum approach, volume elements $dV$ are considered small enough to be treated as points, but still large enough to be described by the hydrodynamic regime. Although such a volume element must contain lots of molecules it will be considered further on as a fluid particle.

Each particle is, from a statistical-physics viewpoint, a thermodynamic equilibrated ensemble that allows for exchange of mass and internal energy with the surrounding medium, i.e. fluid particles. Therefore, the first law of thermodynamics holds for every particle and can be used to describe the internal energy balance of a system. For the full description of the motion of a fluid, information about the velocity field $\mathbf{v}(x, y, z, t)$ and, at least, two additional arbitrarily chosen thermodynamic variables is needed, since the remaining physical properties follow from the EOS relation. A set of hydrodynamic variables, which are namely
the densities of mass $\rho$, momentum $\rho \mathbf{v}$, and energy $\rho \epsilon$, each satisfy a continuity equation of the form
\[ \frac{dA(r,t)}{dt} + \nabla \cdot j_A(r,t) = 0, \quad (2.19) \]
where $A(r,t)$ is the respective density and $j_A(r,t)$ is the corresponding flux [1].

This choice of variables is theoretically explained, since a continuity equation always corresponds to a conservation law. However, for application-oriented reasons, it is appropriate to use more familiar variables, such as $(\rho, U, \mathbf{v})$. Moreover, since the internal energy $U$ is an extensive property, it is more convenient to use the intensive (mass) specific internal energy per particle $u = U/N \mu m_p$, where $\mu$ mean molecular weight and $m_p$ the proton mass.

Mainly responsible for the description of the motion of a fluid (both liquid or gas) is the momentum, or at least the velocity field, which is described by Euler equation. Under consideration of dissipation, such as viscosity the particular equation is named Navier-Stokes equation. Dissipation must also be considered in the energy equation. Furthermore, the energy equation also takes thermal interactions into account, such as thermal conductivity, described by Fourier’s heat law.

In summary, a set of five PDE fully describes the motion of the fluid in three dimensions. These are namely the three components of the momentum equation, and each one equation for the energy and density, which ensure to the conservation of momentum, energy, and mass, respectively.

### 2.2.1 Lagrangian and Eulerian picture

In the context of hydrodynamics, especially with regard to numerical solvers, two different, but formally equivalent, viewpoints have been established. These two pictures of hydrodynamics differ in their frame of reference, but are formally equivalent. They distinguish, in simple terms, between the grid based and the particle based point of view. However, it depends on the actual problem to be solved, which one is preferable to use.

An illustrative description of the differences between the two pictures is given in Figure 2.7. The Eulerian picture is the mathematically more obvious description, where a grid is used that is fixed in space and time. The hydrodynamic equations can then be solved by calculating the mass flow in and through a, so obtained, fixed grid. The second picture is the Lagrangian picture. It is less intuitive, but on the other hand computationally less expensive. It can either be described by streamlines, which are given by the velocity field fixed in time, or by following the trajectories in time of fluid volume elements of fixed mass. Every fluid element can then be understood as the origin of its own frame of reference. Therefore it is commonly referred to as the usage of comoving coordinates.
2.2 Hydrodynamics

Figure 2.7: Visualization of the two reference frames. (a) Grid based Eulerian picture versus Lagrangian picture, with (b) streamlines illustrating the free movement of particles in space, or (c) following the trajectory of one volume element evolving in space and time.

Introducing the convective derivative\(^5\) by the operation

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla,
\]

(2.20)
is explained by the differentiation between the two pictures, where it gives the transition between the Lagrangian and the Eulerian picture. With regard to the two pictures it is necessary to define the frame of reference of the velocity \(\mathbf{v}(\mathbf{r}, t)\), which is conventionally defined as a field in every fixed point in space and time. It must be emphasized that \(\mathbf{v}\) is not the comoving velocity that belongs to a certain fluid element.

2.2.2 Continuity equation

The conservation of mass in hydrodynamics is satisfied by the continuity equation\(^6\). It can be derived by two possible ways to calculate the mass of a given volume \(V_0\). On the one hand, the total mass \(m_0\) of \(V_0\) is given by

\[
m_0 = \int_{V_0} \rho \, dV,
\]

(2.21)

where \(\rho\) is the density. On the other hand, the mass outflow flow per time unit \(\frac{dm_0}{dt}\) through the surface of \(V_0\) can be expressed by

\[
\frac{dm_0}{dt} = \int_{\partial V_0} \rho \mathbf{v} \, df,
\]

(2.22)

\(^5\)This derivative is also sometimes referred to as the substantial, the material, or the total derivative.

\(^6\)Although every conserved properties belongs to a respective continuity equation, in hydrodynamics the term “continuity equation” usually belongs to the mass conservation.
where $v$ is the velocity vector and $df$ is the normal to a surface element of $\partial V_0$. Thus, combination of the equations (2.21) and (2.22) gives
\[
-\frac{\partial}{\partial t} \int_{V_0} \rho \, dV = \oint_{\partial V_0} \rho v \, df.
\] (2.23)

Using Gauss’s theorem, the surface integral is transformed to a volume integral,
\[
\int_{V_0} \left[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) \right] \, dV = 0,
\] (2.24)

which must be fulfilled for any arbitrary volume $V_0$. Thus, the integrand itself must be zero. The continuity equation in the Lagrangian picture follows by use of the product rule for the divergence term and using the substantial derivative
\[
\frac{d\rho}{dt} + \rho \nabla \cdot v = 0.
\] (2.25)

Incidentally, Eq. (2.25) ensures non-existence sources or sinks, which means that mass can neither be created nor destroyed.

### 2.2.3 Momentum equation

The most important equation is the momentum equation. It describes the motion of the fluid, by the time derivative of momentum, i.e. the resulting force on a volume element. It consists of the partial forces with miscellaneous physical origins that are involved to the dynamics of the system.
\[
\delta F = \sum_i \delta F_i, \tag{2.26}
\]
worth mentioning the ideal hydrodynamic $\delta F_H$, viscous hydrodynamic $\delta F_V$, gravitational $\delta F_G$, or external forces $\delta F_{\text{ext}}$. The momentum equation is called Euler equation, when viscous forces and thermal conductivity become negligible small compared to ideal hydrodynamic forces. Therefore, the Euler equation describes the reversible part of the flow. Under consideration of stress terms, such as the viscosity is, the momentum equation is called Navier-Stokes equation. In the latter case the equation is quite easier to handle with the aid of tensors, where the pressure and viscosity are given as tensors of stress.

Nevertheless, the Euler equation can be derived from the definition of pressure, since it has the dimension of a force per unit area [N/m$^2$]. Consider the resulting force acting on an arbitrary volume element $V_0$, which is given by the integral
\[
\delta F_H = -\oint_{\partial V_0} P \, df, \tag{2.27}
\]
using again Gauss’s theorem
\[
\delta F_H = -\int_{V_0} \nabla P \, dV, \tag{2.28}
\]
eventually gives the Euler equation
\[ \rho \frac{d\mathbf{v}}{dt} = -\nabla P, \] (2.29)
in the Lagrangian reference frame. The physical interpretation of the Euler equation, is that the motion of an ideal fluid is solely driven by a local pressure gradient, where the flow is always directed from high to low pressure regions, and inertia effects due to the density term. However, the Euler equation can also be written in tensor notation,
\[ \rho \frac{d\mathbf{v}_\alpha}{dt} = -\frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta}, \] (2.30)
where the pressure is expressed by the so called stress tensor \( \sigma_{\alpha\beta} = \delta_{\alpha\beta}P \). Einsteins summation convention is used, which implies that a repeated index on one hand side of an equation is summed over. The tensor can now be extended to include viscous terms. This is done adding the viscous stress tensor,
\[ \sigma_{\alpha\beta} = \eta \left[ \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \frac{\partial v_\gamma}{\partial x_\gamma} \right] + \zeta \delta_{\alpha\beta} \frac{\partial v_\gamma}{\partial x_\gamma}, \] (2.31)
containing both shear and bulk viscosity effects, controlled by the coefficients \( \eta \) and \( \zeta \), respectively. Thus, the most general form of the stress tensor is given by
\[ \sigma_{\alpha\beta} = \delta_{\alpha\beta}P + \sigma_{\alpha\beta}. \] (2.32)

Using the stress tensor from Eq. (2.32) for Eq. (2.30) gives a generalized form of the momentum equation
\[ \rho \frac{dv_\alpha}{dt} = -\frac{\partial P}{\partial x_\alpha} + \frac{\partial}{\partial x_\beta} \left[ \eta \left( \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \frac{\partial v_\gamma}{\partial x_\gamma} \right) \right] + \frac{\partial}{\partial x_\alpha} \left( \zeta \frac{\partial v_\gamma}{\partial x_\gamma} \right), \] (2.33)
where it can also be given in vector notation,
\[ \rho \frac{d\mathbf{v}}{dt} = -\nabla P + \eta \Delta \mathbf{v} + \left( \zeta + \frac{\eta}{3} \right) \nabla (\nabla \cdot \mathbf{v}), \] (2.34)
which is the so called Navier-Stokes equation.

### 2.2.4 Thermodynamics and energy equation

From a thermodynamic point of view, hydrodynamic processes are always quasi-static. This means, the hydrodynamic time scale is large enough, such that the system can be expected to remain locally in equilibrium. Thus, energy conservation can be expressed by thermodynamics, where the first law of thermodynamics gives an expression for internal energy \( U \). The formulation requires again considering a volume element \( V_0 \). The law is then defined by
\[ dU = \delta Q + \delta W, \] (2.35)
where $U$ is the internal energy, and

$$\delta W = -PdV \tag{2.36}$$

is the work done in the system. The first term

$$\delta Q = TdS, \tag{2.37}$$

takes heat exchange with the surroundings and irreversible dissipative processes that result in an increase of entropy $S$, such as the viscosity, into account. Temperature changes may occur by thermal conduction or by other interaction with the environment, such as coupling to a heat bath. Since $U$ is extensive it is more appropriate to use the intensive mass specific $u$. Let the mass be $m$, so that using $V = m/\rho$ gives $dV = -m/\rho^2 d\rho$. Thus, the contribution to the specific internal energy $u$ from the work term becomes

$$\frac{du}{dt} = \frac{P}{\rho^2} \frac{d\rho}{dt}. \tag{2.38}$$

The time derivative of density is given by the continuity equation (2.25), which eventually culminates in the expression

$$\frac{du}{dt} = -\frac{P}{\rho} \nabla \cdot \mathbf{v}. \tag{2.39}$$

Thermal conduction can be described by Fourier’s heat law, where a heat flux vector is defined by $\mathbf{j}_Q = \kappa \nabla T$, with the in general material and temperature-dependent thermal conductivity $\kappa = \kappa(\rho, T)$. The latter must be positive, since heat can only flow from high to low temperature regions. The rate of change of internal energy due to this heat flux is then given by the negative divergence of $\mathbf{j}_Q$. Thus,

$$\frac{du}{dt} = -\frac{P}{\rho} \nabla \cdot \mathbf{v} - \frac{1}{\rho} \nabla (\kappa \nabla T) \tag{2.40}$$

gives the total change in internal energy for a given arbitrary volume element of the fluid. Note that viscous effects can be included in analogy to the procedure described for the momentum equation, where the notation above is replaced by the tensor notation and the stress tensor, given by equations (2.31) and (2.32), is used [6] and the energy equation reads in the most general form as

$$\frac{du}{dt} = -\frac{P}{\rho} \nabla \cdot \mathbf{v} - \frac{1}{\rho} \nabla (\kappa \nabla T) + \frac{\eta}{2\rho} \left[ \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} - 2\frac{2}{3} \delta_{\alpha\beta} \frac{\partial v_\gamma}{\partial x_\gamma} \right]^2 + \frac{\zeta}{\rho} (\nabla \cdot \mathbf{v})^2. \tag{2.41}$$

Finally, if needed, the specific total energy $\epsilon$ can be obtained by the summation of specific kinetic energy and specific internal energy

$$\epsilon = \frac{1}{2} v^2 + u. \tag{2.42}$$
Algorithms and methods

The set of hydrodynamic equations is a complicated set of coupled PDE. For this reason, it is not surprising that analytical solutions exist only for few special conditions and they can not be solved in general. This is where numerical methods come into play. Numeric in general denotes the subject in mathematics that deals with the calculation of algorithms and iterative methods being used to approximate solutions of mathematical problems in the absence of analytical solutions, for instance algorithms to calculate derivatives and integrals, or to solve equations and sets of equations. Advances in the speed of processors and multi-threading in inter-connected computer systems allow for the calculation of more and more complex systems. Therefore, it becomes attractive for physical problems, such as solving the set of hydrodynamic equations, where adequate solutions can only be achieved by a high computational effort. In the context of hydrodynamics, or more generally fluid mechanics, the subject of numerical approximation commonly known is under the generic term of computational fluid dynamics (CFD). Methods can be approached from two viewpoints. They are either based on the Eulerian reference frame. Such methods are called grid based techniques. In contrast, methods derived from the Lagrangian picture are commonly referred to as particle based techniques.

This chapter gives an overview about the numerical methods used in this work. A comprehensive description of the Lagrangian based smoothed particle hydrodynamics (SPH) method and further modifications to the context of SD will be given. Furthermore, time stepping schemes and symplecticity are discussed. Since the generation of appropriate initial conditions is essential in the context of SD it is also discussed. The program package GADGET-2, used for this work, is described including the basic details of the further methods used by the code, such as tree construction. At last, a discussion of particular analysis methods especially
Chapter 3 Algorithms and methods

for SPH data, related to the SD, such as the calculation of the domain sizes, are discussed.
3.1 Smoothed particle hydrodynamics

Smoothed particle hydrodynamics (SPH) is a numerical method that solves the governing equations of hydrodynamics on basis of the Lagrangian reference frame. The algorithm first approximates the spatial derivative components of the fluid particles, which are needed for the calculation of the temporal evolution by an appropriate time integration scheme solving this set of ordinary differential equations.

The SPH method has many possible realizations, which is due to symmetry operations, based on easy mathematical considerations. The proper choice of the algorithm depends on the respective problem. One formulation has been established as the modern formulation of SPH with adaptive smoothing [28], sometimes also called the “grad-h“ SPH [29]. However, the basic governing equations can be derived on the basis of the original SPH approach, which was originally proposed by Gingold and Monaghan [13], and simultaneously also by Lucy [30]. Both developed the method for astrophysical purposes for numerical simulations on the dynamics of non-spherically symmetrical star formation. In the context of astrophysics the method established in various other fields such as galactic interactions, cosmological structure formation, and became generalized to the magnetohydrodynamic equations. Hydrodynamics in astrophysics mostly deals with low density gases and thus, with compressible fluids and it may even be treated isothermally. Nonetheless, SPH is able to handle incompressible non-isothermal liquids, so that it can also be applied to many other hydrodynamics related problems but astrophysics. Recent progresses have been made in the context of free surface flows, and more general, of multiphase systems, which is closely related to question of how to formulate adequate boundary conditions in terms of SPH, between both solid and fluids.

The ongoing development of phase separating systems is divided in two approaches. On the one hand, the distinct phases are treated severally, wherefore the interaction between the phases must be included extrinsically. In this formulation mass exchange can hardly be realized. In the other approach the system is described by one single EOS. Therefore, the interaction is intrinsically involved and also mass exchange between the phases must not be addressed by additional terms. A first approach to the latter for a SPH using the vdW-EOS was given by Nugent and Posch in 2000 [31], where the formation of single droplets in vapor medium were studied and validation test to the surface tension and oscillation of droplets have been performed. However, the simulations were performed only at a very low resolution and in two space dimensions. Following studies and further developments are mostly related to this first attempt and addressed to this very specific case of single droplet formation [32, 33, 34, 35, 36, 37, 38]. That this approach can be extended easily to three dimensions and to the dynamics of even more complex phase separating systems, such as in spinodal decomposition, is subject of this thesis.

The aim of the present section is just to give a basic overview about the SPH
method. Since the method is recently still in development, there is no claim for completeness. For further studies and for more details the comprehensive reviews of Springel [28], Monaghan [39], Rosswog [29], and Price [12] are recommended.

3.1.1 Kernel interpolation

Although not exactly the topic of SPH, nevertheless, a historic outline is fundamental for the understanding of the method. The main idea is based on a technique used in statistical mathematics to estimate the probability density function from a given set of measurements of a probability variable \( X \). Each measurement \( X_i \) is used as the center of a smooth profile with width \( h \). This smoothing is done by a so called kernel \( W \), where the shape of that kernel could be, for instance a Gaussian

\[
W(x - X_i, h) = \frac{1}{\sqrt{2\pi h^\nu}} e^{-\frac{1}{2}(\frac{x-X_i}{h})^2}, \quad (3.1)
\]

where \( \nu \) gives the number of spatial dimensions. The desired probability density is then obtained by the superposition of all the single profiles. The method is therefore called kernel density estimation (KDE). Figure 3.1 illustrates a KDE for a set of random points at constant \( h \). The idea of summing distance-dependent kernel-weighted grid points in probability theory can be extended to statistical physics, where any arbitrary field quantity \( A(\mathbf{r}) \) at a given time can generally expressed in terms of the integral

\[
A(\mathbf{r}) = \int_V A(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r}'. \quad (3.2)
\]

Note that this expression is valid for both scalar or vector fields not only in one but even in three dimensions. In analogy, the \( \delta \)-distribution is broadened by a kernel
function \( W(|r - r'|, h) \), that smooths the point with a certain width \( h \). However, the equality is no longer valid, but still an approximation.

\[
A(r) \approx \langle A \rangle_V = \int_V A(r')W(|r - r'|, h)dr'
\]  

(3.3)

Obviously, the kernel must satisfy the condition \( \lim_{h \to 0} W(|r|, h) \to \delta(r) \), where the mean value \( \langle A \rangle_V \) converges to the exact value \( A(r) \).

From the Lagrangian viewpoint discrete particles, each of mass \( m_i \), are considered. Furthermore, each particle is equipped with the fluid quantities such as density, pressure, momentum, and internal energy. Using the relation \( m/\rho = d\rho/r \) allows to replace the integral in Eq. (3.3) by a sum

\[
A(r) \approx \sum_j m_j \frac{A_j}{\rho_j}W(|r - r_j|, h),
\]  

(3.4)

where the fluid particles are now used as supporting points for a weighted summation. Thus, Eq. (3.4) can be understood as an interpolation scheme on an irregular grid. This is the most fundamental approach to the SPH method. Due to the interpretation as an interpolation scheme the kernel should fulfill other conditions, that is the normalization \( \int Wdr = 1 \). Furthermore, the use of kernels with compact support are also worth recommended in order to reduce computational effort. Thus, the Gaussian distribution is not forbidden but unadvised. A selection of common choices of kernels is given in Sec. 3.1.4.

In general any quantity can be calculated by expression (3.4). Note that it can be used to calculate the values in any point, not necessarily restricted to the particle positions \(^1\). However, this calculation is not always useful to perform for every quantity, e.g. the pressure is already given by the EOS, but it is very likely for the density. This will be further addressed to in Sec. 3.1.5, since it can be used instead of solving the continuity equation.

### 3.1.2 First and second order spatial derivatives

One of the benefits of the SPH method becomes evident from the calculation of spatial derivatives, such as divergence, gradient or curl. By applying the \( \nabla_r \) operator to \( A \)

\[
\nabla_r A(r) \approx \int_V A(r')\nabla_r W(|r - r'|, h)dr',
\]  

(3.5)

it can be seen that the derivative solely acts on \( W \), since it is the only appearance of \( r \) on the right side of the equation. Again, the transition from the continuous field approximation to the discrete particles picture gives the SPH interpretation by summing over neighbored particles \( j \)

\[
\nabla_r A(r) \approx \sum_j m_j \frac{A_j}{\rho_j}\nabla_r W(|r - r_j|, h).
\]  

(3.6)

\(^1\)This can be useful for the visualization of SPH data.
This interpolation method brings the further requirement on the kernel that the first derivative should be a continuous function as well as the function itself. For the sake of completeness, being a vector quantity $A$,

$$\nabla_r \cdot A(r) \approx \sum_j m_j \frac{A_j}{\rho_j} \cdot \nabla_r W(|r - r_j|, h),$$  \hspace{1cm} (3.7)

$$\nabla_r \times A(r) \approx \sum_j m_j \frac{A_j}{\rho_j} \times \nabla_r W(|r - r_j|, h)$$  \hspace{1cm} (3.8)

are formed in a very similar procedure.

Second order derivatives also appear in the hydrodynamic equations, for example, in the heat conduction term, modeled by Fourier’s heat law in the energy equation (2.40). Therefore, it must be considered in the SPH representation. The most general formulation of the problem is expressed by the term $\nabla(A \nabla B)$, for any arbitrary field quantities $A$ and $B$, whereby the simpler expression, the Laplacian $\Delta B$, is obtained by setting $A = I$. However, the question on how to adequately formulate these second order terms in SPH is still an open issue [40]. Three basic approaches have been proposed. Two approximations are straightforward, but unfortunately giving less accurate results, whereas the third approach gives adequate solutions. The first is in analogy to the construction method of the first derivative by using the second derivative of the kernel. However, this is the poorest in terms of the accuracy and it highly depends on the actual choice of kernel. The second approach is that one could plausibly calculate the derivatives of the derivatives of the sought quantity, but it becomes clear from a computational viewpoint, that it is much more expensive since a second summation loop is required.

However, it is found that a much better formulation is given by a combination of SPH and a simple finite difference scheme. The derivation is described in Refs. [41, 42]. The SPH approximation of a Laplacian $\Delta$ of a field quantity $B(r)$ is

$$\Delta B(r) \approx 2 \sum_j \frac{m_j}{\rho_j} (B(r) - B_j) \frac{r - r_j}{|r - r_j|^2} \nabla W(|r - r_j|, h),$$  \hspace{1cm} (3.9)

which is obtained through Taylor series expansion by neglecting higher order terms. The general expression can be derived by using the identity

$$\nabla(A \nabla B) = \frac{1}{2} \left[ \nabla^2(AB) - B \nabla^2 A + A \nabla^2 B \right].$$  \hspace{1cm} (3.10)

The general second order derivative in SPH is then approximated by

$$\nabla(A(r) \nabla B(r)) \approx \sum_j \frac{m_j}{\rho_i \rho_j} (A(r) + A_j)(B(r) - B_j) \frac{r - r_j}{|r - r_j|^2} \nabla W(|r - r_j|, h).$$  \hspace{1cm} (3.11)

However, there is still degree of freedom in the choice of the term $A + A_j$, since it can be interpreted as arithmetic average, and by this means replaced by another
3.1 Smoothed particle hydrodynamics

average method such as the geometric or the harmonic mean. The harmonic
mean is actually proposed by Cleary and Monaghan [43] who recommended the replacement

\[
\frac{A + A_j}{2} \rightarrow \frac{2AA_j}{A + A_j}, \quad (3.12)
\]

which is still the state of the art for SPH approximation of second order derivatives.

3.1.3 Symmetrization

The set of hydrodynamic variables and their derivatives at a given point can be calculated by the weighted interpolation procedure as previously described. However, it gives only the single state of the system at a certain point in time. The dynamics become effective with consideration of the hydrodynamic equations, where the convective time derivatives of quantities are related to spatial derivatives. The most prominent example is the Euler equation (2.29), where \(\nabla P/\rho\) is responsible for the acceleration of fluid particles. Furthermore, as in the SPH summations only the particle positions and the therewith associated particle quantities (such as density) are required, it is sufficient to calculate only those quantities that are strictly necessary for the temporal evolution, i.e. they appear in the hydrodynamic equations. Moreover, they only need to be evaluated at the actual positions of the particles. Thus, the \(A(r)\)-expression can now be replaced by \(A_i\), indicating the approximated mean quantity corresponding to a particle \(i\) at the position \(r_i\), whereby, e.g. Eq. (3.4) is now given by

\[
A_i = \sum_j m_j \frac{A_j}{\rho_j} W(r_{ij}, h) \quad (3.13)
\]

where an equal sign can now be used, and \(r_{ij} = |r_i - r_j|\) denotes the distance between two particles.

A first attempt to formulate the hydrodynamic equations can now be done. A straightforward formulation of the Euler equation would then be given by

\[
\frac{d\mathbf{v}_i}{dt} = -\frac{1}{\rho_i} \sum_j m_j \frac{P_j}{\rho_j} \nabla^r_i W_{ij}(h), \quad (3.14)
\]

where for the reason of simplification, the abbreviations \(W_{ij}(h) := W(|r_i - r_j|, h)\) and \(\nabla^r_i := \nabla_{r_i}\) are introduced. However, the conservation of momentum is violated by this expression. This can easily be checked by comparison of the force terms \(F_{a,b}\) that act between two particles \(a\) and \(b\), whereby generally \(P_a \neq P_b\) and therefore the particle do not fulfill Newton’s third law \(F_{ab} \neq -F_{ba}\) [29].

This lack of conservation can be handled by mathematical considerations, where the main idea lies in forming symmetric interaction terms. It can be seen from the hydrodynamic equations (2.25), (2.34) and (2.40) that spatial derivatives mostly
appear within a product or fraction with a scalar quantity $\phi$, e.g. the density $\rho$. Due to this finding, one can make use of the two identities

$$\nabla A = A \nabla \phi + A \frac{\partial A}{\partial \phi},$$  \hspace{1cm} (3.15)

which turns out to be very useful especially for pressure term, and

$$\phi \nabla A = \nabla (\phi A) - A \nabla \phi$$  \hspace{1cm} (3.16)

that can be used for the velocity divergence. Both identities provide the possibility to obtain a symmetric SPH formalism and ensure, that every sum term in the sum of particle $a$ concerning a particle $b$ also appears in the sum for this certain particle itself.

Applying Eq. (3.6) to the identities (3.15) and (3.16) gives

$$\nabla_i A_i = \sum_j m_j \rho_j \left[ \frac{\phi_j}{\phi_i} A_i + \frac{\phi_i}{\phi_j} A_j \right] \nabla_i W_{ij}(h),$$  \hspace{1cm} (3.17)

and

$$\nabla_i A_i = \sum_j m_j \frac{\phi_j}{\phi_i} [A_j - A_i] \nabla_i W_{ij}(h).$$  \hspace{1cm} (3.18)

The latter can then be used to obtain the continuity equation (2.25) for SPH by

$$\frac{d\rho_i}{dt} = \frac{1}{\rho_i} \sum_j m_j v_{ij} \nabla_i W_{ij}(h),$$  \hspace{1cm} (3.19)

where $v_{ij} := v_i - v_j$ is used. However, this equation is not being solved and becomes replaced by the common practice of directly estimating the density with Eq. (3.13). Thus, the density at the position of a particle $i$ is given by

$$\rho_i = \sum_j m_j W_{ij}(h).$$  \hspace{1cm} (3.20)

Two reasons are mainly responsible for this choice. On the one hand, the results only slightly differ, whereby the summation by Eq. (3.20) is computationally less expensive. Furthermore, this method is numerically more robust, whereas calculating the time rate of change would generally allow for negative density values. This can happen in regions of extremely low densities and thus only very few particles [29]. The second reason is, that mass is always exactly conserved, when the kernel becomes normalized, and if the masses of the particle are kept constant. However, the considerations concerning Eq. (3.19) are not for nothing, since it can be used for the derivation of the work term of the energy equation (2.40),

$$\frac{d u_i}{dt} = \sum_j m_j \frac{P_i}{\rho_i^2} v_{ij} \nabla_i W_{ij}(h)$$  \hspace{1cm} (3.21)

2Note that both expressions are also true when $A$ is a vector field $\mathbf{A}$. 

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Eventually, applying Eq. (3.15) to the momentum equation by setting $A \rightarrow P$ and $\phi \rightarrow \rho$, yields the SPH equations of motion, yet at a constant smoothing length $h$,

$$\frac{dv_i}{dt} = - \sum_j m_j \left[ \frac{P_i}{\rho_i^2} + \frac{P_j}{\rho_j^2} \right] \nabla_i W_{ij}(h), \quad (3.22)$$

which has become the so called “Standard SPH” originally proposed in Ref. [44]. As it can now easily be seen, linear momentum is exactly conserved by this symmetric representation. Moreover, also angular momentum is conserved as shown in Ref. [12].

### 3.1.4 Smoothing function

Although the kernel has often been mentioned in the previous sections, the actual form of such a kernel has not been further specified and only was referred to this section. It has been strictly emphasized that the outcome of the simulations strongly depend on a proper choice of kernel and its properties. The following lists give a summary of such requirements [45]. The requirements on the properties of a kernel can be differentiated. These are on the one hand, numerical and general mathematical properties, e.g. aspects concerning the stability of the interpolation. Therefore, the function should be

- monotonic,
- symmetric,
- normalized,
- twice continuously differentiable,
- converges in the limit to the $\delta$-distribution: $W \rightarrow \delta$ for $h \rightarrow 0$,

The further requirements are those, satisfying computational and physical demands, e.g. to keep the computational effort as low as possible. From these, a “good” kernel should be

- Gaussian-bell shaped curve - actually this is only a desirable feature from the physical point of view, and not necessarily required, since many other functions yield in the delta distribution.
- a good density estimator,
- $W$ and $\nabla W$ computationally inexpensive,
- stable against pairing.

Many of these properties have already been pointed out in the respective contexts in the sections above, but further problems arise, when considering temporally evolving systems, such as the pairing instability. This is a phenomenon, where particles clump together due to vanishing repulsive net force, when approaching

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3The whole set of hydrodynamic equations with the use of a constant smoothing length $h$ is sometimes also referred to as the “vanilla ice” SPH [29].
each other. The occurrence can be directly attributed to a bad choice kernel whereby the smoothing length was chosen too large. However, there are kernels completely avoiding this problem, independently from smoothing length.

The lists give only an actual view on the demands without the claim to completeness. Moreover, some issues on the lists even overlap, such as that a good density estimation always implies the monotonicity and the $h$-limit in a $\delta$-distribution. Nevertheless, so far, a kernel that adequately satisfies all of these conditions, is still not found, even though some good candidates exist. Thereby, it is much easier, to comply the items on the first list then those of the second list, which is mostly because of that the former requirements are stricter expressions. In the past decades many kernels have been suggested but only few have actually been established.

One important issue should be mentioned before giving any example of a kernel. That is the confusion in common literature between smoothing length $h$ and the radius of a kernels support $H$. Typically kernels are chosen to have compact support, i.e. $W(r, h) = 0$ if $r > H$, since it is computationally more efficient. Note that in this regard the already mentioned normal Gaussian distribution would be a bad choice of kernel. For a given kernel the dependency is given by $H = C \cdot h$ for a kernel dependent constant factor $C$ [45]. The kernel function $W(r, h)$ can be expressed in two ways. It can be given either in terms of the real smoothing length $h$ by the use of a function $\tilde{w}(r/h)$,

$$W(r, h) = \frac{1}{h^{\nu}} \tilde{w}(|r|/h), \quad (3.23)$$

where $\nu$ is the number of spatial dimensions. However, the compact support radius $H$ and, therewith associated, the number of neighbors $N_H$ must also be calculated for actual SPH summation. Another possibility is to directly formulate the kernel in terms of $H$,

$$W(r, h) = \frac{1}{H^{\nu}} w(|r|/H) \quad (3.24)$$

by a normalized function $w$ with $w(q) = 0$ if $q > 1$, which is indeed much more efficient. The smoothing length is typically defined by $h := 2\sigma$, where $\sigma$ is the standard deviation of the kernel. Thus, it expresses a quantity for the resolution and it is certainly best choice in the context of comparing several kernel functions. In contrast, the compact support radius $H$ is way more interesting from the computational point of view, since it is directly connected to the total number of neighbors $N_H$ involved to the summation. In practice, $N_H$ is used as a constant input parameter and $H_i$ of a particle $i$ can be estimated by

$$H_i = \left[ \frac{3}{4\pi} \frac{N_H \bar{m}}{\rho_i} \right]^{1/3}, \quad (3.25)$$

in three spatial dimensions, where $\bar{m}$ is the average particle mass and $\rho_i$ the estimated density of the actual particle. Due to the suitability for practicable
3.1 Smoothed particle hydrodynamics

implementation, the following kernels will be given in reduced variables in the sense of Eq. (3.24). Nevertheless, both descriptions are equivalent. However, apart from the actual functional form of the kernel, the formal description of the governing equations of SPH will be given in terms of $h$ in accordance to literature.

The probably most common choice is the cubic $B$-spline, which is implemented to many publicly available SPH codes. It bases on a 1D Fourier transform of the forth power of the sinc($\cdot$)-function. An elegant representation for these piecewise continuous cubic polynomials is given by

$$W_{b4}(q) = \frac{1}{H^3} \frac{16}{\pi} \left[ (1-q)^3_+ - 4 \left( \frac{1}{2} - q \right)^3_+ \right],$$

using the notation $(\cdot)_+ := \max(0, \cdot)$ and $q = |r|/H$. The factor $16/\pi$ is the normalization coefficient in three dimensions$^4$. The derivative of $W$ can be calculated analytically and is given by

$$\nabla W_{b4}(q) = \frac{1}{H^4} \frac{16}{\pi} \left[ -3(1-q)^2_+ + 12 \left( \frac{1}{2} - q \right)^2_+ \right].$$

The reason for the popularity of this kernel was the formerly recommended low number of neighbors, whereby an adequate density estimation could be obtained by the use of only 32 neighbors in 3D. Unfortunately, this kernel badly deal with the pairing instability. Thus, the actual choice of a kernel must be a balance between high performance of the algorithm and an adequate resolution.

At this point a little paradox occurs. On the one hand, the broader the kernel support and hence the increase of the number of neighbors, the better the estimation becomes, which is indeed highly desired. However, on the other hand, the larger the smoothing length gets, the lower the spatial resolution becomes. Thus, one can not simply enlarge $h$. Hence, the use of other kernels is obvious, which have the similar smoothing lengths but larger kernel support radius. Such kernels can be achieved by using larger power numbers in the derivation via sinc($\cdot$) in order to obtain, for instance, quartic or quintic kernels, although all of these kernels leave the problem of pairing instability unsolved.

It is exactly this pairing instability that is almost completely suppressed by the use of the so called Wendland functions [46, 45]. The recently often used Wendland $C_4$ has been shown to give a good balance between computational effort and very large kernel support. It is used, as it is computationally inexpensive, but has a very large kernel support radius.

$$W_{C4}(q) = \frac{1}{H^4} \frac{495}{32\pi} (1-q)^6_+ \left( 1 + 6q + \frac{35}{3} q^2 \right).$$

The derivative can then directly be calculated by

$$\nabla W_{C4}(q) = \frac{1}{H^4} \frac{495}{32\pi} \left[ \frac{280}{3} \left( 1-q \right)^5_+ - \frac{56}{3} q \left( 1-q \right)^5_+ \right].$$

$^4$The respective constants in 1D and 2D are $8/3$ and $8/(7\pi)$.
A detailed discussion about the benefits of the Wendland kernels can be found in Ref. [45]. Therein, a bias correction

$$\rho_{i,\text{corr}} = \rho_i - \epsilon m_i W(0, h_i)$$  \hspace{1cm} (3.30)

is introduced that further enhances the density estimation, where $\epsilon$ depends on the actually used kernel and spatial dimensions. For instance, in the case of a $C_4$ in three dimensions, the two parameters $(w_{100}, \alpha) = (0.01342, 1.579)$ define

$$\epsilon = \epsilon_{100} \left( \frac{N_H}{100} \right)^{-\alpha}. \hspace{1cm} (3.31)$$

Figure 3.2 shows a plot of the two herein introduced kernels and their derivatives. Both seem similar as they have the characteristic Gaussian bell shape, especially the outer region is found to be very similar, except for support radius, indicated by the arrows. A difference is found in the derivative curves at $q \approx 0$. The Wendland kernel has a more distinct minimum at a lower $q$ than the cubic spline, which can be seen as the descriptive explanation for the higher stability against the pairing problem, since $-\nabla P$, and therewith associated to $\nabla W$, is one of the driving forces for fluid flow. If two particles come closer, the force term vanishes. In the case of $b_4$, the phenomenon becomes apparent at a broader distance and with a lower net force term.

Note that both kernels must satisfy the normalization condition and therefore, in 3D a $r^2$ term appears in the integral, which affects only small contributions to the integral by the values $r \to 0$. 

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3.1 Smoothed particle hydrodynamics

3.1.5 Governing equations of SPH

The designation “Standard SPH” may be misinterpreted as to represent the state of the art, but so far this is only true for at least weakly compressible fluids, where the density deviations are small compared to the actual density. However, it leads to poor results when densities temporally evolve to higher or lower values. Thus, for lowering densities the number of neighbors used for the interpolation becomes also low, which leads to underestimation. Especially, for higher densities, a higher number of neighbors is the consequence, which on the one hand produces overhead. On the other hand, with increasing density, more and more distant particles contribute stronger-weighted than intended and desired to the SPH estimation. Moreover, a higher number of neighbors leads to a higher computational effort. In addition, the pairing instability may occur when distinct particles come close compared to the actual support radius, which reduces the resolution scale significantly. However, a better choice of kernel cannot fully comply this problem, and the kernel width \( h \) should be adjusted to the actual density, that is commonly fulfilled by a constant number of neighbors [47]. Note that the condition of constant neighbor number is not necessary, but it will be shown to be very effective in the following derivation.

For these reasons, “Standard SPH” is not the ultimate solution. The eventual formulation of SPH goes further, that is varying the resolution by the use of adaptive smoothing lengths, where a particular smoothing length \( h_i \) is assigned to each particle. Unfortunately, this is accompanied by the lost of conservation properties such as energy and momentum, which has been achieved by symmetrization.

The governing equations of SPH, now with respect to adaptive smoothing lengths \( h \), must be modified again [47]. To obtain the desired conservation properties it is straightforward to derive the equations of motion from a Lagrangian approach\(^6\). The starting point of this derivation is the hydrodynamic description of an inviscid ideal fluid by the continuum Lagrangian (see e.g. Ref. [48]).

\[
L = T - U = \int \rho \left[ \frac{v^2}{2} - u(\rho, s) \right] \, dr, \tag{3.32}
\]

which turns to the discrete form

\[
L = \sum_j m_j \left[ \frac{v_j^2}{2} - u_j \right]. \tag{3.33}
\]

Hamilton's principle of least action is used to derive the equations of motion, given by the so-called Euler-Lagrange equations

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{v}_i} - \frac{\partial L}{\partial v_i} = 0, \tag{3.34}
\]

\(^6\)It is also possible to derive the equations of motion from a Hamiltonian of the system. However, this is without the reference a continuum limit, as apparent for a Lagrangian.
where \( j \in \{1 \ldots N\} \), and therefore is a set of 3N equations in three spatial dimensions. Analytic differentiation of the Lagrangian with respect to \( \mathbf{r}_i \) gives the first summand
\[
\frac{d}{dt} \frac{\partial L}{\partial \mathbf{v}_i} = \frac{d}{dt} (m_i \mathbf{v}_i) = m_i \mathbf{a}_i, \tag{3.35}
\]
where \( m_i \) is assumed to be constant, and is the net force on a particle \( i \). The partial differentiation with respect to \( \mathbf{v} \) gives
\[
\frac{\partial L}{\partial \mathbf{r}_i} = - \sum_j m_j \frac{\partial u_j}{\partial \rho_j} \frac{\partial \rho_j}{\partial \mathbf{r}_i}. \tag{3.36}
\]
The first product term can be calculated from the first law of thermodynamics Eq. (2.38), giving
\[
\frac{\partial u_j}{\partial \rho_j} \bigg|_s = \frac{P_j}{\rho_j^2}. \tag{3.37}
\]
For the second term, it must be realized that \( \rho(h) \) is now a function of \( h \) and the derivative should then be expressed by
\[
\frac{\partial \rho_j}{\partial \mathbf{r}_i} = \frac{\partial \rho_j}{\partial \mathbf{r}_i} \bigg|_h + \frac{\partial \rho_j}{\partial h_j} \frac{\partial h_j}{\partial \mathbf{r}_i}, \tag{3.38}
\]
where the undesired chain rule term can be eliminated by exactly the assumption that the kernel volume should enclose a constant mass, given by Eq. (3.25). Using the derivative of this equation, the former equation can be expressed by
\[
\frac{\partial \rho_j}{\partial \mathbf{r}_i} = \left[ 1 + \frac{h_j}{3 \rho_j} \frac{\partial h_j}{\partial \mathbf{r}_i} \right]^{-1} \frac{\partial \rho_j}{\partial \mathbf{r}_i} \bigg|_h. \tag{3.39}
\]
So far, not a single SPH approximation has been used for the derivation. However, it is now involved with the use of the density sum (see Eq. (3.20)) for the density gradient estimation at constant \( h \)
\[
\frac{\partial \rho_j}{\partial \mathbf{r}_i} \bigg|_h = m_i \nabla_i W_{ij}(h_j) + \delta_{ij} \sum_k m_k \nabla_i W_{ki}(h_i). \tag{3.40}
\]
Combining the equations above to the Euler-Lagrange equations gives the final SPH expression for the momentum equation with full respect to adaptive smoothing lengths
\[
\frac{d \mathbf{v}_i}{dt} = - \sum_j m_j \left[ f_i P_i^2 \nabla_i W_{ij}(h_i) + f_j P_j^2 \nabla_i W_{ij}(h_j) \right], \tag{3.41}
\]
\(^7^7\)Note that this is only true under the assumption of constant specific entropy \( s \).
where the $f_i$ are the so called “grad-h” correction terms\(^8\) given by

$$f_i = \left[ 1 + \frac{h_i \partial \rho_i}{3 \rho_i \partial h_i} \right]^{-1}. \quad (3.42)$$

One of the advantages by this formulation is, that linear and angular momentum are intrinsically conserved by deriving the momentum equation from the Lagrangian (see e.g. [12]). Note that the derivation from a Lagrangian has solely made use of the density approximation (3.20) and, for instance, did not state the Euler equation. This fact is also true for the energy equation (2.38), which has already been used for the derivation above. The first law of thermodynamics can be formed in an analogous way, determining the time derivative of the density sum with taking the chain rule and the $\rho(h)$-relation into account. The internal energy evolution equation is eventually given by

$$\frac{du_i}{dt} = f_i \frac{P_i}{\rho_i^2} \sum_j m_j (v_i - v_j) \cdot \nabla_i W_{ij}(h_i). \quad (3.43)$$

Note that it is completely equivalent to express the energy evolution equation in terms of the specific total energy $\epsilon$ shown in Eq. (2.42). It can be derived by a Legendre transformation of the Lagrangian, which is the Hamiltonian of the system and thus describes the total energy of the system. The time derivative is

$$\frac{d\epsilon_i}{dt} = m_i \left[ v_i \frac{dv_i}{dt} + \frac{du_i}{dt} \right], \quad (3.44)$$

which is in SPH formalism

$$\frac{d\epsilon_i}{dt} = -\sum_j m_j \left[ f_i \frac{P_i}{\rho_i^2} v_i \cdot \nabla_i W_{ij}(h_i) + f_j \frac{P_j}{\rho_j^2} v_j \cdot \nabla_i W_{ij}(h_j) \right]. \quad (3.45)$$

This completes the derivation from the Lagrangian function, whereby the basic set of governing equations is given by the equations (3.20), (3.41), and (3.43). Further extensions, to yield more physical realistic systems, such as the consideration of viscosity or thermal conductivity will be discussed in the following.

### 3.1.6 Dissipative effects

The basic hydrodynamic equations only describe non-dissipative non-conducting ideal fluids. However, as always, by increasing the complexity of a system the equations become more complex too, wherefore the basic equations need to be extended by taking irreversible processes into account, including transport phenomena such as shear and bulk viscosity or heat transfer.

---

\(^8\)Note that in the literature the term is sometimes also defined by the reciprocal $\Omega_i := 1/f_i$ [29, 12].
For a given functional relation $\kappa_i := \kappa(\rho_i)$, the thermal conduction equation, as shown in the energy equation (2.40), can be used to describe thermal exchange among particles. Using the equations (3.11) and (3.12) for a SPH discretization, thermal conduction is given by

$$\left( \frac{du_i}{dt} \right)_{\text{cond}} = \sum_j m_j \frac{2\kappa_i\kappa_j}{\rho_i\rho_j} \frac{r_{ij}}{|r_{ij}|^2} \cdot \nabla_i W_{ij}
$$

(3.46)

where $W_{ij} = 1/2(W_{ij}(h_i) + W_{ij}(h_j))$ is the arithmetic mean of the two kernel values [43, 42]. Thus, thermal conductivity only requires to adapt the energy equation.

Viscosity, where kinetic energy irreversibly transforms into internal energy, needs to be included to both the momentum and the energy equation. As can be seen from Eq. (2.31), only the spatial derivatives of the velocity components need to be calculated, of which the SPH approximations are given by

$$\frac{\partial v_\alpha}{\partial r_\beta} |_{i} = \frac{1}{\rho_i} \sum_j m_j v_{ij}^{\alpha} r_{ij}^{\beta} \frac{\nabla_i W_{ij}(h_i)}{|r_{ij}|},
$$

(3.47)

where $r_{ij}^{\alpha} := r_i^{\alpha} - r_j^{\alpha}$ is the component $\alpha \in \{1, 2, 3\}$ of $r_{ij}$, and the $v_{ij}^{\alpha} := v_i^{\alpha} - v_j^{\alpha}$ denotes the therewith related velocity difference of the component $\alpha$ between the particles $i$ and $j$. Using the stress in tensor notation $\sigma_i^{\alpha\beta}$ together with Eq. (2.31), viscosity contributes to component $\alpha$ of the momentum equation with

$$\left( \frac{du_i}{dt} \right)_{\text{visc}} = \frac{\eta}{2\rho_i} \left[ \frac{\partial v_\alpha}{\partial r_\beta} |_{i} + \frac{\partial v_\beta}{\partial r_\alpha} |_{i} - \frac{2}{3} \delta_\alpha_\beta \frac{\partial v_\gamma}{\partial r_\gamma} |_{i} \right]^2 + \frac{\zeta}{\rho_i} (\nabla \cdot \mathbf{v})_i^2,
$$

(3.49)

where $\sigma_i^{\alpha\beta} r_{ij}^{\beta} := \sum_{\beta=1}^{3} \sigma_i^{\alpha\beta} r_{ij}^{\beta}$ using the summation convention. Somewhat easier to compute is the rate of change of the internal energy. Using Eq. (2.41) the corresponding entropy production rate can be calculated by

$$\left( \frac{du_i}{dt} \right)_{\text{visc}} = \frac{f_i}{\rho_i^2} \sum_{j=1}^{m} m_j \sigma_i^{\alpha\beta} v_{ij}^{\alpha} r_{ij}^{\beta} \frac{\nabla_i W_{ij}(h_i)}{|r_{ij}|}.
$$

(3.50)

It is obvious that viscosity and thermal conduction are phenomena that only need to be implemented if they are expected to affect the dynamics of the considered system. This must always be declared before the simulating. For instance, viscosity may be negligible, when viscous accelerations are small compared to the pressure gradient contribution to the acceleration, or thermal conduction can be neglected when the system is anyway only weakly conducting or, at least, isothermal.
3.1 Smoothed particle hydrodynamics

3.1.7 Artificial dissipation

Irrespective of whether the considered phase space volume of the modeled fluid is in the relevant regimes for thermal conduction or viscosity, the SPH method exhibits inaccuracies in handling discontinuities in the hydrodynamic variables. This becomes obvious regarding the derivation from the Lagrangian function (see Sec. 3.1.5). It is based on the assumption that \( L \) is differentiable and hence must be a continuous function, which means that it is not able to adequately treat contact discontinuities, such as shocks or large temperature differences. For this purpose, artificial dissipative terms need to be introduced to the SPH method, smoothing discontinuities out to a resolvable scale [12].

To see this explicitly, a “Sod shocktube” (which is actually fluid in rest with a large jump in density in one spatial direction, in this case by a factor of 8.) [51] may be considered. It is an excellent standard test case for the SPH method [12, 28], which reveals most of the undesired features of SPH, such as noise production in the velocity profile and unwanted large jumps in internal energy. A more general description is given by the so called Riemann problem, which can be solved analytically for any arbitrary configuration of hydrodynamic variables by so called Riemann solvers [52].

It is due to the technical nature of these problems that they arise from numerical inaccuracies and that they have no definite solution. As always in SPH, there is some degree of freedom for the eventual formulation. One obvious possibility is to formulate an artificial viscosity (AV) term inspired by a Riemann solver [53], which will be presented here since it was used for simulation in this work [54]. Besides, it has established as the standard form of AV. For detailed descriptions on more advanced formulations of AV, being more accurate and effective, see e.g. Refs. [53, 55, 12]. However, they are only mentioned here for the sake of completeness, since these advanced AV methods are not being used in this thesis.

The standard form of AV is very similar to a real bulk viscosity term, that dissipates kinetic energy from compression into heat to prevent interpenetration of particles. Thus, it shall only appear in the presence of a shock, or more precise, when two particle \( i \) and \( j \) approach each other, which means \( \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} < 0 \). The corresponding AV term between the two particles is then given by

\[
\Pi_{ij} = \begin{cases} 
-\alpha_{av} \frac{\mathbf{v}_{ij} \cdot \mathbf{r}_{ij}}{2\rho_{ij}}, & \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} < 0 \\
0, & \mathbf{v}_{ij} \cdot \mathbf{r}_{ij} \geq 0
\end{cases}
\]  

(3.51)

where \( \mathbf{v}_{ij}^{sig} = c_i + c_j - \mathbf{v}_{ij} \cdot \mathbf{r}_{ij}/|\mathbf{r}_{ij}| \) is the local signal velocity between the particles \( i \) and \( j \), and \( c_i \) is the speed of sound of particle \( i \) that is given by \( \sqrt{\partial P_i/\partial \rho_i} \) which follows from the actual equation of state. The \( \overline{\rho}_{ij} \) denotes the arithmetic average. In this representation the artificial viscosity coefficient \( \alpha_{av} \) is a constant parameter typically between [0, 1]. More advanced representations are using time and particle dependent viscosity coefficients controlled by a differential equation. However, note that the AV term already includes the antisymmetry in \( i \) and \( j \),
which is indicated by the index $ij$. Despite this, it has a form similar to that of the bulk viscosity tensor, but using $v_{ij} \cdot r_{ij}$ instead of $\nabla \cdot v_i$. This means, it has only diagonal entries and can be treated similar to the scalar pressure term. Thus, the contribution to the momentum equations is, in analogy to Eq. (3.48), given by

$$ \frac{dv_i}{dt} \bigg|_{av} = - \sum_j m_j \Pi_{ij} \nabla_i W_{ij}, \quad (3.52) $$

where $W_{ij} = (W_{ij}(h_i) + W_{ij}(h_j))/2$. The corresponding heat production rate that arises from AV is also similar to that of the physical viscosity in Eq. (3.50) and given by

$$ \frac{du_i}{dt} \bigg|_{av} = \frac{1}{2} \sum_j m_j \Pi_{ij} v_{ij} \cdot \nabla_i W_{ij}. \quad (3.53) $$

Although this method is strongly recommended to apply to compressional fluid motion, spurious unexpected forces occur in shear flows [29]. Therefore, it is necessary to significantly reduce the AV in undesired regions, where one possible way is multiplication of $\Pi_{ij}$ with the factor $f_{ij} = (f_i + f_j)/2$, which is the so called “Balsara-switch” [56]. The factors $f_i$ are given by

$$ f_i = \frac{|\nabla \cdot v_i|}{|\nabla \cdot v_i| + |\nabla \times v_i| + \varepsilon_i}, \quad (3.54) $$

where $\varepsilon_i = 10^{-4} c_i / h_i \ll 1$ is due to numerical reasons, preventing a singularity. In this formulation the switch reasonably suppresses artificial viscosity in regions of pure shear whereas the factor $f_i \approx 1$ in the absence of shear flow.

The AV term produces heat from kinetic energy. However, it is also possible that discontinuities occur only across internal energy, which can not be smoothed by the AV procedure. For this purpose, an artificial conduction (AC) term can be constructed in analogy to the physical thermal conduction Eq. (3.46) (see e.g. Ref. [57]) that is given by

$$ \frac{du_i}{dt} \bigg|_{ac} = \sum_j m_j \alpha_{ac} \tilde{v}_{sig}^{ij} \rho_{ij} (u_i - u_j) r_{ij} \cdot \nabla_i W_{ij} |r_{ij}|, \quad (3.55) $$

where $\alpha_{ac} \in [0, 1]$ is the artificial conduction coefficient in analogy to a constant thermal conductivity. However, in contrast to Eq. (3.46) the internal energy $u$ is used directly instead of the temperature $T$.

### 3.1.8 Equations of state

There is one important key issue that has not been mentioned so far, although it has serious impact on the outcome of a simulation. That is the pressure calculation and, if heat transfer is also considered, also the temperature. As discussed in Sec. 2.1.2, both are given by the so called equations of state (EOS), where
the most suitable EOS must be chosen individually as the case arises depending on the actual system under consideration. Incidentally, the sound speed is also derived from the EOS, since it can be calculated by $\sqrt{\partial P/\partial \rho}$. However, even in review articles, a discussion of the topic is often missed out or, at least, only minimally discussed. Although, the importance for hydrodynamics is obvious and it is mainly controlling thermodynamic aspects. This is in particular true for complex fluids, such as in phase separating fluids. One possible reason may stem from the fact that for most astrophysical purposes the ideal gas EOS is a reasonably good approximation, for why alternatives may be considered as less important to discuss. Applying Eq. (2.5) to SPH yields

$$P_i = (\gamma - 1)u_i \cdot \rho_i$$

(3.56)

for a particle $i$, where $\gamma = (f + 2)/f = C_P/C_V$ is the adiabatic index of the actual gaseous system. If the system under consideration is a liquid, pressure should increase at least with $\rho^2$. Thus, the EOS should be replaced by another that better reproduces this dependency. One common EOS for the simulation of liquids is the so called Tait equation (see e.g. Ref. [58]),

$$P_i = \rho_0 c_i^{\gamma'} \left[ \left( \frac{\rho_i}{\rho_0} \right)^{\gamma'} - 1 \right] + P_0,$$

(3.57)

where $c_i$ is the sound speed. Pressure always pushes the system back to a beforehand predicted normal pressure $P_0$, which is due to the increase of pressure as the density deviates from the reference density $\rho_0$. The strength is controlled by an exponent $\gamma'$, which is a numerical parameter and must not to be confused with the adiabatic index. Typical choices are $\gamma' \in \{2, 7\}$. However, this is only an empirically determined equation to fit experimental data of water, that is not based on a phenomenological approach, such as the ideal gas EOS. Moreover, it is just an isothermal EOS.

One EOS that is based on clear and simple physical assumptions (for a detailed discussion see Sec. 2.1.2), is the van der Waals equation of state (vdW-EOS). It can be understood to combine the linear ideal gas approach with a higher order density dependency as in the Tait equation. As it is also based on a phenomenological approach is is an excellent choice for the simulation of liquid-vapor phase transitions. The vdW-EOS are described in detail in Sec. 2.1.2 and given by the two EOS (2.7) and (2.9). They read, applied to a particle $i$, as

$$P_i = \frac{\rho_i k_B T_i}{1 - \rho_i b} - \sigma \rho_i^2,$$

(3.58)

and

$$u_i = \frac{k_B T_i}{\gamma - 1} - \sigma \rho_i,$$

(3.59)
where $\gamma$ is the adiabatic index and $\bar{k}_B = k_B/\mu m_p$, with $k_B$ the Boltzmann constant, $\mu$ the mean molecular weight and $m_p$ the proton mass, and $\bar{a}$, $\bar{b}$ are cohesive pressure and covolume, respectively, given in specific units (see Sec. 2.1.2).

As already mentioned, it is due to the second term in Eq. (3.58) that a negative pressure can occur in a distinct density interval. From a classical point of view, there is no explanation for this behavior, e.g. this should never happen for an ideal gas. However, in the context of SPH this is a well known outstanding problem\(^9\), with a need to comply with artificial numerically controlled conditions. Nevertheless, in the context of phase separation, especially regarding the dynamic evolution of phase transitions, it even seems to be intended in order to obtain an unstable region with negative pressures below the spinodal curve, just as in the vdW theory. Therefore, in this context there is no need to suppress negative pressures, but rather simply initiating the phase separation process.

---

\(^9\)See Ref. [12] for a more detailed discussion on this, so called, tensile instability, which concerns the appearance of negative pressures in SPH. This must not be confused with the pairing instability, which concerns choosing the right smoothing length to prevent particle clumping, as discussed in Sec. 3.1.7.
3.2 Multiphase flows and spinodal decomposition with SPH

Nowadays, the SPH method has a broad range of applications in a variety of fields in fluid mechanics, but originally, the method has been developed for astrophysical purposes [13, 30]. It has been used for star formation, formation of galaxies, merging of galaxies, or structure formation on cosmic scales [28], and there is still ongoing development in this field [59]. Beside this branch, other fields of application comprise the treatment of incompressible flows, and the treatment of free surfaces that can be used for investigations on the breakdown of waves, which is focused on in the context of tsunami prediction [39]. An issue that is closely related to free surface flows, is the question on the correct treatment of rigid bodies, which can be used for simulations of colloidal suspensions or fluid flow through porous media. Therewith related is the more general question about the correct treatment of boundary conditions and interfaces by the SPH method.

Progress has also been made in the context of multiphase systems (for a detailed overview, see e.g. Ref. [60]). Two promising approaches have been established yet. One possibility is given by modeling a one-component systems in SPH, using the vdW-EOS (herein referred to as vdW-SPH). It has first been introduced by Nugent and Posch [31] to simulate nucleation processes in two dimensions, where condensation of single liquid droplets and the dynamics of elongated liquid droplets in a vapor medium were studied, where the main focus was on correctly reproducing surface tension effects. Further studies based on the vdW-SPH approach followed, only slightly modifying the basic ideas. The main questions mostly comprised the formation and deformation of single droplets, and the coalescence behavior of multiple droplets. These early studies were only in two-dimensions and at relatively low resolution (of the order $N \lesssim 10^5$) [32, 33, 34, 35, 37, 36], but have recently also been applied to three dimensional systems [61, 62, 63]. However, the resolutions of these studies were still relatively low.

The alternative approach for modeling multiphase systems is based on the idea of introducing an additional state variable, namely a so called color function. In the context of incompressible binary mixtures this could be the concentration in the mixture (see e.g. [64, 60]). A drawback of this formulation is that, if surface tension is indicated to consider, it is necessary to include an additional force-term to implement surface tension correctly. On the basis of the color function, an interface normal vector and an interface width can be extracted, which can be used to calculate the additional surface tension force term [65]. However, the physically more convenient approach is that the surface tension directly arises from the EOS, which is the phenomenological straight forward derivation. Thus, color function approach is more often used for engineering applications than for real physical issues, since it adequately handles already separated phases, but does

\[^{10}\]Strictly incompressible flows are hard to obtain and often realized by a weakly compressible flow, such as obtained by using the Tait EOS (3.57)
not consider the beforehand occurring separation process itself.

Using the vdW-SPH approach brings some benefits, especially in the context of the dynamics of a vapor-liquid transition. The explicit tracking of an interface, which would be needed by the color function approach, is computationally expensive. Moreover, the application of a color function to a compressible-incompressible two-phase separating fluid is non-trivial, whereas it is an intrinsic feature of the vdW-SPH method. The diffuse-interface width depends on the actual depth of the temperature quench and follows from the EOS, thus diffuse interfaces also form intrinsically by the vdW-SPH method.

However, in the first attempt by Nugent and Posch, the authors suggested to treat long range and short range forces separately with different interaction ranges, which means different smoothing lengths. They recommended to choose a smoothing length $H = 2h$ for the long range force term $-\pi\rho^2$. This procedure was necessary, in order to obtain stable droplets. It has become common practice in all works that based on this vdW approach, although from a methodological point of view, there is absolutely no explanation for this procedure. Moreover, due to this differentiation, a pairing instability may occur due to the large values of $H$ by the use of classical kernels such as the $B$-spline, as discussed in Sec. 3.1.4. A solution is found to be in the use of Wendland kernels (see Eq. (3.28)). These kernels provide a very large support anyway. Thus, a differentiation in long and short range force terms is obsolete.

The method has yet only been applied to already separated individual droplets, which is mainly a simplified nucleation process. It must be addressed to the relative low particle numbers that have been used. However, a larger particle number and thus a higher resolution allows for application to more complex issues such as the dynamics of spinodal decomposition or condensation and evaporation, which has not been done so far. Thus, new analysis methods and modifications on SPH must be explored, whereby it is found that the SPH method brings some benefits which can be made use of. Both will be described in the following.

### 3.2.1 Analysis of domain size and morphology

One of the advantages of SPH in the context of multiphase systems, especially for spinodal decomposition, is that averages of field quantities can easily be calculated by summing over the individual particle quantities. This summation procedure allows, for instance, to show the detailed time evolution of the separated phases in a phase diagram as given in Fig. 2.1.

It is irrespective of the actual system, whether vapor-liquid or binary mixture is considered, that the final volume fraction between the phases of the equilibrated system always strongly depends on the initial quench conditions (namely the initial density $\rho_0$ in a one component fluid or the concentration in case of a mixture). Therefore, it is in fact meaningful to distinct between the phases from the very beginning of separation. An exception is only given for the critical quench in spinodal decomposing binary mixtures (two incompressible liquids), where it is
due to the very similar physical quantities, such as density, conductivity, and compressibility, that the evolution in the phase diagram can be expected to be symmetric to the critical concentration axis. A common method, that is well established for spinodal decomposition in binary mixtures, is the analysis via the structure factor [8], where the mean domain size can be extracted from its first moment. This is indeed an acceptable method when the density of the phases is roughly equal and the concentration of two liquid species is considered as the order parameter. However, even slight deviations from the critical concentration in the initial concentration change the growth rates significantly [26]. Thus, in a liquid-vapor system, it is even more strongly recommended to treat the two phases separately. This is particularly true when using the vdW-EOS (3.58), where the particle temperature react to a change in density by Eq. (3.59). Thus, due to a compression or expansion, the phase temperature will increase or decrease, respectively.

The actual threshold density value that is used for the particle assignment to a certain phase is freely definable. Typically, the critical density $\rho_c$ is chosen to distinguish between the phases, but also the initial quench density $\rho_0$ could be a plausible choice. Note, that the use of several varying thresholds can be used for a morphological analysis, based on so called Minkowski functionals [66, 67, 68, 69]. However, it is not only the threshold that is freely definable, but also the type of averaging a quantity. Plausible choices of mean are the geometric, the harmonic or the arithmetic mean, but also the mode\(^{11}\) or the median\(^{12}\) can be used. The best choice always depends on the actually considered system. It can be evaluated from the density distribution in a histogram. In view of separating phases, and possible broad diffuse interfaces, the density distribution may not be necessarily given by two distinct density peaks for the two phases (in this case the mode would be an appropriate choice), but connected with intermediate densities that form the diffuse interface. Furthermore, in the initial stage of demixing with increasing density fluctuations (even before the second phase is actually formed), the density distribution initially morphs from a symmetric bell-shaped function to a skew function. For a skew distribution, the mode is an inconvenient choice. It turns out that the most stable choice of mean is the median, as it gives best results in all stages and for all quench depths. Therefore, in this work the densities $\rho_{l,v}$ always mean the median of the respective phase.

Using a fixed threshold parameter can additionally be used to calculate phase-related characteristic lengths $\xi_{l,v}$, since they must be considered again to differ in the phases. The quenched system instantaneously initiates to separate in the two phases. A quantity of interest is how the domain sizes evolve in time and expresses the extent of decomposition. The scaling behavior of this quantity can then be assigned to certain growth regimes, such as the hydrodynamic or a diffusion driven

\(^{11}\)In statistics the mode is defined as the maximum value of a density distribution
\(^{12}\)The median separates the higher half of the lower half of a density distribution, and can easily be calculated by a sorting routine or from a histogram
regime. The regimes are discussed in more detail in Sec. 2.1.3. As the characteristic lengths shall be considered separately for each phase, it is a proximate ansatz for the SPH particles to use the same threshold density value from above, which is usually the critical density \( \rho_c = \frac{2}{3} \), in order to obtain liquid and vapor particles, \( i_l \) and \( i_v \), respectively. The mean of the minimum distances to the opposing phase is used to define the characteristic lengths that belong to the certain phases. By this definition the procedure captures not only simple geometries but any arbitrary complex shapes of the domains, such as “sponge”-like structures.

As an example, the characteristic length \( \xi_l \) for the liquid phase is defined by

\[
\xi_l(t) = \frac{1}{N_l} \sum_{i_l} \frac{N_v}{N_l} \min_{i_v} |r_{i_l}(t) - r_{i_v}(t)|, \tag{3.60}
\]

where \( N_l \) is the total number of liquid particles. The characteristic length for the vapor phase can be calculated in an analogous way. Fig. 3.3 illustrates this procedure of finding the nearest particle of the opposite phase for a single liquid droplet for some example particles. Note that the characteristic lengths obtained from this definition leads to smaller values than those from conventional methods, such as structure factor. For example, a spherical liquid droplet in a vapor medium had only a length of 1/4 of its diameter. Nevertheless, the growth rates are not affected by this fact and it is only a linear effect and the analysis results are found to be in excellent agreement with theoretical predictions on the scaling regimes and the corresponding growth laws (see Eq. (2.18)).

It is obvious that the characteristic lengths do not provide all information that
can be extracted concerning the domains of the system. This is firstly due to the fact that the $\xi$ is only formed by averaging the size of one of the phases and secondly, the average process itself reduces the content of information. Thus, a statement on the effective structure is not possible. Moreover, even if $\xi_l$ and $\xi_v$ are directly compared, it is not even possible to decide which of the two phases is the dominant one, i.e. to define a major and a minor phase. This can be seen by the simple example shown in Fig. 3.4, considering a volume that is divided and separated in a number of smaller sub-volumes. The total volume remains constant, whereas the characteristic length of one phase becomes smaller. Besides, the prediction of minor and major phase defines the apparent demixing process, whether to speak of boiling of bubbles in a liquid solvent, or of condensation of droplets in a vapor environment. In turn, the initial quench configuration predicts the dominant process in the further evolution. Moreover, this knowledge is needed to define the relevant phase of which examining the growth behavior is most meaningful. Therefore, another essential quantity is needed to express a proportion between the phases. From this viewpoint, the volume fraction between the phases would be a proper quantity of interest. However, the total volume of a phase is hard to predict in SPH, whereas the masses are easily accessible. In a combination with the respective density values, masses can alternatively be used as an expression for the volume. For this reason the mass fraction is chosen in this work. It is defined per phase by the ratio

$$\mu_i = \frac{M_i}{M_{\text{tot}}}$$

for the liquid phase, where $M_l = \sum_{i_l} N_{l_i} m_{i_l}$ is the total mass of the liquid phase, and $M_{\text{tot}}$ is the overall total mass of all SPH particles.

Using the mass fraction has a great advantage compared to the volume fraction, since it enables to make statements about mass exchange between the phases through diffuse interfaces. This is of principle interest in the early stage of demixing. Due to large temperature deviations among the phases, mass transfer can be addressed to convective heat transfer. However, once separated, the mass fraction is not expected to change in the late stage.
3.2.2 Heat bath coupling

It is the formal framework of thermodynamics that provides the possibility of coupling to a certain heat bath. It is given by the first law of thermodynamics, where thermal heat exchange $\delta Q$ is provided by Eq. (2.37). It allows for controlling both the initial temperature quench and the equilibration during the demixing process. In SPH, as described in Sec. 3.1.6, it is not necessary to treat simulations adiabatic (where $\delta Q = 0$), but also to model on this basis a heat exchange between the particles. Moreover, thermal exchange with an external heat source is also feasible. These so called thermostats are common methods to treat temperature realistic in microscopic simulation methods, such as they are used by molecular dynamics (MD) or Monte Carlo [70]. The transfer of thermostats from MD to SPH is obvious, since both methods are very similar [71].

Fig. 2.1 gives a schematic representation of the evolution in the phase diagram of spinodal decomposition following a certain temperature quench. The stage of decomposition in this figure is shown isothermally, which is in accordance with available theoretical predictions (for example the well-known Cahn-Hilliard equation). However, in general, this is a non-isothermal process and can not withstand a comparison with real phase separating fluids, where temperature locally deviates from the mean system temperature. Thus, for this purpose hydrodynamics must be taken into account. Moreover, considering the vdW-SPH method, it can be seen from Eq. (3.59) that the particle temperatures are expected to increase or decrease with the respective density deviation. It can be declared as cooling and heating that is due to expansion and compression of the fluid, respectively. Thus, depending on the actual initial quench conditions and the corresponding mass fraction, the equation is an explanation for the release of latent heat, if the initial density is chosen large enough. Note that the contrary decreasing mean temperature can hardly be realized for a liquid-vapor system. This is because of the initial density that is needed to be chosen at a very low value in order to obtain an adequate mass fraction, whereby it would transit the spinodal curve and enter the classical nucleation regime. Thus, no spinodal decomposition will be observed.

Release of latent heat needs to be compensated for a comparison with theoretical predictions. Note that the original SPH method, as described above, conserves total energy, where an increase of kinetic energy of the fluid is accompanied with a loss of total internal energy and vice versa. This is a direct consequence of the hydrodynamic equations. Moreover, taking artificial dissipation and thermal conductivity into account, where the dynamic process becomes irreversible, conservation of total energy is still given. This immediately changes when a thermostat is applied for the temperature tuning.

In the following the two realizations of thermostats that have been used for this work will be described. The first thermostat instantaneously scales the mean temperature to a predicted value. This type of thermostat can be used to explain the domain growth behavior of pure non-isothermal systems where the temperature increases during decomposition. This can be done by assigning the growth rates
obtained at different quench depths to certain regimes in the pure thermal system. The second is the time-scale thermostat, where each local particle temperature exponentially decays to the beforehand predicted temperature at a prescribed time scale. By varying the time scale, this is a model for the strength of coupling to an external heat bath. The time-scale thermostat is used to describe a transition from weak to strong coupling between the limits of pure thermal simulations and instantaneously temperature scaled systems.

Scaling thermostat

As already mentioned, it is due to the caloric vdW-EOS (3.59) that the mean temperature $T$ of the system may increase during the phase separation process. If the focus of interest is on the evolution of these separated phases, it might be desirable to keep $T$ at a constant desired value $T_0$. One way would be to keep all particle temperatures $T_i$ fixed at $T_0$, which would generate an isothermal process, but could not preserve thermal fluctuations within the dynamical system. The two remaining possibilities are either shifting or scaling the mean temperature to the desired value. The former is not recommended because particle temperatures below $T$ can become negative. Hence, the temperature scaling approach is implemented in the following way. The new particle temperatures $\tilde{T}_i$ are given by

$$\tilde{T}_i = T_i \cdot \frac{T_0}{\bar{T}}. $$

This procedure will be herein further on referred to as the scaling thermostat. It should be noticed that in molecular dynamics (MD), thermostat methods, especially the velocity rescaling method, are used in a very similar way to realize a constant temperature ensemble \[70\].

Actually, the SPH method in its simplest non-adaptive formulation is closely related to MD \[71\]. The velocity rescaling method for MD does not reflect the proper physical properties of a canonical ensemble and must be extended to more advanced but also common methods (such as the Berendsen coupling or Nosé-Hoover thermostat), because it does not allow for local fluctuations of the temperature. However, for SPH the scaling approach is quite suitable, because it already treats the temperature as a mesoscopic field quantity. Furthermore, it allows the temperature field to fluctuate around a given mean value.

Timescale thermostat

It is apparent that the instantaneous temperature scaling approach is not a realistic model, because it does not take the strength of coupling into account. A somewhat more realistic model is given by the time-scale thermostat. It is inspired by the

\[\text{In statistical physics, this type of ensemble is commonly referred to as the canonical ensemble, or } NVT\text{-ensemble, which generally indicates a system with constant particle number, volume, and temperature values.}\]
so called Berendsen thermostat [72], which is a very common choice for molecular
dynamics simulations. The thermal evolution of the mean temperature is given
by the solution of the ordinary differential equation
\[
\frac{d\overline{T}}{dt} = \frac{1}{\tau} (T_0 - \overline{T}),
\]
where $\overline{T}$ is the arithmetic mean, $\tau$ is a constant that defines the thermalization
time scale and $T_0$ is the desired final mean temperature. For the calculation of $\overline{T}$,
Eq. (2.9) is used to assign a local temperature to each SPH particle. The solution
of Eq. (3.63) depends on the integration timestep $\Delta t$ and is given by
\[
\overline{T}_{\text{new}} = (\overline{T}_{\text{old}} - T_0)e^{-\Delta t/\tau} + T_0,
\]
where $\Delta t = \max_i \Delta t_i$ and $\overline{T}_{\text{new}}(t) = \overline{T}_{\text{old}}(t + \Delta t)$. Note that a more detailed
discussion on integration schemes and conditions on timestep size will be given in
Sec. 3.3.1. The new temperature $\tilde{T}_i$ of a particle $i$ is then obtained by
\[
\tilde{T}_i = T_i \left( \frac{\overline{T}_{\text{new}}}{\overline{T}_{\text{old}}} \right).
\]
It is clear that for the limit $\tau \to 0$, Eq. (3.65) and (3.64) are converge to Eq. (3.62).
In contrast, when $\tau \to \infty$, it corresponds to a pure thermal simulation where no
thermostat is applied.

Note that for molecular dynamics (MD) the Berendsen thermostat is known to
suppress thermal fluctuations, which is true for microscopic simulation methods,
but for our mesoscopic scheme, where only the overall mean temperature is scaled
by the exponential factor to the desired value, thermal fluctuations are conserved.

If latent heat is released, then $\tau$ defines the half time of the process where the
heat is conducted to the heat bath.

Furthermore, the timescale thermostat provides an excellent opportunity for
modeling the initial quench, if the quench is desired to become part of the sim-
ulation. Most important reasons for this procedure is the comparison between
simulation, theory and experiment, where theoretical predictions mostly consider
instantaneous quenches. This is in contrast to experiments, where the quench at
finite quench rate is always part of the experiment and it cannot be considered
separated from the subsequent demixing process.
3.3 GADGET-2 code

The simulations presented in this work have been performed using the publicly available open source code GADGET-2 [73, 54]. Originally written for astrophysical purposes, it has been applied for investigations on structure formation and dynamics on cosmic scales, where it can handle both, ordinary Newtonian-dynamics time integration and integration in comoving coordinates in regards to cosmic expansion. In fact, the applicability covers a wide range of astrophysics, including simulations on pure-gravity dark matter particles, hydrodynamics, but also including more complex physical phenomena, such as star formation, supernova feedback or black holes. The aim of the code to cover this wide field of application by only one single code resulted in a code structure that is easy to comprehend. Furthermore, as it is open for modifications, GADGET-2 provides a perfect basis for further implementations.

The code already has excellent parallelization properties, so that studies on larger systems can easily be performed. GADGET-2 is pursuing the distributed memory parallelization strategy using the message passing interface (MPI) and can therefore be used on nearly every Unix based computer system, ranging from single workstations to supercomputers\textsuperscript{14}.

In the context of spinodal decomposition both, major and minor modifications need to be done on SPH, which have been fully explained in the previous section. Since SPH had not been applied to SD so far, modifications to SPH concerning physical properties were needed anyway. The GADGET-2 code has already implemented several features that can still be used for this work. These are, among others, the basic SPH algorithm with respect to adaptive smoothing lengths just as described in Sec. 3.1.5, periodic boundary conditions\textsuperscript{15}, a leap-frog time integration scheme, or the so called tree construction. The latter two will be described in the following in more detail. Against this, other features needed to be removed. For example, GADGET-2 originally uses the SPH entropy formalism [47], which was reverted back to the common internal energy formulation. Furthermore, the original code uses the cubic B-spline kernel and an ideal gas EOS, which needed to be replaced by the Wendland $C_4$ kernel and the van der Waals EOS. Furthermore, thermal conduction, physical viscosity and the thermostats were implemented additionally.

3.3.1 Time integration scheme

Instead of rational or real numbers, the time integration is performed with integer numbers and a binary hierarchy for the timestep sizes is used. This is due to diffi-

\textsuperscript{14}The latest development version GADGET-3 includes a combined hybrid openmp/MPI parallelization method [59].

\textsuperscript{15}Periodic boundary conditions mean that if a particle crosses the bounds of the simulated box, it re-enters the box from the opposite side. This can be achieved by shifting each component of a position vector of a particle. Furthermore, particle interactions are calculated by repeating the simulation box in every direction.
culties that occur by rounding errors when particles need to become synchronized, since two real timesteps can hardly have the exact same value. The problem is solved by the use of integer numbers that represent the time intervals. The global timestep of the simulation is assigned to the largest available integer number\(^\text{16}\). Both are then subdivided in a power of two hierarchy. Thus, particles can change their timestep only in synchronization with this order.

The SPH algorithm already decouples the set of hydrodynamic equations by solving the partial derivatives and reduces the PDE to a set of second order ODE, which can be solved by a simple time integration scheme. Since every higher order ODE can be brought to the form of a first order ODE, the integration scheme can freely be chosen. Descriptions on different types of integration schemes and discussions of their properties can be found in nearly every book or review about computer simulations. Therefore, it will not be discussed in detail, except for the herein used leapfrog algorithm. However, for the sake of completeness the class of Runge-Kutta methods (see e.g. [74]), or the Verlet algorithms (variations of the original Verlet method are the so called Velocity-Verlet and the so called leapfrog algorithm) (see e.g. [2]) shall be mentioned. The latter Verlet-based methods have very interesting properties in the context of physical systems, because they already are solver of second order ODE and conserve the phase space volume. This property is commonly known as symplecticity, which means that the algorithm can be derived from a Hamiltonian system. A version of the so called leapfrog method is used by \textsc{gadget-2}, namely the Kick-Drift-Kick method (KDK), where the K and D represent operations in the \(6N\)-dimensional phase space. The kick operation \(K(\Delta t)\) assigns the new velocities from the accelerations for a given timestep \(\Delta t\) but leaves the position unchanged. The drift operator \(D(\Delta t)\) gives the new particle positions. The calculation of KDK is shifted by half a timestep, so that \(D\) does not use the velocities at the actual time but half a timestep shifted. Therefore, a formal description of the KDK is

\[
U(\Delta t) = K\left(\frac{\Delta t}{2}\right) D(\Delta t) K\left(\frac{\Delta t}{2}\right),
\]

where \(U(\Delta t)\) is the resulting integration scheme at a given timestep \(\Delta t\). In explicit form for one particle

\[
\begin{align*}
    v(t + \Delta t/2) &= v(t) + \frac{\Delta t}{2} a(t) \\
    r(t + \Delta t) &= r(t) + \Delta t \ v(t + \Delta t/2) \\
    v(t + \Delta t) &= v(t + \Delta t/2) + \frac{\Delta t}{2} a(t + \Delta t),
\end{align*}
\]

where \(a\) is the net acceleration of the particle. It is obvious that the order of execution could also be changed to the DKD. Both are second order energy conserving in the step size. In fact, DKD shows better performance in a \(N\)-body

\(^{16}\)The actual value depends on the precision of the integer that is used for the calculation.
simulation using direct sums. However, using adaptive timesteps is accompanied with the loss of energy conservation, whereafter it is the KDK that shows to be more accurate, which means that larger timesteps can be chosen at a reasonable change of phase space volume [54]. Moreover, calculating the forces with SPH is very time-consuming, whereby the KDK has a better performance. A closer look on the KDK scheme reveals that Eq. (3.69) must only be solved explicitly when a simulation snapshot must be written. Otherwise, \( \mathbf{v}(t+\Delta t) \) can be directly inserted to Eq. (3.67) of the following timestep. This enormously reduces computational effort of the KDK, since it becomes very similar to the simple Euler method. For these reasons it is the KDK scheme that is implemented to gadget-2.

As a first approach for adaptivity, a global adaptive timestep could be chosen that applies to all particles. However, it can be even more effective when taking into account that certain regions can be less active than others, whereby the timesteps can be chosen larger. In order to minimize errors and computational effort, the timesteps are in fact chosen individually for every particle. Thus, the step size of a particle \( i \) is set by choosing the minimum of timesteps predicted by several criteria, lastly bounded by a maximum step size \( \Delta t_{\text{max}} \). The criteria are the acceleration criterion, a Courant-like criterion and a criterion due to temperature changes arising from Eq. (3.46). The total timestep condition is given by

\[
\Delta t_i = \min \left[ \sqrt{\frac{2\eta_1}{h_i}} \frac{\eta_2}{\epsilon_i^{\text{sig}}} \frac{\eta_3(u_i - u_{\text{min}})}{(d/dt)\tilde{u}_i}, \Delta t_{\text{max}} \right],
\]

(3.70)

where \( \eta_{1,2,3} \) are integration accuracy parameters and \( \epsilon_i^{\text{sig}} = \max_j[\epsilon_{ij}] \). The individual timesteps are kept to a binary hierarchy, so that all particles are integrated synchronously at least after the actual existing maximum timestep. The binary hierarchy of the timesteps allows for a distinction between the differing time scales on which the involved physical phenomena are acting, such as conduction or viscosity or the thermostats. As discussed in Ref. [42], energy is barely conserved if particles have unequal timesteps, and therefore, the thermal conduction Eq. (4.9) is only integrated at times of synchronization of all particles. Due to the same conflict of energy conservation that occur with integrating the conduction equation, the synchronization points are also used to update the internal energies by the actual thermostat, such as the scaling or the timescale thermostat, given by Eq. (3.62) or Eq. (3.65), respectively. The KDK scheme in gadget-2 already supports this separation of time stepping [54], although originally employed for a distinction between long-range and short-range gravitational force interaction. Therefore, such a “subcycling” scheme \( \tilde{U} \) is formally given by

\[
\tilde{U} = K_l \left( \frac{\Delta t}{2} \right) \left[ K_s \left( \frac{\Delta t}{2m} \right) D \left( \frac{\Delta t}{m} \right) K_s \left( \frac{\Delta t}{2m} \right) \right]^m K_l \left( \frac{\Delta t}{2} \right),
\]

(3.71)

\footnote{The Euler method is the most simple numerical method for calculating the solution of an initial value problem \( \dot{x}(t) = f(x,t) \) by \( x(t + \Delta t) = x(t) + \Delta t f(t) \).}
where the indexes $s$ and $l$ refer to small and large timesteps, respectively. Fortunately, this does not affect the symplectic nature of the scheme [75].

### 3.3.2 Tree construction

One of the largest portions in the GADGET-code is represented by the tree. The implementation is a complicated issue, but it is a worthwhile investment, because the tree has multiple functions in the code. The main purpose is the calculation of gravitational accelerations as an alternative for the direct summation, which becomes meaningful especially when large particle numbers are simulated. The main idea is that distant clumps of particles, which lie in between an opening angle, can be summarized and represented by one single point mass. This procedure immensely reduces the computational effort. GADGET-2 follows the ideas of Barnes and Hut [76]. However, self-gravity is not being considered in this work. Therefore, it will not be explained in more detail here. A detailed description is given in Ref. [54]. Nevertheless, a relevance is still given due to its further application as efficient neighbor search algorithm for SPH. Furthermore, the tree can be used for the parallelization, where the domain decomposition is managed with the aid of the tree. Besides, the classical self-gravitation has the same scalar potential as the Coulomb potential. Therefore, in general, it should be possible to simulate electrically charged particles with the use of the tree.

The main purpose of the tree is the effective access to particles within a given volume. In a three dimensional system, the tree has an octahedral structure, commonly referred to as octree. The principle is as follows. The simulation box is subdivided in eight boxes (or nodes), which becomes further subdivided. This procedure is continued and only aborts until only single particles remain in the respective box. It is the similarity to a tree that gives the name to the so obtained grid of nodes in a hierarchical structure. The level of a node in this hierarchy gives rise to the size of the corresponding box. Therefore, once calculated, it is a very effective supplier for neighbor lists at a given distant, which is the smoothing length in SPH. By determining a global maximum velocity and, therefore, increasing the radius, the tree must not be reconstructed for every timestep.

Furthermore, the tree construction is closely related to the space-filling Peano-Hilbert curve [77]. Thus, it can excellently be used for domain decomposition that is needed for the parallelization [54]. The tree nodes can be walked-along by the Peano-Hilbert curve with variable order in connection with the hierarchical level of the actual node. The so obtained curve is then evenly divided into segments, representing the different domains that are then processed by their respective thread.

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18The two and one dimensional analogs are the quadtree and binary tree, respectively.
3.4 Initial conditions

It is out of the question that the system initiates to evolve in time, once the simulation is started. Therewith associated, it depends on the stability of the initial state how the system behaves and further evolves. Thus, also the later dynamics and the outcome of a simulation are strongly influenced by this initial configuration. A meaningful simulation will always be based on an unstable initial state. Otherwise, if it was in equilibrium, nothing is expected to occur. However, the latter situation is not fully useless, since it can be used for an investigation on the stability of initial particle distributions. In SPH the initial distribution of the particles is not strictly specified. In fact, it turns out that particles will always start to move slightly in the first timestep of a simulation, where spurious forces rearrange the particles in order to form a more stable configuration. Hence, it can be seen as a relaxation process. This strongly undesired effect in the beginning of a simulation should be reduced to a minimum. Thereby, the intensity of the movement depends on the actual choice of initial particle distribution. Note that this is a drawback of the SPH method, or more precisely the Lagrangian nature of SPH, in contrast to grid based codes, where such a flow can be avoided by an appropriate choice of initial configuration.

Selecting the proper particle distribution in SPH is a science in itself. More detailed comparisons between different distributions can be found in Refs. [29, 12]. There are two general approaches for particle arrangements. They can either be based on regular or on irregular grids. For example the hexagonal closed packed (hcp) lattice is a commonly used regular particle configuration in SPH. A regular distribution has the advantage that the density estimation is very accurate. However, it fails even in a simple test case, such as the Sod shock at a density discontinuity. It does not reproduce accelerations correctly in three spatial dimensions, since artificial forces occur in the directions perpendicular to the propagation. They can be explained by differing lattice constants in the two density regions, where the particles need to adjust in order to fit the discontinuity. An explanation for this behavior is that these particles need to overcome an artificial local minimum in free energy in the direction of propagation. It is obvious that this effect needs to be reduced, which can be done by introducing an artificial dissipation term. However, it is clear that it should be avoided from the outset.

It can be shown that a so called glass-like distribution is a much better choice. It is an irregular distribution, but shows a short range order. For the purpose of preparing a glass-like distribution a repulsive body force is applied to homogeneous randomly distributed particles, which is then integrated in time. This culminates in a long-range correlated stable particle distribution. One advantage in the context of spinodal decomposition is the density distribution of such a particle configuration, which is in fact less accurate than in the case of regular grid, but has a bell-shaped density distribution. Therefore, a glass distribution already contains the initial noise that is required for the initial growth of fluctuations at spinodal decomposition. A standard deviation from the densities can easily be
Chapter 3 Algorithms and methods

Figure 3.5: Cross sections slices of a three dimensional particle distribution of \(10^5\) particles during the repulsive-force settling process at the times 0.0, 0.1, 1.0, 10.0, 100.0. It exemplarily shows the transformation from homogeneously random distributed particles to a glass-like distribution. The final particle distribution is eventually obtained from the last snapshot via SPH relaxation at a given initial temperature and density.

calculated.

3.4.1 Glass distribution

The preparing procedure of a glass-like particle distribution is rather intricate and will now be described in more detail. It majorly consists of two procedures. A 

\(N\)-body simulation that forms a first rough glass distribution, and a fine-tuning particle relaxation that is performed with SPH.

In the first instance particles are placed by random numbers in a cubic box with side length \(L = 1\), which generates a homogeneous density distribution, as shown in Fig. 3.5 at \(t = 0\). However, this first particle configuration leads to a very poor SPH density estimation. A first glass-like distribution of the particles is obtained by applying a repulsive body force to the particles. In practice, this is implemented by a \(N\)-body simulation with a direct summation and periodic boundary conditions, where a force is calculated for each particle by interaction with the other particles. In this work, the force is modeled by a repulsive \(1/r\)-Coulomb potential\(^{19}\). The simulation is integrated in time with fixed timestep size of \(\Delta t = 0.01\) up to the time \(t_{\text{max}} = 100\). Cross section slices of this calculation are shown in Fig. 3.5 for several times in orders of magnitude. It is already at \(t = 0.1\) that the particles appear to be glass-like distributed. Only marginal movements of the particle positions are observed in the further proceed. A progress can hardly be figured out by just comparing these snapshots. However, there is progress, which can be seen with the aid of the so called radial distribution function\(^{20}\) \((\text{RDF})\) \(g(r)\) \[^{2, 1}\]. The RDF provides a very powerful tool, which enables to give an assessment of the progress of forming a glass. The RDF is a well known method in statistical physics that can be used to analyze the molecular structure of a material (such as crystal structures, gases, liquids, or glasses) \[^{5}\]. It is closely related to the

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\(^{19}\)It is not necessary to use Coulomb interaction, also other potentials can be used.

\(^{20}\)The function is sometimes also referred to as pair distribution function
3.4 Initial conditions

structure factor through Fourier transformation, which can easily be measured by experiment [1]. The RDF is formally defined by

\[ g(|\mathbf{r}|) = \frac{L^3}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle, \]

where \( N \) is the number of particles in the simulation [2]. In practice the \( \delta \)-distribution is replaced by a histogram (in three dimensions these are spherical shaped shells at finite width) that is calculated over the pair-wise distances. The so obtained histogram slots are then normalized by the number of particles that would be observed for an homogeneous ideal gas at the same density. Thus, an interpretation of the RDF is the following. The RDF describes the probability to find a particle at a given distance from another particle.

Fig. 3.6 shows the RDF corresponding to the cross section slices shown above. For \( t = 0.0 \) no correlation is observed. This is exactly the expectation of randomly distributed particles. For later times a correlation arises that further expands in time, such that the RDF takes the form which is expected for a glass. It already seems to be reasonably good at \( t = 10.0 \), but with view on the inset box that shows a zoom-in to larger distances, it is clear that the method achieves correlation to much larger distances. Although the correlation between particles increases with time, the amplitude converges, which can be seen by comparison between the \( t = 10 \) and \( t = 100 \). The curves are roughly equal up to \( r \approx 0.2 \). A difference can only be noticed from the inset. The so obtained particle distribution can now be applied to the SPH algorithm to allow for a first estimation of the density and its distribution.

Moreover, this initiates the second part of the whole glass preparing procedure,
because the particle positions are now used as initial conditions for a SPH calculation, where the particles will further relax to a stable configuration. This will give the particle configuration the final touch. This procedure significantly reduces the unavoidable density noise for a glass-like distribution. As compared in Fig. 3.7 (a), the RDF of the final snapshot of the calculation is similar to the one that was finally obtained in the previous step. However, the rearrangement of the particles can be seen from the inset box, where the peaks have slightly moved. In fact, it is observed that the distribution function becomes crouched (and not shifted) during this process, which is in contrast to the former step, where only the amplitudes increased but at fixed distances. Therefore, this second part must be understood to redefine the environmental setting, such as the neighbor numbers (eventually, this defines the smoothing length), which has to be used for all further simulations using these initial conditions. Choosing another number of neighbors at this point would destabilize the configuration. Furthermore, the SPH relaxation will also preset the initial density (here $\rho_0 = 0.5$ is used) and a temperature ($T = 1.5$) for further simulations. In our example, with $10^5$ particles and smoothing lengths $h \approx 0.04$, the most distant peak is barely visible at $r \approx 0.315$, and the standard deviation of the density could be reduced from $\sigma_\rho = 5.7 \times 10^{-4}$ to $3.4 \times 10^{-4}$, where the respective histograms are shown in Fig. 3.7 (b).
Effects of temperature on spinodal decomposition and domain growth of liquid-vapor systems

We present a numerical method for simulations of spinodal decomposition of liquid-vapor systems. The results are in excellent agreement with theoretical predictions for all expected time regimes from the initial growth of “homophase fluctuations” up to the inertial hydrodynamics regime. The numerical approach follows a modern formulation of the smoothed particle hydrodynamics method with a van der Waals equation of state and thermal conduction. The dynamics and thermal evolution of instantaneously temperature-quenched systems are investigated. Therefore, we introduce a simple scaling thermostat that allows thermal fluctuations at a constant predicted mean temperature. We find that the initial stage spinodal decomposition is strongly affected by the temperature field. The separated phases react on density changes with a change in temperature. Although, the thermal conduction acts very slowly, thermal deviations are eventually compensated. The domain growth in the late stage of demixing is found to be rather unaffected by thermal fluctuations. We observe a transition from the Lifshitz-Slyozov growth rate with 1/3 exponent to the inertial hydrodynamics regime with a rate of 2/3, only excepted from simulations near the critical point where the liquid droplets are observed to nucleate directly in a spherical shape. The transition between the growth regimes is found to occur earlier for higher initial temperatures. We explain this time dependency with the phase interfaces that become more diffuse and overlap with approaching the critical point. A prolonging behavior of the demixing process is observed and also expected to depend on temperature. It is further found that the observations can excellently explain the growth behavior for pure nonisothermal simulations that are performed without thermostat.
Chapter 4 Effects of temperature on spinodal decomposition and domain growth

The study in this chapter has been published in the article

- Martin Pütz and Peter Nielaba.  
  *Effects of temperature on spinodal decomposition and domain growth of liquid-vapor systems with smoothed particle hydrodynamics.*  

The original paper from Ref. [78] has been slightly revised and adapted for the publication in this thesis.
4.1 Introduction

The influence of hydrodynamics and temperature on the dynamic process of phase transitions are still open issues. In this work a simulation method for first-order phase transitions of a one-component fluid is introduced. To be more precise, the smoothed particle hydrodynamics (SPH) simulation method is firstly applied to investigate the dynamics of liquid-vapor phase transitions, especially the so called spinodal decomposition (SD), where a spontaneous separation occurs after the fluid was instantaneously quenched to a completely unstable state. With our method the whole separation process is in excellent agreement with theoretically predicted properties for all expected time regimes and results from other simulation methods. In addition SPH evolves the temperature, which is a more realistic approach than most theories that treat the process isothermal.

The separation process splits up into an initial and a late stage time regime. The predictions for the initial stage concern the growth of long-wavelength “homophase fluctuations” [8], which follows from the Cahn-Hilliard-equation (CH) [14, 15, 16], a transition from SD at deep quenches to a rather nucleation-like SD for low quench depths near the critical point [19, 8] and an increase of the mean temperature that is due to latent heat observed at nonisothermal simulations [69]. But also in the late stage of phase separation, the domain growth (DG) regime, the SPH results are in agreement with theoretical predictions. The DG process is divided into different growth regimes [24, 21] that are characterized by different scaling behaviors of the characteristic length of the domains \( \xi(t) \sim t^\alpha \). The exponents can be assigned to different growth processes. A diffusion driven coarsening growth was predicted by Lifshitz and Slyozov (LS) [22] and is expected to yield an exponent of \( \alpha = 1/3 \). The influence of hydrodynamics is subdivided in two regimes, where Siggia predicted a crossover from LS to a viscous hydrodynamic regime (VH) with linear scaling \( \alpha = 1 \) [23], followed by Furukawa’s prediction of an inertial hydrodynamic regime (IH) that corresponds to \( \alpha = 2/3 \) [79]. Nevertheless, it must be mentioned that an all-embracing theory is still not found. Many attempts with several simulation methods have been made to prove these predictions (at least partially) [80, 79, 81, 82, 83, 84, 85, 86, 87, 88] and to find crossovers between the regimes [89, 66, 90, 91, 92, 93, 94]. More recent works take the evolution of temperature into account where a prolongation in the DG regime is observed [69, 95]. The SPH method allows us to evolve through all the above-mentioned time regimes in a single simulation, reaching from the early-stage SD to the late-stage DG regimes.

Most of the mesoscopic methods, and so our SPH method, are based on the simple approach for the modeling of phase separation, which is given by van der Waals (vdW) [7] who proposed an equation of state (EOS) for liquid-vapor phase transitions. The vdW theory predicts both, the existence of a completely unstable region, which is enclosed by the spinodal curve, and, above that a metastable region enclosed by the coexisting curve (binodal curve) that predicts the coexisting liquid and vapor densities. The spinodal and binodal meet at the so called critical
point. Surface tension arises naturally by the use of the vdW-EOS in SPH and thus interfaces become more diffuse when approaching the critical point. This was first shown by Nugent and Posch [31] and, with a modified vdW-EOS where an additional stress tensor is applied, in a very recent work by Sigalotti et al. [38]. Both studied the droplet formation after an instantaneous volume expansion. In this procedure only the mean density of the total volume gets below the spinodal curve, but in fact the dynamical process is only a reshaping of an initial squared (or cubed) liquid droplet to a spherical one. This vdW-SPH approach has been the basis for works on various subjects, such as the oscillation and coalescence of droplets, the determination of the surface tension or modeling multiphase flow in two [32, 33, 34, 35, 37, 36] and recently also in three dimensions [61, 62].

Nugent and Posch pointed out that the attractive and repulsive components of the pressure that are given by the vdW-EOS must be treated separately with different smoothing lengths to obtain sensible results. This practice has become a common method. However, from a numerical point of view there is no explanation for this choice and should even be avoided. Furthermore, all of these works have been performed with low resolutions and could not resolve the demixing process at temperatures near the critical point.

The SPH method used in this work is based on the modern formulation of SPH [28, 12], which is derived from a Lagrangian and yields very good conservation properties. Physical viscosity is already applied to SPH [49, 28] but intentionally not included in our model in order to reduce the complexity. SPH is suitable for very effective parallelization strategies and allows us to perform simulations at very high resolutions in three dimensions. An adequate choice of kernel provides the enlargement of the smoothing range and repeals the requirement of differentiation in long- and short-range components. Instantaneous temperature quenches in the unstable region allow us to observe the growth of “homophase fluctuations” in SD and DG under consideration of hydrodynamics. A thermostat treats the simulation quasi-isothermal, because thermal fluctuations at a fixed mean temperature are expected to give a more realistic sight on the separation process of a thermally quenched system than an isothermal treatment. In the context of phase separation, SPH has some advantages over other common simulation methods, like the also mesoscopic Lattice Boltzmann method. It is easy to determine the mean densities and temperatures, to follow their evolution in a phase diagram, and to directly observe the fluid flow.

The paper is structured as follows. In Sec. 4.2 the governing equations and the SPH method are presented. In Sec. 4.3 first the simulation method and the new scaling thermostat are validated with both static and dynamic test cases. Afterwards, the results of the numerical simulations for the phase separation process without thermostat and with thermostat are presented. The paper is closed by a conclusion in Sec. 4.4.
4.2 Methods

In this section the simulation method and the related governing equations are briefly discussed, with focus on recent developments of the code. The SPH method was simultaneously developed by Lucy [30] and Gingold and Monaghan [13], originally for astrophysical purposes (see, e.g., Ref. [96]). It has been extended and further developed until recent days. Therefore, a lot of SPH code implementations are available at present. Today the development also focuses on smaller length scales, which poses further challenges. In the present study a modification of the massively parallel simulation code GADGET-2 [54] is used. The modifications comprise an equation of state that supports phase separation, a new kernel interpolant, a thermal conduction equation, and a herein newly developed scaling thermostat.

4.2.1 Smoothed particle hydrodynamics

The SPH method is a mesoscopic meshfree simulation method where the volume of a fluid is divided in a set of virtual mass elements $m_i$ (hereinafter referred to as SPH particles). Every SPH particle is assigned to a volume that is specified by a so-called smoothing length $h_i$. These volumes must not be regarded as separated volumes but as rather overlapping each other. Any quantity can be approximated via a weighted interpolation over the neighboring SPH particles. The weighting function $W(r, h)$, which is also called the smoothing kernel, must satisfy the conditions that $W(r, h) \to \delta(r)$ for $h \to 0$, $W(r, h) \geq 0$ is monotonically decreasing and twice continuously differentiable [12]. A class of kernels that fulfill these conditions and should further be stable against pairing are the Wendland functions [45]. Instead of common choices, like the class of B-splines or Lucy, we use the Wendland $C_4$ kernel function that allows a wider smoothing range. It reads in three dimensions as

$$W(r, h) = \frac{495}{32\pi} (1 - r)^6 (1 + 6r + \frac{35}{3} r^2),$$

where $r = |r|/h$ and $(\cdot)_+ = \max(0, \cdot)$. In practice a typical number of neighbors $N$ determines the smoothing length $h_i$ via the estimated density, such that the kernel volume enclose a constant mass [54].

As SPH is a mesh-free method and thus the particles follow directly the flow of the fluid, the hydrodynamic equations can be described in the Lagrangian frame [28]. The governing equations for a heat conducting nonviscous fluid are namely the continuity equation, the momentum equation, and the energy equation, which read as

$$\frac{d\rho}{dt} = -\rho \nabla \cdot v,$$  (4.2)
$$\frac{dv}{dt} = -\frac{\nabla P}{\rho},$$  (4.3)
$$\frac{du}{dt} = -\frac{P}{\rho} \nabla \cdot v - \frac{1}{\rho} \nabla j.$$  (4.4)
where $\rho$, $v$, $u$, $P$, and $j$ are the density, velocity, specific internal energy, pressure, and heat flux vector, respectively. The equations are solved for each SPH particle. One of the main advantages of SPH is that the total mass of the system is exactly conserved, when the total number of particles does not change within a simulation [12]. The continuity Eq. (4.2) must not be solved explicitly and can be replaced by the density estimation

$$\rho_i = \sum_{j=1}^{N} m_j W_{ij}(h_i), \tag{4.5}$$

where $W_{ij}(h_i) = W(r_i - r_j, h_i)$. The resulting density tends to overestimate the correct density. It therefore has to be corrected by a correction term fully described in Ref. [45]. The main feature of SPH is that any spatial derivative of a scalar or vector quantity reduces at least to the product of the quantity itself and the derivative of the kernel. Thus, the momentum Eq. (4.3), with respect to adaptive smoothing lengths, can be derived by a Lagrangian and reads as

$$\frac{dv_i}{dt} = - \sum_{j}^{N} m_j \left[ \frac{f_i P_i}{\rho_i^2} \nabla_i W_{ij}(h_i) + \frac{f_j P_j}{\rho_j^2} \nabla_i W_{ij}(h_j) \right], \tag{4.6}$$

where the $f_i$ are correction factors due to the adaptivity of the smoothing lengths and are defined by

$$f_i = \left[ 1 + \frac{h_i}{3 \rho_i} \frac{d\rho_i}{dh_i} \right]^{-1}. \tag{4.7}$$

The SPH formulation of the first term on the right hand side of Eq. (4.4) can easily be expressed in terms of the velocity as

$$\frac{du_i}{dt} = \frac{f_i P_i}{\rho_i^2} \sum_{j}^{N} m_j (v_i - v_j) \cdot \nabla_i W_{ij}(h_i). \tag{4.8}$$

The latter thermal conduction term includes a second derivative, since the heat flux vector is given by $j = -\kappa \nabla T$, with the material specific thermal conductivity $\kappa$. One possible SPH discretization is given by

$$\left( \frac{du_i}{dt} \right)_{\text{cond}} = \sum_{j=1}^{N} \frac{m_j}{\rho_i \rho_j} (\kappa_i + \kappa_j) (T_i - T_j) \frac{r_{ij}}{|r_{ij}|^2} \cdot \nabla_i \Wbar_{ij}, \tag{4.9}$$

where $\Wbar_{ij} = 1/2(W_{ij}(h_i) + W_{ij}(h_j))$ is the arithmetic mean between the two kernel values [43, 42]. If the thermal conductivity is treated as a constant, the sum $(\kappa_i + \kappa_j)$ in Eq. (4.9) is replaced by $2\kappa$. Otherwise, the conduction can be expressed in terms of the density and temperature.
4.2 Methods

In order to suppress nonphysical behavior at discontinuities, it is necessary to take artificial viscosity into account. A variation of the standard formulation of artificial viscosity [53] is given by

\[ \Pi_{ij} = -\frac{\alpha v_{ij}^\text{sig} w_{ij}}{2\rho_{ij}}, \] (4.10)

where \( \alpha \) is called the artificial viscosity constant with a typical value in [0, 1]. The signal velocity \( v_{ij}^\text{sig} = c_i + c_j - 3w_{ij} \) with \( w_{ij} = v_{ij} \cdot |r_{ij}| \) (only if \( v_{ij} \cdot r_{ij} < 0 \), otherwise \( w_{ij} = 0 \)) and \( c_i \) is an estimate of the sound velocity. The \( \rho_{ij} \) denotes the arithmetic mean of the densities due to the particles \( i \) and \( j \). The implementation is realized by replacing any pressure term \( P_i/\rho_i^2 \), due to a particle \( i \), in Eqs. (4.6) and (4.8), by an interparticle term \( P_i/\rho_i^2 + \Pi_{ij} \) [54]. Note that artificial viscosity is solely implemented for numerical reasons and must not be confused with physical viscosity.

The physical properties of the phase separation process for a one component fluid can be described by the vdW-EOS. The vdW theory predicts a fluid to separate into two phases when the fluid undergoes a certain critical point \( (P_c, T_c, \rho_c) \). The separation process is mainly controlled by two components, which can be expressed in terms of the critical point. The first one is a repulsive component and comes up by the assumption of a covolume \( \bar{b} = \bar{b}_c T_c/(8P_c) \), where \( \bar{b}_c = k_b/\mu m_p \) with \( k_b \) the Boltzmann constant, \( \mu \) the mean molecular weight and \( m_p \) the proton mass. The second component is the cohesive pressure \( \sigma = 27(\bar{b}_c T_c)^2/(64P_c) \) and acts ultimately as an attractive force. These considerations result in the mechanical [Eq. (4.11)] and caloric [Eq. (4.12)] equations of state for a SPH particle:

\[ P_i = \frac{\rho_i \bar{b}_c T_i}{1 - \bar{b}/\rho_i} - \sigma \rho_i^2, \] (4.11)
\[ u_i = \frac{\bar{b}_c T_i}{\gamma - 1} - \sigma \rho_i. \] (4.12)

Note that Eq. (4.12) can be used to compute the actual temperature of a particle, which provides that an expansion or compression in terms of the density leads to cooling or heating of the fluid. Furthermore, a minimum internal energy \( u_{\text{min}} = -\sigma/\bar{b} \) can be derived, since the value of density is not allowed to exceed \( 1/\bar{b} \) and \( T_i \geq 0 \). The vdW equation had first been applied to SPH in order to study the formation of liquid drops in two dimensions [31]. However, common choices for the smoothing kernel like Lucys kernel always required a separation of Eq. (4.11) into two components, which severely had to be applied to different smoothing lengths. This differentiation in a long range attraction and a short range repulsion was necessary to get sensible results. However, the Wendland kernel from Eq. (4.1) supports much wider smoothing ranges than the common kernels like Lucys or the \( B_2 \) spline. Hence, there is no need to differentiate attractive and repulsive pressure terms within the formulation of SPH that is used in this work.
Chapter 4 Effects of temperature on spinodal decomposition and domain growth

The integration in time is done by the generally symplectic leapfrog kick-drift-kick algorithm. The implementation to SPH is described in Ref. [54]. It is reasonable to use adaptive timesteps in order to reduce the computational effort, which, however, is accompanied by the loss of symplecticity of the integration scheme. In order to minimize errors due to the adaptivity, the timesteps are chosen individually. Thus, the step size of a particle $i$ is set by choosing the minimum timestep of several criteria, but bounded by a maximum step size $\Delta t_{\text{max}}$. The criteria are given by an acceleration criterion, the Courant criterion and a criterion due to temperature flow from Eq. (4.9). The total timestep condition is given by

$$\Delta t_i = \min \left[ \sqrt{\frac{2\eta_1 v_i}{\ddot{v}_i}}, \frac{\eta_2 h_i}{\dot{v}_i^{\text{sig}}}, \frac{\eta_3 (u_i - u_{\text{min}})}{(d/dt)\dot{u}_i}, \Delta t_{\text{max}} \right], \quad (4.13)$$

where $\eta_{1,2,3}$ are integration accuracy parameters and $\dot{v}_i^{\text{sig}} = \max_j [v_{ij}^{\text{sig}}]$. The individual timesteps are kept to a binary hierarchy, so that all particles are integrated synchronously at least after the actual existing maximum timestep. As discussed in Ref. [42], energy is barely conserved if particles have unequal timesteps, therefore, Eq. (4.9) is only integrated at times of synchronization.

4.2.2 Scaling thermostat for SPH

The SPH method, as described above, conserves total energy. Thus, an increase of kinetic energy of the fluid is accompanied with a loss of total internal energy and vice versa. This can be seen as a consequence of the hydrodynamic equations. Furthermore, taking artificial dissipation and thermal conduction into account, where the dynamic process becomes irreversible, the total energy is still conserved. Combined with the caloric vdW-EOS Eq. (4.12), the mean temperature $\bar{T}$ of the system may change as the particle densities diverge within the process of phase separation. When the focus of interest is on the evolution of these separated phases, it might be desirable to keep $\bar{T}$ at a constant desired value $T_0$. One way is to keep each temperature $T_i$ fixed at $T_0$, which would generate an isothermal process, but could not preserve thermal fluctuations within the dynamical system. The two remaining possibilities are either to shift or to scale the mean temperature to the desired value. The former is not reasonable since temperatures below $\bar{T}$ could result in negative temperatures. Therefore, the scaling approach is implemented in the way, that the new particle temperatures $\tilde{T}_i$ are given by

$$\tilde{T}_i = T_i \cdot \frac{T_0}{\bar{T}}. \quad (4.14)$$

Due to the same conflicts that occur with integrating the conduction term, the synchronization points are also used to update the internal energies by the additional thermal scaling term $\bar{k}_b (\tilde{T}_i - T_i)$. It should be noticed that in molecular dynamics (MD), thermostat methods, especially the velocity rescaling method, are used in a very similar way to realize a constant temperature ensemble [70].
Actually, the SPH method, in its simplest nonadaptive formulation, is closely related to MD [71]. The velocity rescaling method for MD does not reflect the proper physical properties of a canonical ensemble and must be extended to more advanced but also common methods, e.g., the Berendsen coupling or Nosé-Hoover thermostat, because it does not allow fluctuations in temperature. However, for SPH the scaling approach is quite suitable, because it already treats the temperature as a mesoscopic field quantity. Furthermore, it allows the temperature field to fluctuate around a given mean value.

4.3 Simulation Results

In the past decades several approaches have been made in understanding phase separation processes and effects of hydrodynamics on the dynamical process. Therefore, spinodal decomposition (SD) has been studied extensively, both experimentally and theoretically. Since almost all theoretical derivations commonly treat the process isothermal, which is indeed an appropriate approximation for quenches in the neighborhood of the critical point, thermal SD simulations have been performed with a thermal Lattice-Boltzmann (LB) method [69] where the temperature field and thermal conduction were applied. When the SD occurs the mean temperature is found to increase due to latent heat and the domains grow slower than in the isothermal case. However, the thermal fluctuations that arise from compression and expansion play a decisive role for the evolution of deep-quenched systems. This evolution of dynamics is far from clear and shall be focused on in this work from the early stage, where the phases separate, up to the late stage, where the system reaches local equilibrium and is dominated by domain growth and coarsening. The SPH method allows us to observe the thermal evolution for each phase in a direct manner, whereas the thermostat extension allows us to observe fluctuations at a fixed mean temperature.

First the accuracy of the scaling thermostat is demonstrated by both static and dynamic thermal conduction test cases. This is followed by simulations with and without applied thermostat, where the SD and DG regimes are studied and compared with theoretical predictions in detail. The results for various quench depths and applied thermostat are presented in the last part.

The distribution of the initial SPH particle configuration is realized by a relaxation process. The desired number of SPH particles are uniform randomly distributed in the simulation box before they are integrated in time with an artificial repulsive force term. The particles reach a nearly equilibrated state after a certain number of timesteps. The resulting configuration is a so called glass like distribution. Note that a small noise in the SPH-density estimation (depending on the number of neighbors $N$ and the initial value of the density $\rho_0$) is generated by the nonequidistant spacing of the particles. But in the context of SD a noisy density field is even desired. The simulation box is a cube of side length $L = 1$ and the total mass $M = \rho_0 L^3$. Therefore, the mass of one particle is $m_i = M/N_{\text{tot}}$.
where \( N_{\text{tot}} \) is the total number of particles. For a fixed number of neighbors that is set to \( N = 250 \) for all the simulations hereinafter, and an initial density \( \rho_0 = 0.5 \) the initial standard deviation of the SPH-density is \( \sigma_\rho \approx 5.7 \times 10^{-4} \). The covolume and cohesive pressure are expressed in terms of the critical point \((T_c, P_c, \rho_c) = (32/27, 8/27, 2/3)\), which yields \( \bar{n} = 2.0 \) and \( \bar{b} = 0.5 \). The coefficient in the temperature term is chosen such that \( k_b/(\gamma - 1) = 1.0 \). Further constant parameters in all simulations are thermal conductivity \( \kappa = 0.01 \), artificial viscosity \( \alpha = 1.0 \), the integration accuracy parameters \((\eta_1, \eta_2, \eta_3) = (0.0025, 0.15, 0.1)\) and \( \Delta t_{\text{max}} = 10^{-4} \). Periodic boundary conditions are applied, since boundary effects shall be neglected here.

### 4.3.1 Validation of the scaling thermostat approach

The SPH implementation of the thermal conduction equation with the new approach for a scaling thermostat have not yet been applied to the vdW-EOS. In order to evaluate the performance and accuracy of these, a validation test case is performed with the four resolutions of \( 10^4, 5 \cdot 10^4, 10^5, \) and \( 10^6 \) SPH particles. We consider a planar thermal interface of a homogeneous liquid phase with the initial density \( \rho_0 = 1.5 \). The interface is located at \( x_m = 0.5 \) in \( x \) direction and separates the initial temperatures of \( T_l = 1.0 \) and \( T_r = 0.8 \), where the indices \( r \) and \( l \) denote the right and the left half of the box, respectively. This initial configuration is purposefully chosen to be out of the binodal region. Hence, thermal effects due to phase separation are neglected.

First we are interested in the capability of the thermal conduction to capture a test case, which can be analytically solved [6, 42]. That is the initial configuration described above, but concerning a fluid at rest. To meet this, the velocities are kept fixed at zero. The analytic solution for the temperature is given by an error function term,

\[
T(x,t) = T + \frac{\Delta T}{2} \text{erf} \left( \frac{x - x_m}{2\sqrt{\chi t}} \right),
\]  

where \( \Delta T = |T_l - T_r| \) and \( \chi = \kappa/\rho_0 c_p \) is called thermal diffusivity with \( c_p = 1 \). The internal energy is related to the temperature by Eq. (4.12). Therefore, the internal energy solution is also given by an error function term that is similar to Eq. (4.15). This relation is mainly given by the density weighted cohesive pressure term, which causes a noise at the conversion from temperatures to internal energies, when the glass like distribution is used for the initial particle positions. One of the interesting features of the thermal conduction term is that those noisy temperature differences are instantly smoothed out. That is why the internal energies are used for initialization instead of the temperatures. Note that this procedure does not have any effect on the mean values of the quantities, but on single particle values. As periodic boundaries are applied, they must be taken into account in the analytic solution. Figure 4.1 shows a comparison of the temperature profiles from the simulation results with \( 10^6 \) SPH particles at six different times of the pure thermal conduction equation [Fig. 4.1(a)] and with the additionally
4.3 Simulation Results

Figure 4.1: Time sequences of the temperature field $T$ of a resting fluid with an initial thermal discontinuity at $x_m = 0.5$ with $10^6$ SPH particles and periodic boundary conditions. While in panel (a) the pure thermal conduction equation is used, in panel (b) the thermal conduction equation and scaling thermostat are applied. The symbols represent the simulation results. The corresponding analytic solutions are drawn by the solid lines. The inset boxes show enlargements of the central region of size $(x_m \pm 0.04, T \pm 0.015)$.

Both simulations reproduce the analytic solution well, but a closer look at the inset boxes in Fig. 4.1 reveals that the simulation with pure thermal conduction tends to overestimate the temperature values not only in the central region but in the whole simulation volume. This can be addressed to the kernel interpolation procedure that produces density estimations that are slightly too high. However, this incorrect behavior is compensated by the scaling thermostat, which almost perfectly predicts the temperature values expected from the analytic solution. In order to verify the functionality of the scaling thermostat in dynamic systems the same initial configuration is used but with released particles. In this case the analytic solution is expected to hold only a short period of time, which is just as long as the density can be considered to be approximately homogeneous. In addition these density changes that are due to the particle movement (and therefore the fluid flow) repeal the similarity between the evolution of the internal energy and the temperature. In Fig. 4.2 the evolution of the densities, temperatures, and internal energies for the four different resolutions with applied thermostat are shown. Note that the simulations have also been performed without the scaling thermostat, but they only differ in the poorer temperature estimation as it was observed in the nondynamical case. The comparison reveals a limited ability in capturing this dynamic test case. The simulations with higher resolutions produce very similar results, whereas the lowest resolved simulation with $10^4$ particles differ significantly from these. Therefore, the lowest resolution cannot be expected to adequately describe the dynamics of a vdW fluid. The evolution of the internal
Indeed, the point in time of demixing “homophase fluctuations” [8]. This is almost identical for both of the simulations. Due to the initial density noise, grow in height with time, which is often called to immediately initiate to separate. In this initial stage several density peaks, are set to the spinodal curve and therefore completely unstable, such that the system is expected to immediately initiate to separate. In this initial stage several density peaks, due to the initial density noise, grow in height with time, which is often called “homophase fluctuations” [8]. This is almost identical for both of the simulations. Indeed, the point in time of demixing \( \tau_0 \) (defined as the point where a particle density first exceeds \( \rho_c \)) is the same \( \tau_0 = 0.31 \). However, from this moment on the evolution of the simulations differ significantly. Figure 4.3 shows cross-section slices of the density of both simulations at different times. The simulation without thermostat forms a wider and more diffuse interface between the two phases than the one with thermostat. The critical density is used as a threshold value \( \rho_{th} = \rho_c \) to distinguish between the liquid or vapor phase and to calculate the mean temperature per phase. In Fig. 4.4(a) a comparison of the walk through the temperature-density diagram is shown. The density values are obtained by a median calculation for each phase. The median is chosen instead of more common

\[
\rho \quad \rho \quad \rho
\]

\[
T \quad 1.5
\]

\[
t = 0.01 \quad t = 0.05 \quad t = 0.10 \quad t = 0.25 \quad t = 0.50 \quad t = 1.00
\]

\[
0.25 \quad 0.5 \quad 0.75
\]

\[
x
\]

\[
\tau
\]

\[
\text{Figure 4.2: Time sequences of the temperatures } T, \text{ internal energies } u, \text{ and densities } \rho, \text{ for the calculations with thermostat. The different lines and colors represent the results for the resolutions } 10^4 \text{ (short-dashed blue line), } 5 \cdot 10^4 \text{ (long-dashed green line), } 10^5 \text{ (solid red line), and } 10^6 \text{ (dashed-dotted orange line).}
\]

energies still have the error-functional shape very similar to the analytic solution in the nondynamical test case. However, the effects of the dynamics can be seen in the density field that fluctuates between high and low densities. It is driven by the actual present temperature. Due to the balance between computational expense and reasonably good results the resolution of \( 10^5 \) particles is chosen for all further simulations.

4.3.2 Spinodal decomposition and domain growth

Effect of the thermostat

The effects of the thermostat on the phase separation process are studied on the basis of two simulations with \( N = 10^5 \) particles. They only differ in applying the thermostat. Corresponding to an instantaneous deep quench further initial values are set to \( T_0 = 0.8 \) and \( \rho_0 = 0.5 \) for both of the simulations. This is below the spinodal curve and therefore completely unstable, such that the system is expected to immediately initiate to separate. In this initial stage several density peaks, in the density field that fluctuates between high and low densities. It is driven by the actual present temperature. Due to the balance between computational expense and reasonably good results the resolution of \( 10^5 \) particles is chosen for all further simulations.
4.3 Simulation Results

Figure 4.3: Comparison of density rendered cross section slices from simulation snapshots at the times $t = 0.4$, $0.65$, $1.00$, $4.00$, $7.00$, and $10.00$. The pure thermal simulations with no thermostat (top row) and with thermostat (bottom row), with a side length of the box size $L = 1$. Note that even $t = 10.00$ is far from equilibrium and the actual shapes of the three-dimensional structures cannot be determined in the two-dimensional representation.

Figure 4.4: (a) Temperature-density diagram at equidistant timesteps with $\Delta t = 0.01$ up to $t = 20$ for the $T_0 = 0.8$ and $\rho_0 = 0.5$ simulations without thermostat (red triangles) and with applied thermostat (green dots). The dark and light colors refer to the liquid and vapor phase, respectively. The gray lines represent the binodal (solid line) and spinodal (dashed line) curves from vdW theory and Maxwell construction. The density values are obtained via median and the temperatures are arithmetic means of each phase. The characteristic lengths of the vapor $\xi_v$ and the liquid phase $\xi_l$ for the same simulations are shown in panels (b) and (c), respectively. The arrows point fit intervals and the gray lines refer to slopes of $1/3$ and $2/3$ to guide the eye.
Chapter 4 Effects of temperature on spinodal decomposition and domain growth

choices, such as the arithmetic mean or the modus for the reason that these are very susceptible to the formation of diffuse interfaces at higher temperatures in the initial stage. In the late stage, the density distribution shows two sharp peaks in the histogram and the three types of means differ only slightly. But in the early stage the robustness of the median to single strong density-deviations improves the understanding of the separation process. The points in Fig. 4.4(a) mark equidistant timesteps. It shows that the early stage of the demixing process lasts longer in the pure thermal case. Associated therewith the thermal heating is an important difference to the thermostat case in this early stage. This effect has recently been shown by Gan et al. \[69\] who implemented a thermal model for phase separation to LB simulations. In this case, theoretical predictions are not clear. However, the SPH method provides a direct view on the evolution of the phases, which reveals that in the absence of a thermostat both phases heat up. More precisely the SD process can be divided into the three following parts. The aforementioned heating is followed by a time interval where the heating stagnates and only the liquid density is further approaching the coexistence density. Each of these parts last about $\Delta t \approx 0.1$. In the third part, which lasts longer by two orders of magnitude, temperature is raised again. But the liquid density shows an oscillating behavior until it reaches the coexistence curve. On the other hand, with applying a thermostat the interesting effects are seen on the vapor phase. Instead of a temperature increase, as observed and expected from the pure thermal simulation, the vapor temperature first decreases alongside with a density decrease. This process is followed by a slow temperature increase approaching both the predicted temperature and coexistence density. A contrary evolution is observed for the liquid phase where a density increase is accompanied with an increase in temperature.

Anyhow, the heating and cooling behavior of both simulations can be explained by the caloric EOS and thermal conduction in Eq. (4.4). The initial density noise is intensified by the gradient of Eq. (4.11). These density differences are coupled to the temperature by Eq. (4.12). In the pure thermal case the mass of the liquid phase dominates the simulation volume. With its immense temperature increase the vapor phase is heated via thermal conduction. Therefore, the initial $\rho_0$ and $T_0$, which determine the mass fraction of the separated system predict the equilibrated mean temperature. With a high gas-to-liquid mass fraction the system should decrease in temperature, whereas a low gas-to-liquid fraction leads to heating, as observed here. Note that the vapor temperature decrease that is always observed in simulations with applied thermostat should also be observed in simulations without thermostat for quenches close to $T_c$, where the heating of the liquid phase is minimally extensive.

The late stage of phase separation is dominated by the domain growth and coalescence of droplets. It is quantified by the scaling behavior of the characteristic length scales of the domains, i.e., $\xi(t) \sim t^\alpha$, where $\alpha$ depends on the time regime. Conventionally, $\xi(t)$ can be obtained via several methods, such as the structure factor or a two-point correlation function \[8\]. However, there are several reasons
to define $\xi(t)$ in a different way. The calculation of a structure factor goes along with a Fourier transformation and, therefore, requires a regular grid. Also, the maximum value that can be obtained via two-point-correlation is half the box size, even though the domain sizes in our simulations exceed this value. Therefore, in this work $\xi(t)$ is calculated straightforward as the mean of the minimum distances from one phase to the other. There are several advantages of this calculation method. The resolution does not depend on the grid sizes, which must be chosen for the Fourier transformations or histogram calculations. In addition, it allows us to distinguish between liquid and vapor phase, thus, the lengths can be treated separately. The characteristic length, e.g., for the liquid phase, is then defined as the arithmetic mean of the particle wise calculated minimum distance to the vapor phase,

$$
\xi_l(t) = \frac{1}{N_l} \sum_{i_l} \min(|r_{i_l}(t) - r_{j_v}(t)|),
$$

(4.16)

where $i_l$ and $j_v$ belong to the liquid and vapor phase, respectively, and $N_l$ is the total number of liquid particles. This method is actually very robust and allows us to trace the phase separation process even until the very late stage, where the coalescing process is almost completed and only the single separated domains remain in local equilibrium. Note that the values obtained by Eq. (4.16) are smaller compared to conventional methods; e.g., for a spherical-shaped droplet $\xi_l$ would be $1/4$ of the diameter of the sphere. Calculations of the characteristic lengths of vapor $\xi_v$ and liquid $\xi_l$ for both simulations are presented in Figs. 4.4(b) and 4.4(c). The comparison between the two simulations reveal only slightly different behavior. The already mentioned initial stage “homophase fluctuations” exceed $\rho_c$ in both cases and end up with crossing the spinodal curve. This is were the liquid curves $\xi_l$ show a slight kink from where the growth process is dominated by the LS mechanism with $\alpha = 1/3$. In both simulations the very late stage that is dominated by inertial hydrodynamics (IH) with $\alpha = 2/3$, is observed. One of the main differences is that the pure thermal simulation exhibits a regime with $\alpha = 1/2$ between these two growth rates. This may be understood as a transition regime where LS mechanism is overlaid by IH effects. Regarding the higher temperature of this simulation it also shows that the regime of hydrodynamics is not temporally fixed and may depend on temperature. Nevertheless, in the simulation with thermostat the two regimes can clearly be distinguished and identified. Note that the model does not include physical viscosity and, therefore, it is not expected to observe the intermediate introductory described viscous hydrodynamic regime.

In Table 4.1 the results for the exponents from a least-square regression analysis to the corresponding fit intervals from Fig. 4.4 are presented. Note that the intervals are only suggestions by the authors based on the shapes of the curves and the evaluated exponents may vary within rearranged intervals. But it should further be mentioned that the fitted $\alpha_l$ in the suggested arrangement of intervals are in very good agreement with the theoretical predictions for both types of simulations [23, 79]. The $1/2$ exponent in a thermal, in contrast to the $2/3$ exponents
Table 4.1: The exponents \(\alpha\) (with asymptotic standard error \(\delta\alpha\)) are least-square fitted within the fit intervals suggested in Fig. 4.4. The abbreviation nt and wt denote the simulations “no thermostat” [Fig. 4.4(b)] and “with thermostat” [Fig. 4.4(c)].

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Time</th>
<th>(\alpha_l \pm \delta\alpha_l)</th>
<th>Time</th>
<th>(\alpha_v \pm \delta\alpha_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nt</td>
<td>1.00 − 3.30</td>
<td>0.333 ± 0.001</td>
<td>1.00 − 4.30</td>
<td>0.419 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>3.31 − 6.00</td>
<td>0.509 ± 0.001</td>
<td>4.31 − 11.3</td>
<td>0.502 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>6.01 − 10.3</td>
<td>0.667 ± 0.008</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>wt</td>
<td>0.65 − 7.00</td>
<td>0.329 ± 0.001</td>
<td>0.65 − 7.00</td>
<td>0.424 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>7.01 − 10.9</td>
<td>0.671 ± 0.006</td>
<td>7.01 − 9.90</td>
<td>0.621 ± 0.004</td>
</tr>
</tbody>
</table>

\(^1\) Asymptotic standard error expresses the accuracy in accordance to the calculated characteristic lengths.

...
4.3 Simulation Results

Figure 4.5: Temporal evolution of the kinetic energies for the temperatures $T_0 = 0.60$, $0.70$, $0.75$, $0.80$, $0.85$, $0.90$, $0.95$, $1.00$, $1.05$, and $1.10$ (from left to right). The inset box shows an enlargement of the curves in the main box at the end of simulation times.

applied thermostat to improve the understanding of the phase separation process, with special attention to the temperature evolution and thermal fluctuations. This provides one of the main features of the SPH method in contrast to other fully isothermal approaches.

Quench depth variation with thermostat

Simulations with different quench depths are performed in order to compare the dynamic behavior and the growth rates. The quench depth means the relative distance from the critical point $1 - T_0/T_c$. We focus primarily on the late stage, where the demixing process is almost completed and the domains are growing. Therefore, various initial temperatures, ranging from a deep-quenched $T_0 = 0.6$ to low-quenched $T_0 = 1.1$, are set. The simulations are all scaled by the thermostat. The initial density is independently from the quench depth set to $\rho_0 = 0.5$. The total simulation time ranges from $\approx 20$ to $\approx 50$, depending on the dynamics of the system in order to simulate up to a time where finite-size effects influence the dynamics. Note that the simulations are not evolved until the total equilibration long-time limit is reached, which is mainly due to the absence of physical viscosity in our model. Exemplarily, a representative set of simulations is chosen of which cross-section slices of the density in a temporal evolution are shown in Fig. 4.6. An interesting correlation is observed. The evolutions of the simulations depend significantly on the temperature. The initial fluctuations that are expected to finally form the liquid phase arise much slower with decreasing the quench depth. This is also supported by a comparison of the total kinetic energies $E_{\text{kin}} = \sum m_i v_i^2/2$ (shown in Fig. 4.5). The maximum value of kinetic energy is
located between $\tau_0$ and $\tau_1$ and decreases with increasing $T_0$. A further look on the inset box reveals, that for the simulation with $T_0 = 1.1$ local equilibrium could not be reached within the simulation time and the kinetic energy is even growing at $t = 50$. Therefore, this simulation is considered separately later on. A qualitative comparison between the remaining simulations regarding the arise of “homophase fluctuations” and the formation of “sponge”-like structures in the initial stage reveals a very similar growth behavior even though the temporal evolutions differ. However, in correspondence with the prolonged dynamical evolution it is clearly visible that not only the number of initially growing nuclei is lowered with increasing temperature but also the wavelength of the fluctuations increase. Thus, the interfaces between separated phases become broader and more diffuse. In the simulations with $T_0 = 0.95$ and upwards the interfaces of actually separated liquid drops are found to be diffuse enough to overlap (e.g., Fig. 4.6 and $T_0 = 0.95$ at $t = 20$ in the top left of the box). Moreover, the simulations suggest that high temperatures near $T_c$ (and therefore a long wavelength of the initial fluctuations and the increase in time of demixing) affect more of a nucleation-like demixing behavior than the SD. This phenomenon is also predicted by a theory discussed in Refs. [19, 8] (see also Fig. 2.4) and indeed already observed here at $T_0 = 1.1$. Such a formation of a spherical-shaped droplet is shown in Fig. 4.7. The cross-section is positioned at the center of the left droplet. At $t = 40$ a stable droplet with a homogeneous density inside and a diffuse interface is formed. The main portion of
kinetic energy of the system is in the interfaces. The fluid velocity vanishes beside the interfaces. A second droplet forms at the same time in a lower level of the box. It is barely identifiable in the density plot on the right-hand side of the box, but becomes visible in the temperature plot with velocity field vectors. The heating of the liquid and cooling of the vapor medium is also observed. In the further temporal evolution the temperature peak vanishes due to thermal conduction and results in a homogeneous temperature within the whole simulation volume. Also, the droplets do not remain static. At later times the nuclei grow and undergo coalescing processes as it does at deeper quenches.

The effects of the temperature field and thermostat shall now be studied in a more detailed manner. Therefore, the thermal evolution is plotted in Fig. 4.8 in the temperature-density phase diagram. Here the density and temperature values are also obtained as already described in the previous section. The dependency between quench depth and prolongation can be confirmed. The distances between the marked points at equidistant times with $\Delta t = 0.005$ become shorter in the initial stage of separation with higher $T_0$. This rapid change in the density values of the separated phases is coupled to the temperature by the caloric vdW-EOS. Thus, the liquid phase is heated and the vapor phase is cooled. The faster the phase separation occurs and, hence, the density changes, the stronger the temperature deviations become. In the further evolution $\rho_v$ and $\rho_l$ continue to approach the binodal and the temperature deviations vanish. Since the thermostat only scales the $T_i$ by a factor [see Eq. (4.14)] in order to satisfy the condition $\bar{T} = T_0$, it cannot level out the thermal fluctuations. Hence, this process must be due to thermal conduction, which explains also why the temperature deviations are higher at deeper quenches. The effect of conduction becomes too weak to compensate the cooling and heating of the phases that occur as a result of the change in density.

In the late-stage time regime, where DG is dominant, latent heat is fully released and, therefore, the thermostat becomes less important for the demixing process. In Fig. 4.9 the characteristic lengths for the liquid $\xi_l$ are shown. Because the curves actually overlap, they are shifted by an exponential temperature-dependent factor for reasons of clarity and better comparability. Concerning the growth rates,
it is found that the theoretical predicted LS mechanism is correct for the deeper quenched simulations. A time regime with a $\alpha = 1/3$ scaling, right after the initial stage, can be clearly identified for the simulations with $T_0 = 0.6$ up to $T_0 = 0.95$. This $1/3$-scaling either ends due to finite-size effects (as it is for $T_0 = 0.6$ and $T_0 = 0.7$) or the $1/3$ exponent changes to a value slightly around $2/3$, which is in accordance with the theoretical predictions for IH growth. Our simulations show that the transition time $\tau_2$, that marks the crossover, depends on $T_0$. One possible suggested dependency for this transition is highlighted with the bold bar in Fig. 4.9. Even the slight kink in the $T_0 = 1.0$ curve may be due the crossover between the two growth regimes. For lower quench depths the growth rate of $2/3$ appears immediately after the initial stage. See Appendix (see Sec. 4.5) for detailed listing of one possible realization of fit intervals and the corresponding fitted exponents.

This time dependency can also be interpreted with Fig. 4.6 in view. The domination of the hydrodynamic regime in the very late stage can be explained with the growth of $\xi$. It means that facing domains (actually still separated, but of the same phase) approach each other and coalescence becomes the dominant growth process over the coarsening. As it was mentioned above the width of the interfaces increases with increasing $T_0$. This might be understood in terms of surface tension $\sigma$, which is mainly responsible for the coarsening of the phases. A theoretical approach can already be derived from the vdW theory [7]. It takes the form $\sigma \approx (1 - T/T_c)^\gamma$, where $\gamma \approx 11/9$ [25]. Hence, for higher temperatures the surface tension decreases. Several studies show the capability of the vdW-SPH method to capture the surface tension phenomenon well [31, 38]. In addition, the theoretical
4.3 Simulation Results

Figure 4.9: Log-log representation of the evolution of the characteristic lengths $\xi_l$ for various temperatures in time [color coding as in Figs. 4.5 and 4.8, from $T_0 = 0.6$ (top) to 1.10 (bottom)]. For reasons of comparability the lengths are each shifted by a factor $E_0 = \exp((T_c - T_0)/\alpha)$ that depends on the initial $T_0$. The gray lines are guides to the eye and highlight the transitions from LS to IH growth (bold line) and the two growth rates of $1/3$ and $2/3$ (thin lines). Note that the growth of $\xi_l$ for deeper quenches is limited due to finite-size effects before the crossover to IH regime occurs.

expression for planar interfaces from vdW theory relates $\sigma$ to the thickness of the interface $L$, since it can be calculated by an integration of the square of the density gradient [97]. Based on the vdW theory, the density profile perpendicular to the interface can be described by a tanh($2\pi/L$) function and, therefore, the interface width diverges as $T$ approaches the critical temperature $T_c$ [98]. Moreover, the diffuse interfaces of separated domains overlap, such that they can interact hydrodynamically even if the drops are far away from each other. Thus, the interface thickness explains that the transition from LS to IH occurs earlier in time, and, therefore, depends on $T_0$. This transition point in time $\tau_2$ actually scales with the quench depth $(1 - T_0/T_c)$. To this a least-square regression is shown in Fig. 4.10. As it was discussed above the slope of the fitted curve should be determined by the mean distance between the separated droplets, i.e., taking the domain size and the interface width into account. Thus, changing the values of $\pi$ or $\beta$ would affect the interface widths and thus also the slope of the transition line. But the question as to which quantity can affect this transition line to shift in time must be addressed to the thermal conductivity. It is responsible for the compensation of thermal fluctuations and the driving force for the LS mechanism. In accordance with the results from thermal LB simulation [95], a higher value of $\kappa$ is expected to reduce the duration of the SD regime and could affect a shift of the transition line.

Figure 4.10 shows also the scaling behavior of the times $\tau_0$ and $\tau_1$. It also
supports the statement that the whole demixing process becomes slower with decreasing quench depth. The times of demixing $\tau_0$ and the point in time $\tau_1$, where $\xi_v$ reaches the minimum, can be fitted with an exponential growth (the simulation with $T = 1.1$ was not taken into account because of its spherical non-SD-typical nucleation growth behavior). This is in agreement with the results that are obtained from deep quench simulations of binary mixtures [83] where a similar correlation is found.

For a final remark, the pure thermal simulation ($T_0 = 0.8$, without thermostat) from Sec. 4.3.2 is compared to the results that are obtained with different quench depths and applied thermostat. As it was already mentioned, the initial demixing progress (concerning the wavelength of “homophase fluctuations”) is very similar to $T_0 = 0.8$ with thermostat. The differing further evolution might be due to the thermal heating. The comparison between Figs. 4.3 and 4.6 reveals a similarity to the $T_0 = 1.1$ simulation in a later stage. Indeed, the simulation without thermostat seems to cross between the thermostat simulations with the rise of temperature. That explains the observed $1/2$ exponent from Fig. 4.4(b). As it was already expected in the previous section, it is truly the result of an overlap between the $1/3$ LS growth, driven by the fluctuations that raised in the early time regime, and the $2/3$ IH exponent that occurs earlier in time for higher mean temperatures.
4.4 Conclusion

The SPH method in its modern formulation with extensions to vdW-EOS and thermal conduction is proved to capture the dynamics of phase transitions such as spinodal decomposition. This is even possible without complicated extensions such as density gradient forces or the separation of the vdW-EOS in short-range repulsive and long-range attractive components. Only minor improvements due to newest findings and developments to SPH such as the Wendland kernel and the thermostat are necessary. The internal energy and, therefore, also the thermal evolution is an inherent part of the method. Due to the massive parallelization algorithms the method provides the choice of very high resolutions (up to $\sim 10^7$). But in the context of phase separation it produces already satisfactory results with spatial and temporal resolutions that are even smaller by an order of magnitude than the resolution requirements for comparable mesoscopic simulation methods such as thermal-LB. Thus, the time range can be chosen much longer and the computational cost is reasonably low. A typical simulation run with $10^5$ particles and $T_0 = 0.8$ up to a time $t = 50$ is performed on 32 CPU and lasts about 48 h, and, thus the complete calculation of the initial SD regime at $t \approx 1$ is completed within 1 h.

The correctness of the SPH interpretations of the thermal conduction equation and the newly developed scaling thermostat are verified with a number of validation test cases with both, static and dynamic tests. The static test has shown that the thermostat corrects temperature deviations that arise by density estimation errors. The dynamical test reveals that for sensible results an adequate resolution must be chosen.

The dynamics of spinodal decomposition are studied both with a pure thermal simulation and with a scaling thermostat. It is found that “sponge”-like structures are formed in three dimensions. The pure thermal evolution is characterized by an increase in temperature in the initial stage due to latent heat. The growth rates are in accordance with the observations from the thermostat simulations. The initial quench depth is expected to determine the intensity of thermal fluctuations and, thus, the duration of the diffusive LS growth. With the increase in temperature, the interfaces broaden and IH growth becomes dominant. Therefore, a transition growth rate between the two regimes is found. This is expected to result from an overlap of the two growth rates. Although the pure thermal evolution seems more realistic with regard to experiments, this temporal overlapping of the growth regimes makes it more difficult to clarify the physical origins of the growth processes. But the comparison with simulations with various initial temperatures and applied thermostat supports the hypothesis of overlap. These simulations confirm the dependency between temperature and prolongation in the initial stage. The initial demixing is found to be strongly correlated with heating and cooling of the phases, where the deviations from the mean temperature become stronger if the quench depth increases. A crossover (which is also theoretically predicted) between the two growth mechanism (LS and IH) in the late stage time regime is
observed for several initial temperatures. Moreover, it is found that the time of crossover increases with increasing the quench depth and follows a scaling law. Thus, deep quenches show pure LS and low quenches pure IH growth. The line of transition might be shifted in time with changing the thermal conductivity. This is in accordance with results from thermal-LB simulations. For very low quenches (near the critical temperature) the dynamic becomes slower and the separation process is rather more nucleation like than SD which is also in accordance with theoretical predictions. We note that the described SPH method also produces SD-nucleation even at higher temperatures than here presented, but therefore the initial density should be set to a value below the spinodal.

For future works there are several appropriate investigations. For the reason of a better comparability with experimental results we expect that an extended thermostat model that allows finite quench rates will be straightforward. In this work we observe a correlation between the hydrodynamic interaction range and the interface width. We did not focus on it in detail, although it would improve the understanding of the role of hydrodynamics. But for this purpose it is rather reasonable to use a more simple model and to study therein the fluid flow and temperature field evolution of the late-stage IH regime. One possible model could be the coalescence of actually equilibrated liquid droplets in a vapor medium and vice versa. The vdW-SPH method is also a promising candidate for sensible dynamic simulations of evaporation phenomenons like hydrodynamic cavitation and jet formation.
Figure 4.11: Log-log representation of the evolution of the characteristic lengths for the temperatures $T_0 = 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.00, 1.05,$ and $1.10$ (from top to bottom) for (a) the liquid phase $\xi_l$ and (b) the vapor phase $\xi_v$. The curves are also shifted as described in the legend for Fig. 4.9. The fit intervals from Table 4.2 are each highlighted by enlarged (lighter) points and the corresponding fitted exponents are shown with straight lines.

4.5 Appendix - Fit intervals and exponents

In Fig. 4.9 only the characteristic lengths for the liquid phase $\xi_l$ are presented, whereas the $\xi_v$ are not shown. Moreover, the crossover between the different growth regimes is only schematically illustrated. For the sake of completeness, we present in Table 4.2 one possible choice of fit intervals and the corresponding fitted exponents for both, the liquid and the vapor phase. Note that the suggested time intervals represent only one out of many possible realizations. Therefore, the fitted exponents $\alpha$ are also just suggestions. In Fig. 4.11 the fit intervals and the corresponding growth rates are highlighted on the characteristic lengths for (a) the liquid and (b) the vapor phases.
Table 4.2: The exponents $\alpha$ (with asymptotic standard error $\delta\alpha$) are least-square fitted and refer to the characteristic lengths for the liquid phase presented in Fig. 4.9 and their corresponding lengths for the vapor phase.

<table>
<thead>
<tr>
<th>$T_0$</th>
<th>Time</th>
<th>$\alpha_l \pm \delta\alpha_l$</th>
<th>Time</th>
<th>$\alpha_v \pm \delta\alpha_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0.40 - 9.00</td>
<td>0.365 ± 0.001</td>
<td>0.40 - 9.20</td>
<td>0.390 ± 0.002</td>
</tr>
<tr>
<td>0.70</td>
<td>0.47 - 10.00</td>
<td>0.352 ± 0.001</td>
<td>0.47 - 10.20</td>
<td>0.379 ± 0.001</td>
</tr>
<tr>
<td>0.75</td>
<td>0.55 - 8.70</td>
<td>0.333 ± 0.001</td>
<td>0.55 - 8.70</td>
<td>0.403 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>10.7 - 13.7</td>
<td>0.443 ± 0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td>0.65 - 7.00</td>
<td>0.329 ± 0.001</td>
<td>0.65 - 7.00</td>
<td>0.424 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>7.01 - 10.9</td>
<td>0.671 ± 0.006</td>
<td>7.01 - 9.90</td>
<td>0.621 ± 0.004</td>
</tr>
<tr>
<td>0.85</td>
<td>0.81 - 5.70</td>
<td>0.404 ± 0.001</td>
<td>0.80 - 5.30</td>
<td>0.442 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>8.6 - 11.90</td>
<td>0.659 ± 0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>1.20 - 3.6</td>
<td>0.417 ± 0.002</td>
<td>1.20 - 9.60</td>
<td>0.482 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>3.90 - 5.40</td>
<td>0.619 ± 0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>1.70 - 3.10</td>
<td>0.386 ± 0.003</td>
<td>1.72 - 10.00</td>
<td>0.487 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>3.11 - 7.2</td>
<td>0.582 ± 0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>2.90 - 6.40</td>
<td>0.652 ± 0.002</td>
<td>2.90 - 8.70</td>
<td>0.617 ± 0.001</td>
</tr>
<tr>
<td>1.05</td>
<td>6.00 - 14.0</td>
<td>0.687 ± 0.002</td>
<td>6.00 - 16.5</td>
<td>0.766 ± 0.001</td>
</tr>
</tbody>
</table>

$^2$ Asymptotic standard error expresses the accuracy in accordance to the calculated characteristic lengths.
We report the influence of the strength of heat bath coupling on the demixing behavior in spinodal decomposing one component liquid-vapor systems. The smoothed particle hydrodynamics (SPH) method with a van der Waals equation of state is used for the simulation. A thermostat for SPH is introduced that is based on the Berendsen thermostat. It controls the strength of heat bath coupling and allows for quenches with exponential temperature decay at a certain thermalization time scale. The present method allows us to bridge several orders of magnitude in the thermalization time scale. The early stage is highly affected by the choice of time scale. A transition from exponential growth to a 1/2 ordinary power law scaling in the characteristic lengths is observed. At high initial temperatures the growth is logarithmic. The comparison with pure thermal simulations reveals latent heat to raise the mean system temperature. Large thermalization time scales and thermal conductivity are figured out to affect a stagnation of heating, which is explained with convective processes. Furthermore, large thermalization time scales are responsible for a stagnation of growth of domains, which is temporally embedded between early and late stage of phase separation. Therefore, it is considered as an intermediate stage. We present an aspect concerning this stage, namely that choosing larger thermalization time scales increases the duration. Moreover, it is observed that diffuse interfaces are formed during this stage, provided that the stage is apparent. We show that the differences in the evolution between pure thermal simulations and simulations with an instantaneously scaled mean temperature can be explained by the thermalization process, since a variation of the time scale allows for the bridging between these cases of limit.
The study in this chapter has been published in the article

- Martin Pütz and Peter Nielaba.
  *Insights from inside the spinodal: Bridging thermalization time scales with smoothed particle hydrodynamics.*

The original paper from Ref. [99] has been slightly revised and adapted for the publication in this thesis.
5.1 Introduction

The coexistence of separated phases, especially between liquid and vapor, but also separation of liquid mixtures or foam formation and growth, are fundamental dynamic processes in our everyday life. However, it is not yet fully clarified which physical processes are totally involved to it. The understanding of the dynamics of phase separation contributes to the understanding of even more complicated systems, such as in colloidal suspensions or polymer solutions. Still open issues concern the role of hydrodynamics and the thermal evolution of the phases from the very beginning on, when the fluid is still in the initial state and not separated. For the purpose of demixing, an initially stable system is quenched to an unstable state below the coexistence region. The quench is typically driven by a temperature change via coupling to an external heat bath, but also volume quenches are technically feasible. The depth of the quench defines the responding kind of demixing. Close beneath the coexistence region the state becomes metastable, which is the case for superheated liquids or supercooled vapor, and the separation occurs as a rare event induced by statistical superposition of fluctuations or by adding an external nucleus. As the quench deepens the system becomes completely unstable and a special type of phase separation takes place. It is called spinodal decomposition, wherein the system isotropically initiates to separate throughout the whole volume. A detailed review can be found in Ref. [8].

Once separated, the type of coupling to an external heat bath, computationally realized by so called thermostats [70], is also a decisive factor in the further evolution of the system. Thus, a very strong coupling results in isothermal systems [86] or, at least, quasi-isothermal with thermal fluctuations [100]. However, there is strong evidence for non-isothermal behavior [69, 78]. Contrarily, very weak coupling allows for a pure thermal treatment of the system, consequentially followed by the latent heating of the system [69]. The comparison between experimental practice [101, 102] and numerical [69], but also theoretical concepts [14], reveals a discrepancy. The limits of both pure thermal and instantaneous-scaling thermostats are hardly realizable. Therefore, the most natural and closest to experiment approach is to model a thermostat that allows for time dependent temperature relaxation at a certain rate.

One approach for the theoretical description is to implement all physical principles, that are relevant to the dynamics of phase separation. The demixing behavior of the system naturally arises from the principles, such as the cohesive pressure and covolume in the van der Waals (vdW) theory [7] for liquid-vapor systems. These basic ideas of vdW are further extended to binary mixtures, culminating in the phenomenological Cahn-Hilliard (CH) equation [14, 15]. The CH approach excellently reproduces the behavior of isothermal systems, but it does not include hydrodynamic interactions [103]. However, our approach is to describe the fluid flow with the hydrodynamic equations, which are given by a set of partial differential equations. The set is closed by the vdW equation of state (EOS) [104, 105]. This vdW-approach naturally provides surface tension and can intrinsically form
diffuse interfaces [78].

The dynamics of spinodal decomposition splits up in an early and a late stage, even though they are not clearly separated and depends on the actual choice of system parameters.

In the early stage spontaneous demixing occurs. The so called “homophase fluctuations” arise and depend on initial noise of density fluctuations. This growth of fluctuations happens very fast and is, therefore, hardly observable in experiments. A discussion about the growth and the importance of finite quench rates for realistic models can be found in Ref. [8]. However, in the further evolution a stagnation in the growth can occur, which is interpreted as an intermediate stage [106, 83, 86, 69, 107]. The late stage manifests, where the actually separated domains begin to grow. The growth of the characteristic length scale of the system can generally be described by ordinary power law scaling. Various former theoretical studies focus on predictions for the coarsening process in this late stage and the driving physical processes [23, 24, 79], whereas the actual growth rates are given by the diffusion driven Lifshitz-Slyozov (LS) growth [22] and the viscous (VH) and inertial hydrodynamics (IH) growth regime [21]. A crossover between regimes has been found [89]. Moreover, there is also evidence for a connection between the actual local temperature and the time of initialization of the hydrodynamic regime, such that the regimes can even overlay each other [78]. Since many investigations and comparisons exist concerning this late stage and has become a well studied phenomenon, only few exist for the early stage. Therefore, the main focus of our work will be on the dynamics of the latter.

We use the smoothed particle hydrodynamics (SPH) method for our simulations, which has several advantages in the context of phase separation compared to other simulation techniques. Thus, it allows us to directly follow the path of the separated phases through the phase diagram. Furthermore, the characteristic lengths of the domains are easily calculated without difficult calculations via structure factor and Fourier transforms [78]. Our simulation method expands the fund of methods for realistic treatment of spinodal decomposition and provides deeper insights to the physics involved in phase separation processes.

5.2 Method

For this work a modification of GADGET-2 [54], a massively parallelized tree based smoothed particle hydrodynamics (SPH) code, is used, originally written for astrophysical purposes. The modifications comprise a smoothing kernel, an equation of state that provides phase separation, a thermal conduction equation and an SPH thermostat. Here, only a brief summary of the governing equations and modifications of the basic SPH algorithm is given. More detailed descriptions of the concepts of SPH can be found in the latest reviews by Springel [28], Price [12], and Monaghan [39].
5.2 Method

5.2.1 Smoothed particle hydrodynamics

The SPH method is a Lagrangian based meshless particle method, which means, that the interpolation grid is not fixed, but given by comoving, so called, SPH-particles, where every particle is the origin of its own comoving reference frame. The objective of SPH is to solve the hydrodynamic equations, a set of partial differential equations. In Lagrangian formulation the first is the continuity equation, which is described by

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v}, \quad (5.1)$$

where $\rho$ is the mass density, $\mathbf{v}$ is the velocity and $d/dt = \partial/\partial t + (\mathbf{v} \cdot \nabla)$ denotes the convective derivative. Depending on whether viscosity is taken into account or not, the momentum equation is called the Navier-Stokes equation, or Euler equation, respectively, and is written as

$$\frac{d\mathbf{v}}{dt} = -\nabla P/\rho, \quad (5.2)$$

where $P$ is the pressure. For the Navier-Stokes equation, $P$ can be understood as the stress tensor. It additionally has viscous stress terms included. In contrast, in the case of the Euler equation, $P$ has only diagonal pressure entries. The third equation corresponds to the first law of thermodynamics $dU = \delta Q + \delta W$, where $\delta Q$ expresses the thermal exchange with an external heat bath and $\delta W$ is the work done in the system, the energy equation. In hydrodynamics, it is mostly described in terms of a specific internal energy $u$

$$\frac{du}{dt} = -\frac{P}{\rho} \nabla \cdot \mathbf{v} - \frac{1}{\rho} \nabla \mathbf{j}, \quad (5.3)$$

where $\mathbf{j}$ is the heat flux vector. Note that the traditional formulation of SPH is adiabatic, and therefore there is no heat exchange $\delta Q = 0$, although it is basically not obligatory and will be used in this work for the implementation of a thermostat. Thermal exchange within the simulation volume is given by the heat flux vector $\mathbf{j} = \kappa \nabla T$, where $T$ is the local temperature and the $\kappa$ is the thermal conductivity.

Following the main idea of SPH, the simulation volume is subdivided into a set of elements of a given constant mass $m$, the SPH particles. Every SPH particle is spatially extended, where a smoothing length $h$ determines the width of the smoothing profile, which is based on a Gaussian shaped kernel function. In practice, the Gaussian distribution itself is not first choice, whereas normalized polynomials with compact support are commonly used to enhance the computational efficiency. Here, the Wendland $C_4$ kernel

$$W(\mathbf{r}, h) = \frac{495}{32\pi} (1 - r)^6 (1 + 6r + \frac{35}{3} r^2) \quad (5.4)$$

is used, where $h$ is the smoothing length, $r = |\mathbf{r}|/h$ and $(\cdot)_+ = \max(0, \cdot)$ [46]. Thus the support of the kernel depends only on $h$. The class of Wendland kernels
has been shown to yield excellent results and has outstanding features compared to other common choices [45, 108]. The smoothed particles are penetrating each other and affect the behavior of their neighboring particles, within the smoothing range. Instead of integrating Eq. (5.1), the density is estimated by a summation over all SPH particles, where the masses contribute to the density with a weighting given by the kernel, thus, in practice, only the neighboring particles need to be considered. The estimation for a particle \( i \) reads as

\[
\rho_i = \sum_{j=1}^{N} m_j W_{ij}(h_i), \tag{5.5}
\]

where \( W_{ij}(h_i) = W(r_i - r_j, h_i) \). One of the main advantages of the method can be seen from Eq. (5.5). Since the number of particles in the simulation volume is constant and the kernel is normalized, the total mass of the system is conserved [12]. The smoothing length \( h_i \) is usually adaptively chosen and determined iteratively, such that the volume, defined by \( h_i \), encloses a constant mass [54], where the number of neighbors \( N \) has turned out to be a suitable initial parameter for this calculation. Note that any physical quantity can be expressed in an analogous way. The SPH expression of the spatial derivatives from Eqs. (5.2) and (5.3), but also for any other physical quantity, are also reduced to a sum, where the derivatives only operate on the kernel function, since the quantity is only scalar and the field properties are reduced to the kernel, of which the derivative can easily be calculated analytically. In the symmetrized formulation with adaptive smoothing lengths, Eq. (5.2) reads as

\[
\frac{dv_i}{dt} = -\sum_{j} \rho_j \left( f_i \frac{P_j}{\rho_i} \nabla_i W_{ij}(h_i) + f_j \frac{P_i}{\rho_j} \nabla_j W_{ij}(h_j) \right), \tag{5.6}
\]

where the \( f_i \) are correction factors, defined by

\[
f_i = \left[ 1 + \frac{h_i}{3\rho_i \, dh_i} \right]^{-1}. \tag{5.7}
\]

The SPH expression for the change of internal energy in Eq. (5.3) is subdivided into the work term,

\[
\frac{du_i}{dt} = \frac{f_i P_i}{\rho_i^2} \sum_{j} \rho_j \left( \mathbf{v}_i - \mathbf{v}_j \right) \cdot \nabla_i W_{ij}(h_i), \tag{5.8}
\]

and the heat term, which is the spatial derivative of heat flux and, therefore, a second derivative of the temperature [42, 43, 78]. It is given by

\[
\frac{du_i}{dt} = \sum_{j=1}^{N} m_j \left( \kappa_i + \kappa_j \right) \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|^2} \cdot \nabla_i \mathbf{W}_{ij}, \tag{5.9}
\]
where $W_{ij} = 1/2(W_{ij}(h_i) + W_{ij}(h_j))$ is the arithmetic mean between the two kernel values. The thermal conductivity $\kappa$ is modeled by a density dependency

$$\kappa_i = \kappa_0 \rho_i,$$

where $\kappa_0$ is a constant parameter [109]. The SPH method is known to produce unphysical behavior in the presence of shocks. In order to improve the method, the standard implementation of artificial viscosity in GADGET-2 is used [54]. The main idea is to suppress unphysical behavior in shocks, that arises, when SPH-particles approach each other. Artificial viscosity acts like real physical viscosity by an interparticle term

$$\Pi_{ij} = \frac{\alpha v_{ij}^s w_{ij}^2}{2\rho_{ij}},$$

which is added to the pressure in Eq. (5.6) and (5.8), with the artificial viscosity constant $\alpha = 1$ and a signal velocity is defined by $v_{ij}^s = c_i + c_j - 3w_{ij}$ with $w_{ij} = v_{ij} \cdot r_{ij}/|r_{ij}|$ (but only if $v_{ij} \cdot r_{ij} < 0$, otherwise $w_{ij} = 0$). The $c_i$ is an estimate of the sound velocity and $\bar{\rho}_{ij}$ is the arithmetic mean of $\rho_i$ and $\rho_j$. Note that artificial viscosity is only improving the numerical stability and must not be confused with real physical viscosity.

The set of hydrodynamic equations are closed by an equation of state (EOS). In the context of phase separation of one-component fluids, it is appropriate to follow the van der Waals (vdW) approach [7, 104, 105], which is given by two EOSs, namely the mechanic

$$P_i = \frac{\rho_i k_b T_i}{1 - \bar{b} \rho_i} - \bar{a} \rho_i^2,$$

and the caloric equation

$$u_i = \frac{\overline{k_b} T_i}{\gamma - 1} - \overline{a} \rho_i,$$

where $\overline{k_b} = 1, \overline{a} = 2.0$ and $\overline{b} = 0.5$, are the reduced units of the Boltzmann constant, the cohesive pressure and the covolume, respectively. Furthermore, the coefficient in the temperature term is set to $\overline{k_b}/(\gamma - 1) = 1$. The vdW theory predicts a certain unstable region, of which a system, quenched into this region, initiates to separate in liquid and vapor phases, where thermal equilibrium is reached on the so called binodal curve of phase coexistence. A quenched fluid becomes more and more inseparable with increasing temperature culminating in the critical point $(P_c, T_c, \rho_c)$, where the state of the phase becomes undefinable. The covolume and cohesive pressure can also be expressed in terms of the critical point; see, e.g., Ref. [78]. The vdW EOSs have already been applied to SPH for droplet formation, deformation, and coalescence [31, 33, 35, 36, 38]. All former studies have in common, that appropriate results were only produced if the force
calculation was split in long and short ranging components, with unequal smoothing lengths. From the SPH point of view, there is no explanation for this choice. It is also one of the advantages that must be addressed to the Wendland kernels, that produce excellent results without the splitting procedure [78].

The time integration is done by the kick-drift-kick algorithm. An adaptive time-stepping leapfrog scheme with excellent conservation properties is used, where the timesteps are chosen individually, based on a binary hierarchy [54], bounded by a maximum stepsize $\Delta t_{\text{max}}$. A detailed description of the time-step conditions, used herein, can be found in Ref. [78]

### 5.2.2 Thermalization by heat bath coupling

As mentioned in Sec. 5.2.1, it is not necessary to treat the simulations as adiabatic, where $\delta Q = 0$, but to model thermal exchange with an external heat source. These so called thermostats are common methods to treat temperature realistic in microscopic simulations, such as molecular dynamics (MD) or Monte Carlo [70]. The transfer of thermostats from MD to SPH is obvious, since the methods are very similar [71] and a simple scaling thermostat has already been applied to SPH [78]. The time-scale thermostat, used in the present work, is inspired by the Berendsen thermostat [72], a very common choice in molecular dynamics simulations. The thermal evolution of the mean temperature is given by the solution of the ordinary differential equation

$$\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T),$$  \hspace{1cm} (5.14)

where $T$ is the arithmetic mean, $\tau$ is a constant that defines the thermalization time scale and $T_0$ is the desired final mean temperature. For the calculation of $T$, Eq. (5.13) is used to assign a temperature to each SPH particle. The solution of Eq. (5.14) depends on the integration timestep $\Delta t$ and is given by

$$\bar{T}_{\text{new}} = (\bar{T}_{\text{old}} - T_0)e^{-\frac{\Delta t}{\tau}} + T_0,$$  \hspace{1cm} (5.15)

where $\Delta t = \max_i \Delta t_i$ and $\bar{T}_{\text{new}}(t) = \bar{T}_{\text{old}}(t + \Delta t)$. The new temperature $\bar{T}_i$ of a particle $i$ is then obtained by

$$\bar{T}_i = T_i \left(\frac{\bar{T}_{\text{new}}}{\bar{T}_{\text{old}}}\right).$$  \hspace{1cm} (5.16)

Due to energy conservation in the time integration the particles are only collectively updated according to Eq. (5.16) only at the maximum size of timesteps $\Delta t$.

Note that for molecular dynamics (MD) the Berendsen thermostat is known to suppress thermal fluctuations, which is true for microscopic simulation methods, but for our mesoscopic scheme, where only the overall mean temperature is scaled by the exponential factor to the desired value, thermal fluctuations are conserved.

If latent heat is released, then $\tau$ defines the half time of the process where the heat is conducted to the heat bath.
5.2 Method

5.2.3 Domain size analysis

The quenched system instantaneously initiates to separate in two phases, the liquid and the vapor phase, respectively. A quantity of interest is how the domain sizes evolve in time, that expresses the extent of decomposition. A common method, that is well established for spinodal decomposition of binary mixtures, is the analysis via the structure factor [8], where the mean domain size can be extracted from its first moment. This is indeed an acceptable method when the density of the phases is roughly the same and the concentration of two liquid species is considered. However, liquid-vapor systems differ in density and, therefore, the growth rates are also expected to differ. Moreover, the mean domain size is not efficient to characterize the dynamics of the system [66], especially for liquid-vapor systems. Therefore, the characteristic length shall be considered separately for each phase [78]. A natural ansatz for the SPH method is to define a threshold density value, usually the critical density \( \rho_c = 2/3 \), and divide in liquid and vapor particles, \( i_l \) and \( i_v \), respectively. The mean of minimum distances to the opposing phase is used to define the characteristic lengths, that belong to the certain phases. Thus, the characteristic length \( \xi_l \) for the liquid phase reads as

\[
\xi_l(t) = \frac{1}{N_l} \sum_{i_l} \min_{i_v} \| \mathbf{r}_{i_l}(t) - \mathbf{r}_{i_v}(t) \|,
\]

where \( N_l \) is the total number of liquid particles. Note that the characteristic lengths obtained from this definition leads to smaller values than those from conventional methods. For example, a spherical liquid droplet in a vapor medium had only a length of \( 1/4 \) of its diameter. However, the growth rates are not affected by this fact and it is only a linear effect. Furthermore, the analysis results are found to be in excellent agreement with theoretical predictions [78].

5.2.4 Initial conditions

The particles are initially glasslike distributed. For this purpose, a repulsive body force is applied to randomly distributed particles, which evolve in time until a relaxed state is obtained. Theupon, the particles are further relaxed by applying the SPH algorithm to the particles at a supercritical temperature, where the system is expected to be stable. The initial configuration is distributed in the described way with \( N_{\text{tot}} = 10^5 \) SPH particles, and \( T_0 = 1.5 \). The resulting homogeneous initial density \( \rho_0 = 0.5 \) is used for all simulations. This procedure has the advantage of very small fluctuations with a standard deviation of \( \sigma_\rho = 3.5 \times 10^{-4} \). Periodic boundaries are applied to a cubic box with side lengths \( L = 1 \). Thus, the total mass is \( M_{\text{tot}} = \rho_0 \ast L^3 = 0.5 \) and the particle mass is given by \( m_i = M_{\text{tot}}/N_{\text{tot}} \). The density specific thermal conductivity is set to \( \kappa_0 = 0.05 \), which causes the restriction \( \kappa(\rho) = \kappa_0 \rho \in [0, 0.1] \), because \( \rho \leq 2.0 \) due to the vdW theory. In order to reduce numerical errors, it is found that a reasonable maximum integration
timestep is $\Delta t_{\text{max}} = 5 \times 10^{-4}$, evolving up to $t_{\text{max}} = 50$, where all runs are eventually in local equilibrium. The number of smoothing neighbors for the kernel interpolation is set to $N = 250$.

### 5.3 Simulation results

The evolution of the early stage of spinodal decomposition is usually described by the rise of fluctuations. So far, the early stage received little attention compared to the late stage of domain growth and coarsening. The time scale of the thermalization shows to be responsible for the type of growth in the early stage. Therefore, it indirectly affects also the late stage. The process of thermalization also influences the evolution of the mass fraction between the phases, where shorter time scales lead to a faster mass allocation to the phases. The density evolution is also affected. A slow thermalization causes the once separated heated phases to evolve along the coexistence curve, as long as the relaxation to the desired temperature is in progress.

The simulations begin right after the instantaneous quench, which is realized by setting both thermostat parameters, namely the initial and the desired temperature $T_0$, to a value lower than the critical temperature, such that the system is completely unstable. First, the deep quenches with $T_0 = 0.8$ are presented, where the time scales $\tau$, defined by Eq. (5.14), are varied by several orders of magnitude between $10^{-4}$ and $10^1$. Additionally, a pure thermal (PT) simulation without any thermostat and a simulation with a scaling thermostat (ST) are also performed to facilitate the comparison. Due to the expectation, that the dynamics are affected by the actual system temperature, it is further examined by a comparison of several off-critical quenches of varying depths. For this purpose, simulations with the desired temperatures $T_0 = 0.6, 0.7, 0.8, 0.9$ and 1.0 are performed. For each temperature the time scale $\tau$ is varied from $10^{-4}$ to $10^1$ by factors of 10.

In Fig. 5.1 a comparison of the rendered densities of cross sections from snapshots of the early stage of decomposition for the $T_0 = 0.8$-quench is shown up to $t = 3.0$, when the phases are expected to already be separated and the late stage of domain growth has started in all simulations. The snapshots already reveal several features, which will be focused on in more detail later. It becomes apparent that all simulations are very similar in the early evolution, whereas the further evolution can generally be distinguished between two different types. This can mostly be seen by a comparison between the snapshots at $t = 1.5$ and 3.0, where the interfaces are still diffuse for the larger time scales $\tau \gtrsim 1$, such as $\tau = 10^1$ and $10^0$ and the PT simulation. In contrast, sharp interfaces are formed for the shorter time scales $\tau \ll 1$, particularly $\tau = 10^{-3}$ and $10^{-4}$ and the ST simulation. A transition point between these contrary images can qualitatively be placed at $\tau \approx 10^{-1}$. This particular run seems to start similar to the $\tau \gtrsim 1$ simulations, but eventually evolves similar to the $\tau \ll 1$ runs. Despite the respective evolution, all simulations have in common, that the phases, once separated, undergo a coarsen-
5.3 Simulation results

Figure 5.1: Density rendered cross-section slices (with thickness 0.02 in z direction and only half of the box in y direction is shown) of the early stage at the times \( t = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, \) and 3.0. Exemplarily the simulations with \( \tau = 10^1, 10^0, 10^{-1}, 10^{-2}, 10^{-3}, \) and \( 10^{-4} \) (from top to bottom), compared with the runs of pure thermal evolution (PT) and scaling thermostat (ST), are shown with a side length of size of the box \( L = 1 \). Note that the actual shapes of the 3D structures can not be determined in this 2D representation.

In Fig. 5.2 the phase diagram for the \( T_0 = 0.8 \)-runs is shown, wherein the median of the density values and the mean temperatures for the respective phase are plotted in steps of \( \Delta t = 0.05 \). The calculation starts with the exceed of the threshold density at \( \rho_c = 2/3 \), whereby this point in time is 0.35 and unaffected by the actual choice of \( \tau \). The use of the median of the density values, instead of the commonly used arithmetic mean, has some advantages. Mainly, it is the robustness to single strong density deviations, which is usually present, when diffuse interfaces are formed [78]. The respective similarities in the evolution between PT and large time scales \( \tau \gtrsim 1 \), and between ST and short time scales \( \tau \ll 1 \), are further assured by the evolution of the separated phases in the temperature-density phase diagram. The simulations ST, \( \tau = 10^{-4} \) and \( 10^{-3} \) almost perfectly coincide. Also the early evolution of PT and \( 10^1 \) evolve roughly equal. So far, it is clear, that the late evolution of the \( \tau = 10^1 \)-run must diverge from PT, because of the time scale thermostat that decreases the temperature. However, the process is very slow and these simulations do not reach the desired final temperature within the simulated time range. Note that the discrepancy between the end up vapor density values...
that is reached, corresponds to a higher temperature than the predicted characteristic for thermal simulations. The coexistence density of the liquid phase of the density dependent thermal conductivity in Ref. [78]. This must be addressed to the physically more accurate formulation from the PT and ST simulations in this work slightly differ from those obtained which is followed by an increase of the overall mean temperature. The results of heating of the liquid phase until the vapor is heated up to thermal equilibrium, possible for the heating of the vapor by the hotter liquid. This leads to a stagnation behind the liquid temperature. It can be explained by conduction, which is responsible for the heating of the vapor by the hotter liquid. This leads to a stagnation of heating of the system. In contrast, in PT simulations both phases, liquid and vapor, are observed to heat up, but with the vapor temperature temporally lagging behind the liquid temperature. It can be explained by conduction, which is responsible for the heating of the vapor by the hotter liquid. This leads to a stagnation of heating of the liquid phase until the vapor is heated up to thermal equilibrium, which is followed by an increase of the overall mean temperature. The results from the PT and ST simulations in this work slightly differ from those obtained in Ref. [78]. This must be addressed to the physically more accurate formulation of the density dependent thermal conductivity $\kappa(\rho)$, given by Eq. (5.10).

Both the $\tau = 10^1$ and $10^0$ runs show the stagnation of heating, which is actually characteristic for thermal simulations. The coexistence density of the liquid phase that is reached, corresponds to a higher temperature than the predicted $T_0$. Later and the theoretically predicted binodal value mainly belongs to the resolution, since the vapor phase has only very few particles. However, it also belongs to the choice of mean, because the median is namely very robust, but does not coincide with the peak value of the density distribution.

### 5.3.1 Early stage demixing

The behaviors of PT and ST are well examined [78, 69, 95], more precisely, the quasi-isothermal ST behavior, where the vapor and liquid phase are observed to contrarily cool down or heat up, respectively. This phenomenon becomes clear from Eq. (5.13), where the thermal conductivity is finally responsible for the equilibrium of the system. In contrast, in PT simulations both phases, liquid and vapor, are observed to heat up, but with the vapor temperature temporally lagging behind the liquid temperature. It can be explained by conduction, which is responsible for the heating of the vapor by the hotter liquid. This leads to a stagnation of heating of the liquid phase until the vapor is heated up to thermal equilibrium, which is followed by an increase of the overall mean temperature. The results from the PT and ST simulations in this work slightly differ from those obtained in Ref. [78]. This must be addressed to the physically more accurate formulation of the density dependent thermal conductivity $\kappa(\rho)$, given by Eq. (5.10).

Both the $\tau = 10^1$ and $10^0$ runs show the stagnation of heating, which is actually characteristic for thermal simulations. The coexistence density of the liquid phase that is reached, corresponds to a higher temperature than the predicted $T_0$. Later
5.3 Simulation results

Figure 5.3: The characteristic lengths of the liquid phase $\xi_l$ for $T_0 = 0.8$, plotted in steps of $\Delta t = 0.05$, additionally connected by lines. PT and ST are highlighted by open dots. The data sets are each vertically shifted by factors of $10^{0.1}$ due to a better comparability. The factor is also shown true to scale. The black lines indicate power laws to guide the eyes.

in progress, in the simulations with thermostat, the temperature decreases and evolves along the coexistence curve to the desired temperature. Solely, the PT run persists in that heated state.

The demixing process and the growth of the domains can be investigated by means of the characteristic lengths $\xi$, defined in Eq. (5.17). The lengths are shown in Figs. 5.3 and 5.4 for the liquid and vapor phase, respectively. For the reason of better comparability the curves are each shifted by factors of $10^{0.1}$. It is due to the initial density $\rho_0 = 0.5$ that per definition the one-component fluid is vapor in the initial state. That means in effect $\xi_v(0) = 1$, followed by a rapid decrease, whereas the liquid phase initiates at $\xi_l(0) = 0$, which further strongly increases. The initial state also determines the composition that eventually manifests in the separated system [100]. Here, a minor liquid phase in a major vapor phase is expected, which is why the main focus is on the liquid phase, whereas the vapor is only considered as solvent.

The early stage takes place right after the instantaneous quench, and the very early dynamics are dominated by the rise of so called “homophase fluctuations” [8], which arise from the initial noise of the density field. The point in time of demixing is unaffected by the choice of $\tau$. Therefore, it appears to suggest it also for the rise of fluctuations. However, the further evolution of the $\xi_l$-curves in Fig. 5.3 differ. It can be distinguished between the two beforehand mentioned different procedures. First, for ST and $\tau \ll 1$, the initial growth has rather more exponential growth character, which is followed directly by a power law scaling in the late stage. In contrast, for PT and for $\tau \gtrsim 1$, the initial growth seems to scale with an ordinary power law, which is followed by a plateau, where the growth of
Chapter 5 Insights from inside the spinodal: Bridging thermalization time scales

The characteristic lengths of the vapor phase $\xi_v$ for $T_0 = 0.8$, plotted in steps of $\Delta t = 0.05$ connected by lines (coding as in Fig. 5.3). The data sets are each vertically shifted by factors of $10^{0.1}$ due to a better comparability. The black lines are shown to guide the eyes. The inset shows a non-logarithmic plot of the $\tau = 10^{-2}$ curve in the early stage.

$\xi_l$ stagnates, also followed by the ordinary power law scaling of the late stage. It is obvious that the type of initial growth, whether it is described by an exponential or an ordinary power law, depends on the choice of $\tau$. The change is, as already qualitatively mentioned, placed at $\tau \approx 10^{-1}$, more precisely, between $\tau = 10^{-2}$ and $10^{-1}$.

Since this growth behavior in the early stage is also expected to be strongly affected by the actual temperature of the system, it will now be discussed in more detail by comparison of several quench depths.

The type of growth of the domains in the early stage is found to differ between the simulations. Interfaces become diffuse, unless the interfaces will not be formed before the intermediate stage. These are the simulations with slow thermalization $\tau \gtrsim 1.0$, which increase the temperature, or apparently those with the temperature already above the threshold, i.e. $T_0 \gtrsim 1.0$. In Fig. 5.5 a comparison of the early stages of the characteristic lengths $\xi_l$ for different quench depths is shown. As discussed in Appendix A (see Sec. 5.5), the $\xi_v$ are not suitable to realistically capture the growth behavior in the early phase, which is due to the initial rapid decrease of the curves. Therefore, only the lengths of the liquid phases are evaluated here. Representatively chosen for the fast and slow thermalization are the simulations with $\tau = 10^{-4}$ and $\tau = 10^{4}$, respectively. The $\xi_l$ in the very early stage are used for a least square regression. It turns out that the best fitting regression function strongly depends on both, the actual depth of the quench and thermalization time scale. The fitting parameters, which belong to the overlaying straight curves in Fig. 5.5, are listed in Table 5.1. The corresponding functions, that are used for the regression, are as follows. Three different types of growth can
be distinguished. An exponential increase $\xi \sim e^{\beta t}$, is observed for $\tau = 10^{-4}$ and deep quenched systems with $T_0 = 0.6, 0.7, 0.8, 0.9,$ and $1.0$. As $\tau$ becomes larger, the growth rates successively alter and follow an ordinary power law scaling, given by $\xi \sim t^\beta$. The best fitting values for this range of $\tau$ appear to suggest an exponent $\beta \approx 1/2$. For higher $T_0$ values, e.g., the $T_0 = 1.0$ run, the growth of fluctuations seems to be unaffected by the choice of $\tau$. Furthermore, the type of growth of the $\xi_l$ curves has changed to logarithmic scaling of the form $\xi \sim \log_{10}(\beta t)$, for both, $\tau = 10^{-4}$ and $10^1$, not least qualitatively, but also supported by the fitted values.

The differing behavior in the early stage can be clarified with a view on the temperature-density plane of the phase diagram, which is shown for all quenches in Fig. 5.6 for the simulations with $\tau = 10^1$ and $10^{-4}$. Note that the $\tau \ll 1$ simulations are very similar to the corresponding ST runs, for which, as recently described in Ref. [78], both phases evolve in different directions, forced by the caloric vdW EOS in Eq. (5.13). The volume expansion of the vapor phase causes a temperature decrease of the phase, and the liquid temperature increases, caused by the increase of $\rho_l$. Eventually, thermal conductivity forces the system to thermal equilibrium. However, the $\tau \gtrsim 1$ simulations show contrary behavior, because the mean temperature of the system is allowed to deviate from $T_0$, which is an effect of the slow thermalization. Therefore, the mean temperature is expected to finally evolve in the same direction of that phase that accretes most of the mass. Therefore, it depends on the initial $\rho_0$. In our setup, the liquid becomes the mass rich phase, whereas the vapor phase still tends to decrease the temperature. Therefore, the vapor phase gets heated through thermal conduction, which affects

\[1\] Asymptotic standard error expresses the accuracy in accordance to the calculated characteristic lengths.
Table 5.1: The parameters $\beta$ (with asymptotic standard error $\delta\beta$) are obtained via least square fitting of the $\xi_l$ in Fig. 5.5 within suggested best fit intervals. The expected types of growth are exponential (exp), power law scaling (scale) or logarithmic (log). The appearance of an intermediate stage is synonymous to the plateau in the $\xi$ curve.

<table>
<thead>
<tr>
<th>$T_0$</th>
<th>$\log_{10}(\tau)$</th>
<th>type</th>
<th>fit interval</th>
<th>$\beta(\pm\delta\beta)$</th>
<th>plateau</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>−4</td>
<td>exp</td>
<td>0.15 - 0.30</td>
<td>6.88(43)</td>
<td>no</td>
</tr>
<tr>
<td>0.7</td>
<td>−4</td>
<td>exp</td>
<td>0.20 - 0.40</td>
<td>4.56(25)</td>
<td>no</td>
</tr>
<tr>
<td>0.8</td>
<td>−4</td>
<td>exp</td>
<td>0.35 - 0.70</td>
<td>2.23(4)</td>
<td>no</td>
</tr>
<tr>
<td>0.9</td>
<td>−4</td>
<td>exp</td>
<td>0.90 - 1.60</td>
<td>0.73(1)</td>
<td>no</td>
</tr>
<tr>
<td>0.6</td>
<td>+1</td>
<td>scale</td>
<td>0.15 - 0.40</td>
<td>0.43(1)</td>
<td>yes</td>
</tr>
<tr>
<td>0.7</td>
<td>+1</td>
<td>scale</td>
<td>0.20 - 0.45</td>
<td>0.460(8)</td>
<td>yes</td>
</tr>
<tr>
<td>0.8</td>
<td>+1</td>
<td>scale</td>
<td>0.35 - 0.65</td>
<td>0.46(1)</td>
<td>yes</td>
</tr>
<tr>
<td>0.9</td>
<td>+1</td>
<td>scale</td>
<td>0.90 - 1.45</td>
<td>0.52(3)</td>
<td>yes</td>
</tr>
<tr>
<td>1.0</td>
<td>−4</td>
<td>log</td>
<td>4.05 - 5.55</td>
<td>0.401(3)</td>
<td>no</td>
</tr>
<tr>
<td>1.0</td>
<td>+1</td>
<td>log</td>
<td>4.10 - 5.25</td>
<td>0.430(5)</td>
<td>yes</td>
</tr>
</tbody>
</table>

1 Asymptotic standard error expresses the accuracy in accordance to the calculated characteristic lengths.

Figure 5.6: Phase diagram for several quench depths for the thermalization time scales $\tau = 10^4$ (open) and $\tau = 10^{-4}$ (filled) up to the simulation time $t_{\text{max}} = 50$. 

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the vapor temperature to generally lag behind the liquid phase in relation of the total heating of the system. A stagnation of heating in the liquid phase is observed for all initial temperatures except for the $T_0 = 1.0$ simulations. Note that the exceptional role of the latter also manifests in the differing type of scaling of $\xi_l$, which is logarithmic. It can be explained by the prolongation of the dynamics with higher system temperatures [78, 69], in the way that thermal conductivity already directly affects the demixing in the very early stage. Moreover, $T_0 = 1.0$ is above this temperature, where the heat stagnation can be observed in the remaining simulations.

The equilibration of the temperature imbalance in the early stage can be expected to be mainly driven by thermal conductivity, which is certainly true for $\tau \ll 1$ and for large $T_0$. For the $\tau \gtrsim 1$ range it is found, that also convective heat transfer plays a decisive role for spinodal decomposition [102]. Convective heat transfer is also responsible for the $\tau$ dependent reduction of the growth rate in Fig. 5.5. This can be seen from the liquid mass fraction, which is defined by

$$\mu_l = \frac{M_l}{M_{tot}},$$

where $M_l$ is the total mass of the liquid phase. It is due to our definition of the threshold density $\rho_c = 2/3$, that the liquid mass fraction initializes with $\mu_l = 0$, which is followed by a strong increase. A comparison of the liquid mass fractions for several quenches is shown in Fig. 5.7. Again, only the curves for $\tau = 10^{-4}$ and $\tau = 10^1$ are exemplarily shown, for $\tau \ll 1$ and $\tau \gtrsim 1$, respectively.

For the latter, a comparison with the temporal evolution in the phase diagram reveals an unexpected coinciding feature. Mass becomes not only reduced, but a backflow from liquid to vapor is observed in the $\mu$ curves. It takes place at
exactly the same time, when the stagnation of heating is observed for the deep quenched simulations $T_0 = 0.6, 0.7, 0.8$ in the phase diagram. The strength of this convection driven mass flow increases with the depth of the quench. The $\mu_l$ of the deep quenches further undergo local minima, followed by a slow increase until equilibrium is reached, whereas for $T_0 = 0.9, 1.0$ the backflow diminishes and only a halted increase is observed. The minima are found to take place at exactly the same time, where the liquid density starts to decrease in the phase diagram (see Fig. 5.6) at the reflection point. Moreover, the further evolution of the $\mu$ curves coincide with the time interval, where the plateau appears in the characteristic lengths.

However, for high temperatures the morphological evolution slows down and droplet nucleation dominates spinodal decomposition and the diffuse interfaces are formed simultaneously with the separation of the phases [78]. This leads to the instantaneous formation of spherical-shaped droplets. The mass backflow in the evolution of $\mu$ vanishes, e.g., at the $T_0 = 1.0$ curve, as it can be seen in Fig. 5.7. Additionally, a prolonging behavior of the dynamics is also observed for larger $\tau$, which must be mainly due to the rapid increase in temperature. In contrast, the thermal relaxation, back to the desired temperature $T_0$, in these systems is slow. Therefore, the temperature is allowed to exceed a certain threshold value, which is at $T_{th} \approx 1.0$, as it can be seen in Fig. 5.6.

### 5.3.2 Intermediate stage and diffuse interfaces

The physical origin of the stagnation of growth in the characteristic lengths $\xi_l$ in Fig. 5.3 temporally placed at $t \approx 1$, has been a basis for discussion. Thereby, this growth stagnation is expected to depend on several system parameters, such as surface tension, quench depth, thermal conduction, or intensity of the initial noise [83, 86, 69, 107, 110]. This growth stagnation will be further on referred to as plateau. However, the appearance and, therewith related, the duration of this plateau in the $\xi_l$ curves is strongly connected to the actual choice of $\tau$. It is not observed for $\tau \leq 10^{-2}$ and ST. Furthermore, it is associated with the beforehand described change in the type of scaling behavior of the early stage. The plateau becomes observable at $\tau = 10^{-1}$ and achieves longer durations for larger $\tau$ values.

An explanation for the plateau can be given by taking a closer look at the phase diagram in Fig. 5.2. It is placed right after the stagnation of heating at the reversal point of the liquid density. At this point the density is about to decrease and the temperature starts to increase again. For both runs, the $\tau = 10^1$ and PT, the density reaches a local maximum value at $t = 0.7$ and does not further increase until $t \approx 2.0$. The distinctness of the two reflection points in time appear to suggest it as an intermediate stage. During the time interval both phases, the liquid and the vapor, simultaneously decompress, which could plausibly be explained by two reasons. One is that both phases expand their volume. However, this is not possible due to the finite size of the simulation box. The second is that at least one phase excludes mass to form diffuse interfaces.
5.3 Simulation results

Exemplarily, the density histograms of the $\tau = 10^4$ and $10^{-4}$ runs for $T_0 = 0.8$ at different times are compared, as shown in Fig. 5.8. It reveals that the latter explanation is more reasonable. A movement of the peaks in the direction of lower densities is accompanied by the broadening of both the vapor and the liquid density distribution in the $\tau = 10^4$ data in Fig. 5.8(a). In the $\tau = 10^{-4}$ simulation in Fig. 5.8(b), the density peaks drift apart and the interface remains sharp even at late times. This can be seen in more detail from the inset box in Fig. 5.8(b), where a zoom to the vapor phase is shown. The expectation, that the phases are excluding mass to form interfaces for large $\tau$ and PT is supported by the inset box in Fig. 5.8(a), where the zoom to the liquid phase is shown. Along with the process of phase separation, the liquid peak is rising (light-red arrow), and moves in the following to a lower density value (dark-red arrow). Simultaneously, a second peak arises at the corresponding coexistence density (black arrow) as indicated by the arrows.

Therefore, the duration of the plateau in Fig. 5.3 is not only affected by the rapidity in achieving the coexistence density, but also by forming diffuse interfaces. As it is shown in Fig. 5.1, diffuse interfaces are only formed in simulations with large $\tau$ and PT, in contrast to the evolution of the remaining simulations. Thus, only for high temperatures $T \gtrsim 1.0$, interfaces become diffuse [78]. This is why the plateau can only be observed for simulations that exceed this temperature threshold. This even applies for simulations with higher initial temperatures but also for large $\tau$ values, since the latter allow for latent heating of the system. The temperature dependency will now be discussed in more detail.

As already mentioned above, the subsequent dynamic growth behavior is directly connected to the heating. It is characterized by two possible scenarios. Due to the actual choice of $\tau$ the late stage can directly follow the early stage. The domain growth in the late stage can then be described by theoretically predicted scaling laws. A detailed discussion can be found in Appendix B (see Sec. 5.6).
the second scenario, an intermediate stage occurs, which manifests in the formation of a plateau in the $\xi_l$ curves. The intermediate stage is placed right between the early stage, where homophase fluctuations arise, and the late stage, where coarsening and domain growth are the dominant processes. It shall be clarified here how the occurrence and the duration of this intermediate stage is affected by both, quench depth and the choice of $\tau$.

It has already been clarified in the previous section that the plateau can only be observed for a certain range of parameters, such as $\tau \gtrsim 1$. This is assured by the $\xi_l$ curves in Fig. 5.5, where the plateau is only apparent for the $\tau = 10^1$ curves. The appearance of the plateau is correlated to the formation of diffuse interfaces. A further quantification is given with the phase diagram in Fig. 5.6. The plateau starts exactly at the reflection point $t_1$, where the density value of the liquid phase $\rho_l$ begins to decrease. The end of the intermediate stage is given by the second reflection point $t_2$, where $\rho_l$ initiates to reincrease. The corresponding time interval, defined by the two reflection points, gives a duration $\Delta t_{\tau,T_0}$, which depends on the actual choice of $\tau$ and $T_0$. The values for those simulations, where the intermediate stage is apparent, are summarized in Table 5.2. They are additionally visualized in Fig. 5.9, where the relevant region in the phase diagram is shown. It can be seen, that this phenomenon only occurs in the metastable region, between the spinodal and binodal curves. Moreover, it is an effect of slow thermalization, where the largest $\Delta t_{\tau,T_0}$ are found for the PT runs and become smaller with decreasing $\tau$. Note that the first inflection points $t_1$, obtained via the phase diagram, are all consistent with the end times of the fit intervals of the early stage scaling analysis, given in Table 5.1. The PT and $\tau = 10^1$ have identical $t_1$ values. The intermediate stage becomes smaller with shorter thermalization time scales and eventually vanishes at $\tau = 10^{-1}$. That shows that the intermediate stage is a phenomenon of systems of weak heat bath coupling.

5.4 Conclusion

Our investigation mainly focuses on the dynamics in the early and intermediate stages of spinodal decomposition. The late stage is expected to only slightly influence the actual separation process, since it is dominated by the growth of domains of the already separated phases. Moreover, the late stage is probably the already best investigated of these three stages. The therein involved physical processes are well understood and can be described by scaling laws for the growth of the characteristic lengths. However, the dynamics through the meta- and unstable regions, which lie below the binodal and spinodal curves, respectively, are placed in the early and intermediate stages of the separation process. There is a lack of knowledge concerning the thermal evolution and its effect on the dynamic evolution in that stage. Moreover, the respective temperature evolution is also influenced by the strength of coupling to an external heat bath.

The SPH method, which is herein used for the simulations, can give deeper
Table 5.2: The table gives the time interval $\Delta t_{\tau,T_0}$ that corresponds to the two reflection points $t_1$ and $t_2$ in the evolution of the liquid phase. Listed are only the simulations, where the intermediate stage exists.

<table>
<thead>
<tr>
<th>$T_0$</th>
<th>$\log_{10}(\tau)$</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$\Delta t_{\tau,T_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>PT</td>
<td>0.50</td>
<td>2.35</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.50</td>
<td>1.75</td>
<td>1.25</td>
</tr>
<tr>
<td>0.7</td>
<td>PT</td>
<td>0.55</td>
<td>2.35</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.55</td>
<td>2.10</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>+0</td>
<td>0.7</td>
<td>0.90</td>
<td>0.20</td>
</tr>
<tr>
<td>0.8</td>
<td>PT</td>
<td>0.65</td>
<td>2.75</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>0.65</td>
<td>2.65</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>+0</td>
<td>0.90</td>
<td>1.35</td>
<td>0.45</td>
</tr>
<tr>
<td>0.9</td>
<td>PT</td>
<td>1.55</td>
<td>4.25</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>1.55</td>
<td>3.40</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>+0</td>
<td>2.00</td>
<td>2.50</td>
<td>0.50</td>
</tr>
<tr>
<td>1.0</td>
<td>PT</td>
<td>6.20</td>
<td>9.70</td>
<td>3.50</td>
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<td></td>
<td>+1</td>
<td>6.25</td>
<td>7.15</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Figure 5.9: Evolution in the phase diagram for several quench depths and thermalization time scales, where the intermediate stage is apparent. Color coding as in Fig. 5.6. The time intervals $\Delta t_{\tau,T_0}$ are highlighted.
insights to the thermal evolution of the early phase. Moreover, it is easy to follow the evolution of the separated phases in the phase diagram, and characteristic lengths can easily be calculated by the use of the SPH method. Besides, the computational effort is very modest, as a typical single simulation with $10^5$ particles on 48 cores only takes about 15 h.

An exponential decaying thermostat is introduced that allows for the predefinition of a thermalization time scale, on which the heated system relaxes to a desired temperature. The comparison to an instantaneous scaling thermostat shows that the respective choice of the thermostat has a serious effect on the resulting dynamics of the phase separation process. Moreover, the scaling thermostat can be understood as a system with very fast thermal relaxation, as well as in the opposing limit a very slow relaxing system can be understood as a pure thermal simulation. This is shown by a successive variation of the time scale. Note that the matches with these limits are observed to be independent from the actual temperature of the system. The final equilibrated states are in excellent agreement with vdW theory and unaffected by the strength of coupling. The meaningfulness of varying the thermalization time scale is clarified by a closer view on these limits. Isothermal simulations are close to theoretical approaches, which have mostly only phenomenological nature and are, therefore, hard to put into practice. In contrast, a pure thermal evolution is experimentally unrealizable, since already the quench to the spinodal region must be performed. Therefore, it is more realistic to consider systems in between, which allow for both, latent heating and thermal relaxation at a certain time scale.

In contrast to the common analysis methods, the requirement for a separated analysis of the liquid and vapor phase is stated. A comparison of the evolution of fast thermalization systems in the phase diagram shows that the two phases evolve contrarily in both, density and temperature.

In the early stage, the type of growth of the characteristic lengths differs by the actual choice of thermalization time scale. Short time scales show a fast exponential increase in the characteristic length, whereas at long time scales the lengths grow slower, which is described by an ordinary $1/2$ power law. The slower growth rate arises from a mass transfer between the phases which is directed contrary to the expected demixing behavior. The mass flow, which is directed backwards from the arising liquid phase to the vapor phase, is interpreted as thermal convection. In systems with high temperatures the type of growth is independent of the time scale, where the fit calculations suggest a logarithmic scaling behavior.

In slow thermalization systems, the system temperature initially increases due to latent heat followed by a stagnation of that increase in temperature in the liquid phase, while the density further increases. This is not observed at short time scales. By comparison, the nearly identical evolution of pure thermal simulations shows that the stagnation of heating is no effect of the thermostat. It is rather driven by thermal conduction, where the colder vapor phase tends to retard the increase in temperature. Additionally, an intermediate stage appears in systems
with slow thermalization, where the growth of the characteristic lengths is reduced and forms a plateau. This halted growth is explained by the formation of diffuse interfaces between the separated phases. They only form at high temperatures, which explains that the plateau appears either at systems that already reached high temperatures or at systems that heat up.

The thermalization thermostat excellently closes the gap between the pure thermal and scaled temperature simulations. This is not only assured by a comparison of the snapshots, but also by the evolution in the phase diagram and by the comparison of the characteristic lengths. At short time scales the results are nearly identical to the scaling thermostat even up to the late stage. The large time scales converge to the pure thermal simulation only in the early and intermediate stage. The late stage must differ, which is due to the absence of a thermal relaxation process in PT simulations. However, it is clear that simulations with even larger time scales will also excellently match with the late stage.

For a realistic dynamic behavior, the time scale must be chosen carefully in between the range of the two limits. It is shown that the strength of coupling has a serious impact on the dynamics while the system is in a completely unstable or, at least, metastable state. Moreover, this argumentation is also shown to be supported by the qualitative comparison with both experimental and numerical results of other studies. Thus, the SPH method equipped with the time scale thermostat provides a powerful instrument for the simulational modeling of phase separation dynamics.

5.5 Appendix A - Distinction between liquid and vapor

It is not only the initial density, but also the involvement of temperature and, therewith associated, the strength of coupling to the heat bath that are observed to affect the scaling of the domains. The direct comparison between \( \xi_v \) and \( \xi_l \) of the same \( \tau \) value further emphasizes the requirement for a distinction between the two phases, e.g., the different power law scalings in the late stage or the differing final equilibrium lengths, where the \( \xi_v \) is generally larger than the belonging \( \xi_l \). The latter fact is more distinctive in the curves for \( \tau \gtrsim 1 \) and PT. The differences in the curves is also mainly due to the asymmetry of the quench and the resulting density distribution.

Note that the plateau can also be observed in the \( \xi_v \) curves of the weakly coupled systems, plotted in Fig. 5.4. It is due to the assumption, that both phases are involved to interface formation, as it can be seen in Fig. 5.8(a). The characteristics of the vapor \( \xi_v \) curves are generally very similar to that of \( \xi_l \), but less distinctive than the characteristics of the \( \xi_l \) curves. Due to the rapid decrease of the \( \xi_v \) in the early stage, the type of scaling of initial rise of fluctuations can hardly be worked out from the vapor phase. Moreover, for the large \( \tau \) and PT simulations, the plateau, where the interfaces are formed, is less distinctive in the \( \xi_v \), than it is in the \( \xi_l \) curves.

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Nevertheless, it must be noted that the characteristic lengths are in excellent qualitative agreement with observations from experiments of spinodal decomposition of binary mixtures by Poesio et al., where the effect of the quenching rate on the demixing process is investigated [101]. The inset in Fig. 5.4 exemplarily shows a linearly scaled part from the early stage of demixing of the $\tau = 10^{-2}$ curve, which can be qualitatively compared. Even the initial rapid decrease of the curve and a plateau like stagnation in growth, which is due to their evaluation method via structure factor, can be confirmed by our data. Poesio et al. postulate a linear growth law for the late stage regime, which indeed might be suggested for the small time range, where the growth process is observed. Our simulation method allows us to evolve the system much longer in time, which allows us for a better estimation of the late stage scaling behavior.

5.6 Appendix B - Late stage domain growth

Theoretical predictions for late stage domain growth rates, are mainly given for symmetric quenches in binary mixtures and have recently been shown by simulations to deviate in asymmetric quenches [26]. Moreover, the similarity between binary mixture and liquid-vapor is only valid for such symmetric quenches. However, a symmetric mass distribution can hardly be preset in liquid vapor systems, which is contrary to binary mixtures, where a critical quench predetermines the end up composition. Therefore, the resulting growth rates differ from theoretical expectations. Also, the yielded growth exponents strongly depend on the size of the respective choice of fit intervals [100]. For these reasons, it must be emphasized that we do not claim for the observation of new growth exponents, but rather use the existing predictions for our interpretation.

The late stage, where the phases are eventually fully separated, is dominated by the coarsening and the coalescence of droplets. It is expected that the time evolution of the characteristic domain size $\xi$ can be described by a scaling law $\xi \sim t^\alpha$. The value of $\alpha$ gives rise to the actual physical process, that is responsible for the respective growth behavior. The driving processes are namely, the diffusive LS regime ($\alpha = 1/3$), the VH ($\alpha = 1$), and the IH regime ($\alpha = 2/3$) [21]. Note that our simulations have no physical viscosity included, hence, the VH regime is none of the expected regimes here. Thus, it is only expected to observe exponents localized between 1/3 and 2/3. As it was already mentioned, we do not claim new exponents. Therefore, only slope expectations are shown in Figs. 5.3 and 5.4 to guide the eyes. However, for large $\tau$ and PT, for which the mean temperatures significantly increase, the physical processes that are responsible for the scaling regimes, are expected to overlap. They give rise to a variation of the exponents, because the IH regime becomes relevant earlier at higher temperatures [78]. Furthermore, it has recently been shown that growth rates are strongly connected to the actual temperature of the system[69, 78]. In comparison with our earlier works the exponents from this work are in very good qualitative agreement. Both,
the type of growth in the early stage and the formation of the plateau, must be considered to affect the late stage scaling behavior.

The respective choice of \( \tau \) affects the final mass distribution between the phases. For \( \tau \ll 1 \), the mass separates instantaneously and also the \( \rho_l \) and \( \rho_v \) reach their final coexistence values. In the case of \( \tau \gtrsim 1 \), the demixing process lasts much longer, so that the masses do not reach the final fraction at the end of the simulations. This prolonged demixing behavior is also in qualitative agreement with the results of other numerical simulations [69]. Moreover, mass transfer is apparent even in the late stage, indicating that the growth processes in the late stage are overlayed by early stage processes. This is one more reason for the difficulty in using theoretical predictions for the late stage, when thermal processes are taken into account. Note that the very final mass fraction in the totally equilibrated state is hard to predict from the beginning. It is not only predefined by \( \rho_0 \), but also by the \( T_0 \) and \( \tau \). Since thermal conduction is present in both the simulations with small and large \( \tau \), the thermal balance for the latter must be rather driven by convection than by conduction. Furthermore, the characteristic mass transfer, which is given by \( \mu_l \), is not observed in the \( \tau \ll 1 \) simulations. Thus, convection only appears if the latent heat from the phase separation process is not led away fast enough.
The aim of this thesis is to give a better understanding of the fundamental processes of spinodal decomposition in liquid-vapor systems. For this purpose, simulations were performed taking the hydrodynamic equations with the van der Waals equation of state, thermal conduction, and coupling to an external heat bath by a thermostat into account. As a first step towards this work, an existing program package (namely the astrophysical hydrodynamics code GADGET-2) was modified by the aforementioned extensions to apply for one component multiphase systems. The basic numerical method that is herein applied to spinodal decomposition for the first time is the smoothed particle hydrodynamics method, which shows to have some benefits in the context of simulating dynamics of phase separation. For instance, it already allows us to follow the evolution of the temperature and gives easy access to local densities. Therefore, it is possible to directly decide whether a certain region is vapor or liquid. Furthermore, the evolution of each of the phases in the phase diagram, even in the very early stage of the separation where the phases are still in an unstable state, can easily be observed. Due to its rapid exceed, this initial growth of fluctuations is hardly observable in experiments. Moreover, the smoothed particle hydrodynamics method is shown to allow for simulating through all stages of the demixing process in one single simulation. The three time regimes of demixing are the early stage, an intermediate stage, and the late stage. Although, the intermediate stage is theoretically not fully justified by a certain physical process, there is experimental and numerical evidence for such an intermediate stage, such as that the domain growth shows unexpected behavior, usually a stagnation of growth. The late stage is certainly the best investigated regime. Corresponding to the observation of a certain domain growth rate, a respective theoretically predicted physical processes can be assigned that arise from the scaling assumption. The herein expected driving physical processes
are the diffusion driven Lifshitz-Slyozov scaling regime, where the mean domain size grows proportional to $t^{1/3}$, and the hydrodynamic regime, which splits up in viscous and inertial hydrodynamic regime, scale with exponents $1$ and $2/3$, respectively. However, it must be emphasized that these predictions are based on isothermal assumptions by neglecting temperature effects and were originally formulated for binary liquid-liquid mixtures.

By additionally taking the temperature into account this classical picture is expected to completely change, even more when considering a liquid-vapor decomposition. In fact, it is an overall finding in all simulations performed with this method, that the liquid and vapor phase must always be treated separately. This statement challenges the conventional wisdom that spinodal decomposition in liquid-vapor system (with an asymmetric phase diagram) is comparable to that of binary mixtures (with a symmetric phase diagram). However, the two phases behave totally different, which is mostly due to the change of the densities in the early stage. A rapid decrease of density of the vapor phase in the early stage tends to cool down the system temperature. In contrast the liquid phase, where density increases, tends to increase the temperature. Eventually, the thermal equilibration is driven by the thermal conduction. However, it becomes not only apparent from the phase diagram but also from the very different growth rates that are obtained for the two phases. Therefore, the investigations are focused on one phase and expect the other as the surrounding medium, where a meaningful decision always depends on the actual initial condition.

In the first study of this thesis, simulations were performed introducing a simple scaling thermostat that instantaneously scales the mean system temperature to a predicted temperature (published in Ref. [78]). This investigation mainly focuses on the effect of the quench depth on the late stage domain growth behavior, where the densities already have reached their coexistence values and the domain growth is found to be rather unaffected by thermal fluctuations. Temperature scaled simulations with differing quench depths, i.e. different temperatures, were compared. The numerical method is shown to excellently reproduce the late stage behavior concerning the theoretical predictions in this quasi-isothermal environment. A transition from the diffusion driven time regime (which scales with $1/3$) to the inertial hydrodynamics regime (with the exponent $2/3$) is observed. An exceptional role play the simulations near the critical point where liquid droplets are observed to nucleate directly in a spherical shape. The time of the transition between the growth regimes is found to occur earlier for higher initial temperatures. Thus, for deep quenches purely diffusion driven growth is observed, whereas for shallow quenches the domain growth is mainly driven by hydrodynamics. We explain the time dependency with the interfaces between the phases that become more diffuse and overlap when approaching the critical point. A prolonging behavior of the demixing process is observed and also concluded to depend on the actual temperature. It is further found that the observations can excellently explain the growth behavior of pure thermal simulations that were performed without a thermostat. The pure thermal simulation heats up due to latent heat and the therein suggested
growth rates can be explained by an overlap of the two regimes.

In a second study the influence of the strength of heat bath coupling on the demixing behavior in spinodal decomposing one component liquid-vapor systems is reported (published in Ref. [99]). This investigation mainly focuses on the early and the intermediate stage, since these stages were shown to be strongly affected by effects of temperature. For this investigation another thermostat was introduced that is based on the Berendsen thermostat. It controls the strength of heat bath coupling and allows for quenches with exponential temperature decay at a certain thermalization time scale. In this form, the present method allowed us to bridge several orders of magnitude in the thermalization time scale. The early stage is highly affected by the choice of time scale. A transition from exponential growth to a $1/2$ ordinary power law scaling in the characteristic lengths is observed. At high initial temperatures the growth is logarithmic. The comparison with pure thermal simulations reveals latent heat to raise the mean system temperature. Large thermalization time scales and thermal conductivity are figured out to affect a stagnation of heating, which is explained with convective heat transfer. Furthermore, large thermalization time scales are responsible for a stagnation of growth of domains, which is temporally embedded between early and late stage of phase separation. Therefore, it is considered as intermediate stage. Concerning this stage, a further aspect is presented, namely that choosing larger thermalization time scales increases the duration of it. Moreover, it is observed that diffuse interfaces are formed during this intermediate stage, because they only form along with the heating at higher temperatures, and provided that the stage is apparent. As a last universal finding it is shown that the differences in the evolution between pure thermal simulations and simulations with an instantaneously scaled mean temperature can excellently be explained by the thermalization process, since a variation of the time scale allows for a continuous bridging between these two cases of limit.

**Outlook**

The studies presented in this thesis show that the smoothed particle hydrodynamics method in the present extended form is perfectly suited for the simulation of phase transition phenomena. Various subsequent investigations can be imagined.

Obviously in this work the initial density has been set to one single value. However, there is reason to assume, that another initial density strongly affects the demixing. Moreover, so far, the simulations neglect physical viscosity, which should, however, be considered for a realistic environment. Thus, a separate study on these cases would be necessary clarifying the role of viscosity and initial density.

Furthermore, in this work the simulations always start right after the quench (which actually means an infinite quench rate). However, the method could also perform simulations with finite quench rates. When a quench is performed at finite rate, the density fluctuations already start to rise and the phases initiate to
separate even before reaching the desired quench depth. This would give a more realistic picture of the whole process and make it more comparable to experimental results that need to be of course quenched at finite rates.

Another future perspective is to perform simulations of shocks. So far, analytic solutions of shock propagation in a medium are normally assuming an ideal gas. However, those shocks can also be studied using the van der Waals equation of state, especially for the case of a dense gas or a liquid. Thereby, this method is a promising candidate for simulations of shock induced phase transitions, such as evaporation or cavitation.

At last, although it was not mentioned herein, coalescing droplets were observed to build temperature bridges in the moment right before they were actually coalescing, and the vapor between the droplets was pressed outwards. There is experimental evidence for the vapor behavior (see e.g. [111]). We expect the diffuse interfaces of separated droplets to overlap before droplets coalesce. Due to this expectation, this hydrodynamics interaction should be studied in an additional study on droplet coalescence.


Bibliography


Bibliography


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List of publications

Refereed articles

- Martin Pütz and Peter Nielaba. 
  *Effects of temperature on spinodal decomposition and domain growth of liquid-vapor systems with smoothed particle hydrodynamics.* 

- Martin Pütz and Peter Nielaba. 
  *Insights from inside the spinodal: Bridging thermalization time scales with smoothed particle hydrodynamics.* 

Conference proceedings

- Marcus Beck, Andreas Haller, Daniel Kawetzki, Manuel Matt, Martin Pütz, Markus Ring, Ralf Schmid, Kristian Scholz, Ullrich Siems, and Peter Nielaba. 
  *Structures and phases in (nano-) systems in confined geometry.* 
  NIC Symposium 2016, pages 229-239, 2016 (see Ref. [112]).