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MASTER'S THESIS

Theory of gas bubbles around heated nanoparticles

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Abstract

Vapor generation by hot nanoparticles in liquid has attracted recent interest and different experiments have been performed to study it. Although equilibrium systems are properly understood, these non-equilibrium fluids with temperature gradients remain theoretically poorly explored. This thesis introduces the required theory to describe such systems and gives a thermodynamical analysis of the dynamics that are involved. Different systems are simulated, corresponding to different experiments, and their results are presented and discussed. Interestingly, although these fluids are not in equilibrium, it turns out that on a picosecond timescale one can still define their thermodynamic state.

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1 Introduction

Heating of nanoparticles immersed in liquid has recently gained a lot of attention, ranging from generating vapor by solar heated nanoparticles [1] to the kinetics of nanobubbles induced by laser excited particles [2, 3]. These systems are promising tools for a wide variety of applications, and many aspects of the dynamics governing these systems are yet to be discovered. In a recent article (2013) by Neumann et al. [1] the results of an experiment are shown where carbon or metal nanoparticles (with a radius of about 100 nanometers) in liquid water at room temperature generate vapor when exposed to sunlight. Within a few seconds after exposure, steam temperatures well above 100°C are observed without the liquid water heating up. Since no energy is lost to the heating of the water to its boiling point, the steam generation is very efficient. This system allows for small scale solar power generation, sterilization and also yields possibilities for solar distillation. With nanoparticles dispersed in an ethanol-water mixture, distillation yields a distillate substantially richer in ethanol than what would be obtained using conventional heat sources [1]. Other works on the subject include Ref. [2, 4](2015) covering a thermodynamic analysis of the short-lived nanobubbles around gold nanoparticles (10 nm) heated up by femtosecond laser pulses. These systems have been investigated experimentally [3] and the existence of such vapor bubbles has been confirmed. Due to their biochemical compatibility, gold nanoparticles can accumulate in diseased areas and the bubbles can be used to manipulate and destroy cancer cells. The size of the bubbles is of the order of several nanometers allowing very localized destruction of cellular structure.

The article about the solar vapor experiment [1] gives some estimates of quantities like bubble size and the amount of generated vapor. A rigorous theoretical model to describe this system, however, is not provided. The lack of a theoretical analysis of nanoparticle heating was the main motivation for the research done for this thesis. Although equilibrium (inhomogeneous) fluid systems are well understood, the behavior of systems with temperature gradients has not been covered as much.

The goal of this research is to explore the dynamics of vapor bubbles around nanoparticles in water, including both the kinetics and steady state behavior. A sketch of the system is shown in Figure 1. The system is assumed to be spherically symmetric and instead of considering the dynamics of heating up the nanoparticle, the scope of this research is limited to the behavior of the liquid when an (effective) heat flux is applied to the system.

The steady state solutions of the system are interesting considering the vapor bubbles in the solar heating experiment. These bubbles are stable as long as they surround the hot nanoparticle. As such, the bubble together with the nanoparticle rises to the surface of the container so that the vapor can be released and the nanoparticle sinks back down after which the process is repeated. One objective of this research is to calculate the required amount of heat to be emitted from the nanoparticle in order to sustain a stable vapor bubble and thus find a relationship between the amount of emitted heat and the size of a *steady state bubble*. These results can subsequently be compared to the estimates given in Ref. [1].

Another objective is exploring the *kinetics* of vapor bubble nucleation. When gold nanoparticles are excited by a laser pulse, a vapor bubble nucleates but only lives during an extremely short timescale when compared to the bubbles in the solar experiment. For nanoparticles with a radius of 10 nanometer, the vapor bubbles have a radius that is not much larger than two or three times the nanoparticle radius and only live for a few hundreds of picoseconds. Density and temperature profiles, heat fluxes and bubble pressures are just some of the quantities that will be investigated and compared with recent results in Ref. [4].



Figure 1: Sketch of the system studied in this research: a nanoparticle surrounded by a layer of vapor, immersed in liquid water. The nanoparticle can emit energy in several ways, for example by a (picosecond) heat pulse or a continuous constant flow of heat. All physical quantities are assumed to respect spherical symmetry and the simulated fluid ranges from r_{\min} (the radius of the nanoparticle) to r_{\max} (a cut-off). The vapor bubble has a radius denoted by R_b .

This thesis is outlined as follows: In Chapter 2 the required theory will be introduced which is split into two parts, the first of which covers equilibrium phase transitions and the second describes nonequilibrium hydrodynamics. Next, Chapter 3 will cover the numerical methodology involved in solving the differential equations associated with the theory, discussing the numerical method itself, its correctness, as well as any issues that were encountered. Then, in Chapter 4 the results of the research will be presented together with an analysis and comparison to other works. Finally a conclusion and discussion of the research is given in Chapter 5.

2 Theory

This thesis builds on two types of theories for fluids which will be introduced separately. The thermodynamics associated with liquid-gas phase transitions is a vital part of the system description, however, this equilibrium theory is not enough. Hydrodynamics is required to describe the behavior of a non-equilibrium system with particle and energy flows. Section 2.1 will introduce the necessary components of thermodynamics after which the hydrodynamic equations will be covered in Section 2.2.

2.1 Van der Waals Theory

The ideal gas law $p = Nk_BT/V$ (where p, N, T, V are pressure, number of particles, temperature and volume, respectively) is a good approximation to the behavior of many gases at high temperatures and low pressures [5] A liquid-gas phase transition is not incorporated into this model, however, making it unsuitable for many purposes. One of the simplest models that satisfies the requirement of describing both a liquid and gas phase is the Van der Waals model which is a modification to the ideal gas law. The ideal gas law can be derived analytically under the assumption that the particles are point masses and undergo only elastic collisions with the sides of the container. The particles also possess no potential energy. Van der Waals proposed two corrections that improve the equation for systems where these assumptions cannot be made. The first modification is based on the idea that every molecule has some volume b (instead of being a point mass) and therefore the volume that is available to the other molecules is no longer V but V - Nb. Secondly the molecules attract each other which reduces the pressure, and Van der Waals argued that the pressure is reduced by an amount $a\rho^2$ for some constant a > 0 where $\rho = N/V$ is the number density. The resulting equation of state therefore becomes

$$p = \frac{Nk_BT}{V - Nb} - a\rho^2 = \frac{\rho k_BT}{1 - b\rho} - a\rho^2,$$
(1)

of which the ρ -dependence is plotted in Figure 2(a) for a temperature above and below the so-called critical temperature T_c that will be derived below. It should be noted that the Van der Waals model does not provide rigorous quantitative results when compared to real systems below the critical temperature [5]. It does however provide proper qualitative predictions about the liquid-gas phase changes and as the purpose of this work is to give a qualitative description of the thermodynamics of the system of interest, the Van der Waals model is an appropriate choice.

2.1.1 Free energy and entropy

A closed system that is connected to a heath bath will minimize its total Helmholtz free energy when in equilibrium. The Helmholtz free energy that belongs to the Van der Waals equation of state (1) is given by

$$f(\rho,T) = \rho \ k_B T \left(\log \left(\frac{\rho \Lambda^3}{1 - \rho b} \right) - 1 \right) - a \rho^2 \qquad ; \qquad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \qquad ; \qquad \rho = \frac{N}{V}. \tag{2}$$

Here f is the free energy per unit volume and Λ is the thermal de Broglie wavelength. This free energy can be obtained from the relation $py = -(\partial F/\partial V)_{N,T} = -f + \rho(\partial f/\partial \rho)_T$ which leaves room for an integration constant. This integration constant is the Λ term and is chosen in such a way that f gives the free energy of an ideal gas in the limit $\rho \to 0$. Since Λ is but a shift of the free energy, any measurable physical quantity (like the pressure) will not depend on Λ (and thus on the Planck constant h) as expected. Figure 2(b) shows a plot of the ρ -dependence of the free energy. It shows that for certain temperatures T, the pressure is not monotonically increasing as a function of density as one might expect, and for this temperature the free energy has a concave part, since $(\partial p/\partial \rho) = \rho(\partial^2 f/\partial \rho^2)_T$. Below it will be shown that this corresponds to the existence of a phase



Figure 2: Pressure (left) and Helmholtz free energy (right) for the Van der Waals model as function of density for different temperatures in units of critical values. The definitions of ρ_c, p_c, f_c can be found in Appendix A.

transition.

The free energy of a thermodynamic system can be obtained from the internal energy and entropy by the relation F = U - TS where U is the internal energy and S is the entropy. For the Van der Waals model, the internal energy density e = U/V and entropy per particle s = S/N (so that ρs is the entropy density) are given by [6]

$$e = \frac{3}{2}\rho k_B T - a\rho^2,\tag{3}$$

$$s = -k_B \left(\log \left(\frac{\rho \Lambda^3}{1 - \rho b} \right) - 1 \right) + \frac{3}{2} k_B, \tag{4}$$

which satisfy $f = e - T\rho s$.

Equations (3) and (4) above satisfy the following thermodynamical relations which will be used later

$$\rho\left(\frac{\partial s}{\partial e}\right)_{\rho} = \frac{1}{T} \tag{5}$$

$$-T\left(\frac{\partial(\rho s)}{\partial\rho}\right)_e = \mu \tag{6}$$

2.1.2 Liquid-gas phase transition

As stated before, the Van der Waals model exhibits a liquid-gas phase transition. This can be derived from the free energy using a so-called common tangent construction. For certain temperatures, the free energy as a function of density has a convex part as can be seen in Figure 3.

To see how this allows for phase separation, consider a system of N particles in a box with volume V. The overall density $\rho = N/V$ is fixed, but the system is allowed to organize itself to have regions with different local densities. If the fluid is homogeneous then the free energy of the system will be given by $F_{\text{hom}} = f(\rho, T)V$. If the fluid separates into two regions with volumes V_1, V_2 and densities ρ_1, ρ_2 respectively, then the free energy of the system is given by $F_{\text{split}} = f(\rho_1, T)V_1 + f(\rho_2, T)V_2$. The restrictions $V_1 + V_2 = V$ and $V_1\rho_1 + V_2\rho_2 = N = \rho V$ allow rewriting the free energy to

$$\frac{F_{\text{split}}}{V} = \frac{\rho_2 - \rho}{\rho_2 - \rho_1} f(\rho_1, T) + \frac{\rho - \rho_1}{\rho_2 - \rho_1} f(\rho_2, T), \qquad \rho \in [\rho_1, \rho_2].$$



Figure 3: Helmholtz free energy (in blue) at $T = 0.9 T_c$ as function of density in units of critical values. The common tangent construction is shown in gray. The solid gray line shows the free energy of a phase separated system (F_{split}/V) and the blue line shows the free energy of a homogeneous system (f). The optimal free energy is given by the gray line if $\rho_{\text{gas}} \leq \rho \leq \rho_{\text{liq}}$ and blue line otherwise. The definitions of ρ_c, f_c can be found in Appendix A.

As a function of ρ this is exactly a straight line through $(\rho_1, f(\rho_1, T))$ and $(\rho_2, f(\rho_2, T))$. This means if one can draw a straight line through two points on the graph of the free energy f, and this line (the part between the points) lies below f itself, then the system can lower its free energy by separating into two different densities. This is possible exactly when f has a convex part which is true if and only if $T < T_c$. The temperature T_c is known as the *critical temperature*. Above this temperature, the free energy has no convex part and the pressure is a monotonically increasing function of density. Below the critical temperature however there are densities for which $(\partial p/\partial \rho)_T < 0$. To find the highest temperature for which $(\partial p/\partial \rho)_T = 0$, the second derivative can be set to zero as well, which yields

$$\begin{pmatrix} \frac{\partial p}{\partial \rho} \\ \rho_{c,T_{c}} \\ \begin{pmatrix} \frac{\partial^{2} p}{\partial \rho^{2}} \end{pmatrix}_{\rho_{c},T_{c}} = 0 \\ \end{pmatrix} \implies \begin{cases} \rho_{c} = \frac{1}{3b}, \\ k_{B}T_{c} = \frac{8a}{27b}. \end{cases}$$
(7)

The next task is computing the densities ρ_1, ρ_2 for which F_{split} is optimal (that is, as low as possible) at a given temperature $T < T_c$. In Figure 3 the so-called common tangent construction is shown. It should be clear from the graphic that there is no other straight line (connecting two points of the graph of f) that is lower than this one anywhere in the convex region. The line of F_{split}/V should be tangent to that of f at ρ_1 and ρ_2 . This means

$$\left. \frac{\partial f}{\partial \rho} \right|_{\rho_1} = \left. \frac{\partial f}{\partial \rho} \right|_{\rho_2} = \left. \frac{1}{V} \frac{\partial F_{\text{split}}}{\partial \rho} \right|_{\rho_1,\rho_2} = \frac{f(\rho_2,T) - f(\rho_1,T)}{\rho_2 - \rho_1}.$$

These two equalities have a physical interpretation. The chemical potential is given by $\mu = (\partial f / \partial \rho)$, so the first equality implies that the chemical potential of the two phases are equal: $\mu(\rho_1) = \mu(\rho_2)$. As stated before, the pressure is related to the free energy through $p(\rho) = -f(\rho) + \rho \cdot \mu(\rho)$ and this allows us to rewrite the last term in the equation to

$$\frac{f(\rho_2, T) - f(\rho_1, T)}{\rho_2 - \rho_1} = \frac{(-p(\rho_2) + \rho_2 \mu(\rho_2)) + (p(\rho_1) - \rho_1 \mu(\rho_1))}{\rho_2 - \rho_1} = \frac{p(\rho_1) - p(\rho_2)}{\rho_2 - \rho_1} + \mu(\rho),$$

showing that $p(\rho_1) = p(\rho_2)$, meaning the two phases have equal pressure.



Figure 4: Temperature-density coexistence diagram for the Van der Waals model. The definitions of ρ_c, T_c are given in Equation (7) The black dot shows the critical point, the blue line (outer) is the coexistence curve and the orange line (inner) shows the spinodal curve.

A related phenomenon of interest is the so-called spinodal decomposition. It was just derived that the total free energy is lowest when the system is split into regions with densities ρ_1 and ρ_2 . Although this is the global minimum of the free energy, it is possible that there are other states with a global density between the coexistence densities which are stable with respect to small density fluctuations. This occurs when $(\partial^2 f/\partial \rho^2)_T > 0$ and the resulting states are metastable. Systems with values of ρ, T which satisfy $(\partial^2 f/\partial \rho^2)_T < 0$ are unstable with respect to infinitesimal density fluctuations and will spontaneously decompose into coexisting states. This process is called spinodal decomposition. The points ρ, T separating the metastable region form the spinodal curve and satisfy $(\partial^2 f/\partial \rho^2)_T = 0$.

Computing the coexistence densities ρ_1, ρ_2 for every temperature $T < T_c$, as well as the spinodal densities, one obtains the so-called coexistence diagram as shown in Figure 4. When a system is initialized at some point (ρ, T) outside (above) the shown coexistence curve, it will be stable and in equilibrium (assuming no other external forces or effects). Initializing the system below the spinodal curve will cause spontaneous phase separation, and the region between the blue and orange lines is a metastable region where the transition takes place through a nucleation-and-growth mechanism.

The derivation in this section assumes that the total free energy is the sum of the energies of the two sub-volumes. This is accurate for system volumes that are thermodynamically large. The next section will introduce a method that provides a correction to this simplification that becomes relevant when there are interfaces in the system.

2.1.3 Density Functional Theory - Diffuse interface method

The equation of state (1) yields two stable phases, a bulk gas and a bulk liquid, but a description of two-phase coexistence also needs to account for the interface between these phases. The so-called diffuse interface method associates an energy with the interface by introducing an energy cost to the spatial change of the density. It is assumed that the density is a smooth function of space, varying rapidly at the interface. This idea was considered already by Van der Waals.

The central idea of Density Functional Theory is that one considers the total free energy to be a functional of the density. In this case we consider the so-called square-gradient approximation

$$F[\rho(\mathbf{r})] = \int_{V} d\mathbf{r} \left(f(\rho(\mathbf{r}), T(\mathbf{r})) + \frac{M}{2} (\nabla \rho(\mathbf{r}))^{2} \right).$$
(8)

The first term is a local density approximation and the second term is the so-called square-gradient term. It accounts for the energy cost of the interface, where M is the phenomenological gradient energy coefficient, assumed not to depend on ρ and satisfying M > 0. Note that a term linear in $\nabla \rho$ is not allowed by symmetry. The square-gradient term is the lowest order non-trivial term, and any other gradient terms can be safely neglected for simplicity [6].

The same idea can be applied to the entropy and energy to obtain

$$S[\rho, e] = \int_{V} d\mathbf{r} \left(\rho \ s(\rho, e) - \frac{C}{2} (\nabla \rho)^{2} \right), \tag{9}$$

$$U[\rho, e] = \int_{V} d\mathbf{r} \,\left(e + \frac{K}{2} (\nabla \rho)^{2}\right),\tag{10}$$

with s and e as defined in Equations (3) and (4) and C, K constants. The **r** dependence of ρ and e has been omitted for readability. Note that there is a minus sign in the square-gradient term of the entropy because the entropy is maximized instead of minimized. The different constants are related by M = K + CT, so that the equality F = U - TS holds. Often M is chosen to be a constant (corresponding to vanishing C, and K a constant) for simplicity. Note that in this context, ρ and e are being considered as independent so that the temperature $T(\rho, e)$ is not an independent variable itself.

The next step is to find the particle density profile $\rho(\mathbf{r})$ and energy density profile $e(\mathbf{r})$ that maximize the entropy, under the constraint that the total number of particles N and the total energy U are fixed. This is accomplished using Lagrange multipliers, by defining a new functional W as

$$W[\rho, e] = \frac{1}{k_B} S[\rho, e] + \nu N[\rho] - \beta U[\rho, e],$$

where N is simply given by $N = \int_V d\mathbf{r} \rho(\mathbf{r})$ and where ν, β are the Lagrange multipliers. Maximizing W with respect to e can be done with a variational derivative to e, and yields that $T(\mathbf{r})$ must be constant:

$$\frac{\delta W}{\delta e(\mathbf{r})} = 0 \qquad \Longrightarrow \qquad \frac{1}{k_B} \rho \left(\frac{\partial s}{\partial e}\right)_{\rho} - \beta = 0 \qquad \Longrightarrow \qquad \beta = \frac{1}{k_B T(\mathbf{r})},$$

where $T(\mathbf{r})$ is shorthand for $T(\rho(\mathbf{r}), e(\mathbf{r}))$ and Equation (5) was used. Using the relation F = U - TSand the fact that T is constant, W can be rewritten to

$$W = -\frac{1}{k_B T} \left(F - \mu N \right),$$

where $\mu = k_B T \nu$ is a rescaled Lagrange multiplier. This shows that maximizing the entropy under fixed U, N is equivalent to minimizing the Helmholtz free energy F under fixed N. Maximizing W (or minimizing F) with respect to ρ now gives the following Euler-Lagrange equation

$$\frac{\delta W}{\delta \rho} = 0 \quad \Longrightarrow \quad \frac{\partial f(\rho, T)}{\partial \rho} - M \nabla^2 \rho - \mu = 0, \tag{11}$$



Figure 5: Density ρ as function of Cartesian coordinate z: the planar solution to Equation (11) at temperature $T = 0.5T_c$. The definition of ρ_c is given in Equation (7), and the length scale l shown on the horizontal axis is chosen such that result is independent of the parameter M, derived in Appendix A. Entering typical values of water, one finds $l \approx 1.0$ nm, $T \approx 55^{\circ}$ C and $\rho_c \approx 2 \cdot 10^2 \text{ kg/m}^3$.

It is this equation that admits a two-phase coexistence as solution. Solving the equation in one dimension with planar symmetry can be insightful. Assume ρ only depends on z and there is a bulk fluid at $z \to \pm \infty$. This means $\rho(\infty) = \rho_+$, $\rho(-\infty) = \rho_-$, and $\rho'(\pm \infty) = \rho''(\pm \infty) = 0$. Entering this into Equation (11) yields $\frac{\partial f}{\partial \rho}(\rho_{\pm}, T) = \mu$. This has the physical interpretation that the chemical potential of the two asymptotic phases must be equal, as was the case in the common tangent construction. Equation (11), in one dimension, can be rewritten to show the phases have equal pressure as well. By multiplying with $\partial \rho/\partial z$ and using the chain rule, the equation is equivalent to

$$\frac{\partial f(\rho, T)}{\partial \rho} \frac{\partial \rho}{\partial z} - M \frac{\partial^2 \rho}{\partial z} \frac{\partial \rho}{\partial z} - \mu \frac{\partial \rho}{\partial z} = 0;$$

$$\frac{\partial}{\partial z} \left(f(\rho, T) - \frac{M}{2} \left(\frac{\partial \rho}{\partial z} \right)^2 - \mu \rho \right) = 0;$$

$$-f(\rho, T) + \mu \rho + \frac{M}{2} \left(\frac{\partial \rho}{\partial z} \right)^2 = p_{\rm cx},$$
 (12)

with p_{cx} a constant. For $z \to \pm \infty$ and using $p = -f + \rho(\partial f/\partial \rho)$ this gives the equal pressure requirement $p(\rho_{\pm}, T) = p_{cx}$. A similar result can be derived in three dimensions (see Section 2.2.3), but the pressure conservation law will be of tensorial form, $\nabla \cdot \mathbf{P} = \mathbf{0}$ for some second rank tensor \mathbf{P} . After using the common tangent construction to find ρ_{gas}, ρ_{liq} one can solve the differential equation of which the solution at $T = 0.5T_c$ is shown in Figure 5. The graph shows that the interface width at this temperature is roughly 2 nm, if parameters are taken that mimic water. The thickness of the interface depends on M and T and diverges as $T \to T_c$.

The energy cost of the interface can be related to the surface tension of the liquid-gas interface. The grand potential Ω is given by the Legendre transformation $\Omega = F - \mu N$ where μ is the chemical potential. Since the Lagrange multiplier μ used before turned out to be the chemical potential, it follows that the functional W is equal to $W = -\frac{1}{k_B T} \Omega$ so maximizing the entropy under fixed U, N is equivalent to minimizing the grand potential Ω . The grand potential can be evaluated for a one

dimensional planar solution $\rho(z)$ satisfying Equation (12) yielding

$$\Omega = \int_{V} d\mathbf{r} \left(f(\rho, T) + \frac{M}{2} (\nabla \rho)^{2} - \mu \rho \right)$$

= $A \int_{-\infty}^{\infty} dz \left(f(\rho, T) + \frac{M}{2} \left(\frac{\partial \rho}{\partial z} \right)^{2} - \mu \rho \right)$
= $A \int_{-\infty}^{\infty} dz \left(-p_{cx} + M \left(\frac{\partial \rho}{\partial z} \right)^{2} \right)$
= $-p_{cx}V + A \int_{-\infty}^{\infty} dz M \left(\frac{\partial \rho}{\partial z} \right)^{2},$ (13)

where A is the area of the system perpendicular to the z-direction.

This expression for Ω can be compared to another form of Ω in terms of the surface energy γ . If the interface area A is large enough then the surface energy is linear in A and the grand potential can be written as [7]

$$\Omega(\mu, V, T, A) = -p(\mu, T)V + \gamma(\mu, T)A.$$

Comparing this with Equation (13), an expression for the surface tension follows:

$$\gamma = M \int_{-\infty}^{\infty} (\rho'(z))^2 dz.$$
(14)

Note that the surface tension depends on the temperature T because the optimal density profile $\rho(z)$ depends on T, and $\gamma > 0$ because M > 0.

2.1.4 Young-Laplace law

The total free-energy cost of a liquid-gas interface is proportional to its area thus causing the system to minimize the size of such an interface. In the case of a single vapor bubble of radius r_{bubble} immersed in liquid, the interface area is proportional to r_{bubble}^2 and as such, smaller bubbles (or no bubble at all) cost less energy. This is under some constraints, because having no bubble requires more particles (they fill up the bubble region) meaning the density of the liquid becomes lower which could cost more (cohesive) energy. This means that in an infinite system with a single bubble, the bubble can not be stable as there are always enough particles to fill up the bubble region. In a finite system, there will be a balance in energy resulting in some bubble size. The preference of a smaller bubble can be seen as an effective inwards force from the outside and to have a steady system an additional force from the inside is needed. This effect is manifested by a pressure difference between the inside and outside of the vapor bubble. This pressure difference is given by the Young-Laplace law [8]

$$\Delta p = \frac{2\gamma}{r}.\tag{15}$$

It can be derived by minimizing the Grand potential $\Omega = -pV + \gamma A$ [7]. The volume is split into a bubble of radius r, at pressure $p + \Delta p$, and the remaining part at pressure p.

$$\Omega = -(p + \Delta p) \cdot \left(\frac{4}{3}\pi r^3\right) - p \cdot \left(V - \frac{4}{3}\pi r^3\right) + \gamma \cdot 4\pi r^2.$$

Minimizing Ω with respect to r immediately gives Equation (15).

2.2 Hydrodynamics

Density Functional Theory only provides a framework to describe fluids in equilibrium. In the previous section a calculation showed that the temperature T must then be a constant throughout space. Extending the theory to systems with non-uniform temperatures requires the use of hydrodynamic equations. This section will introduce the basic concepts of hydrodynamics and derive some equations. It will be shown that the equations reduce to the equilibrium equations if a constant temperature is assumed.

2.2.1 Equations

Hydrodynamics revolves around the fluid being considered as a continuum, where an infinitesimal fluid volume is assumed to be large compared to the molecular size. There are three independent variables, all a function of space and time: the particle number density ρ , the energy density e, and the fluid velocity \mathbf{v} . The first two variables, together with the (Van der Waals) equation of state, characterize the thermodynamic state of the system. The velocity is a kinetic variable describing the motion of the system. Note that the temperature is a function of ρ and e through Equation (3). Instead of ρ and e, any other two thermodynamic quantities, say the pressure and temperature, could be used since all other thermodynamic quantities will be determined by the equation of state. The mass density is given by $m\rho$ where m is the molecular mass, so $m\rho\mathbf{v}$ is the momentum density. Looking back at Equation (10), the local internal energy contribution to the system is given by

$$\hat{e} = e + \frac{K}{2} (\nabla \rho)^2. \tag{16}$$

Define the total energy density as $e_T = \hat{e} + \frac{1}{2}m\rho \mathbf{v}^2$ where the last term accounts for the kinetic energy of the fluid in motion. There are three equations governing the system, and they are conservation laws for the number of particles N, the momentum $m\rho \mathbf{v}$ and the energy U. In tensorial form, these equations take the form

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \tag{17}$$

$$\frac{\partial(m\rho\mathbf{v})}{\partial t} + \nabla \cdot ((m\rho\mathbf{v})\mathbf{v}) = -\nabla \cdot (\mathbf{P} - \sigma), \tag{18}$$

$$\frac{\partial e_T}{\partial t} + \nabla \cdot (e_T \mathbf{v}) = -\nabla \cdot [(\mathbf{P} - \sigma) \cdot \mathbf{v}] + \nabla \cdot (\kappa \nabla T).$$
(19)

Here **P** is the pressure tensor and σ the dissipative stress tensor, given later in Section 2.2.3 by Equations (34) and (25). The heat flux $\mathbf{J} = -\kappa \nabla T$ will be derived in Section 2.2.2. The notation $\nabla \cdot \mathbf{A}$ for a second-rank tensor **A** refers to $(\nabla \cdot \mathbf{A})_j = \sum_i \nabla_i A_{ij}^{-1}$.

Using the first two equations one can obtain

$$\frac{\partial}{\partial t} \left(\frac{1}{2} m \rho \mathbf{v}^2 \right) + \nabla \cdot \left(\frac{1}{2} m \rho \mathbf{v}^2 \mathbf{v} \right) = - \left(\nabla \cdot \left(\mathbf{P} - \sigma \right) \right) \cdot \mathbf{v},$$

so that the third equation can be rewritten to get an expression for $\partial \hat{e} / \partial t$ instead of $\partial e_T / \partial t$

$$\frac{\partial \hat{e}}{\partial t} + \nabla \cdot (\hat{e}\mathbf{v}) = -(\mathbf{P} - \sigma) : \nabla \mathbf{v} + \nabla \cdot (\kappa \nabla T), \tag{20}$$

where the notation $\mathbf{A} : \nabla \mathbf{b}$ means $\Sigma_{ij} A_{ij} \nabla_i b_j$.

 $^{^{1}}$ Since all tensors in the equations here are symmetric, it does not matter whether one contracts over the first or second index.

The equations can be interpreted as local conservation laws of which a derivation will now follow. Equation (17) corresponds to the conservation of the number of particles and indicates no particles can be created from the vacuum. One can also express these laws using an integral formulation [9]. Consider some control volume Ω . The total number of particles in Ω is given by $\int_{\Omega} \rho \, dV$. Let $\partial \Omega$ be the surface of Ω , and $\hat{\mathbf{n}}$ an outwards pointing normal vector of the surface, then the number of particles flowing (outwards) through the surface in one unit of time is given by $\oint_{\partial\Omega} \rho \mathbf{v} \cdot \hat{\mathbf{n}} \, dS$ where dS is the area of a surface element. Since no particles can be destroyed or created from nothing, the decrease per unit time of the number of particles in Ω must equal the amount flowing out through the boundary, so

$$-\frac{\partial}{\partial t}\int_{\Omega}\rho \ dV = \oint_{\partial\Omega}\rho \mathbf{v} \cdot \hat{\mathbf{n}} \ dS = \int_{\Omega}\nabla \cdot (\rho \mathbf{v}) \ dV.$$

The minus sign is present because a positive right hand side indicates *outgoing* particles. The second equality is obtained by Gauss's theorem. The following equation must hold

$$\int_{\Omega} \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right] \, dV = 0$$

and since this is true for any volume Ω the integrand must vanish, yielding Equation (17) also known as the continuity equation.

In a similar way, Equation (18) represents the conservation of momentum $(m\rho\mathbf{v})$ but instead of being conserved, momentum can be generated by forces. This can be derived based on the fact that the total force acting on a control volume Ω is given by the total stress acting on the boundary. This stress includes both forces due to pressure and so-called drag or friction forces. The stress component along a vector \mathbf{n} is given by the product of the stress tensor $\mathbf{P} - \sigma$ and that vector: $(\mathbf{P} - \sigma) \cdot \mathbf{n}$. The stress tensor itself will be derived in Section 2.2.3. Using Gauss's law again, one finds

$$-\oint_{\partial\Omega} (\mathbf{P} - \sigma) \cdot \hat{\mathbf{n}} \, dS = -\int_{\Omega} \nabla \cdot (\mathbf{P} - \sigma) \, dV,$$

which shows that the force acting on an infinitesimal fluid element is equal to $-\nabla \cdot (\mathbf{P} - \sigma)$. There is a minus sign because the normal vector is pointing outwards, whereas the force is the force acting on the fluid element. By Newtons law the force can be set equal to $m\rho \frac{d\mathbf{v}}{dt}$. However one has to pay attention to the fact that the fluid element is moving through space. Consider some physical quantity $\varphi(\mathbf{r}, t)$ of a fluid element moving through space at location \mathbf{r} . The total derivative with respect to time is given by

$$\frac{d\varphi(\mathbf{r},t)}{dt} = \frac{\partial\varphi}{\partial t} + \frac{d\mathbf{r}}{dt} \cdot \nabla\varphi.$$

Since the fluid velocity field is given by \mathbf{v} (and is taken to be in the same reference frame as \mathbf{r}), one has $\frac{d\mathbf{r}}{dt} = \mathbf{v}$. This results in the so-called material derivative

$$\frac{D\varphi}{Dt} = \frac{\partial\varphi}{\partial t} + \mathbf{v} \cdot \nabla\varphi.$$

It can be interpreted as the change in time of some quantity when following the fluid element around in space. Going back to the force acting on an infinitesimal fluid element, it follows that

$$m\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot (\mathbf{P} - \sigma),$$

which is the so-called Navier-Stokes equation when σ is given by $\sigma = \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)$, and in the case of frictionless flow (vanishing σ) it is called the *Euler equation*. The left hand side of this equation can

be combined with Equation (17) and is equal to $\frac{\partial m \rho \mathbf{v}}{\partial t} + \nabla \cdot ((m \rho \mathbf{v}) \mathbf{v})$ so that the above equation is equivalent to Equation (18).

The third conservation law, Equation (19), is the energy conservation equation. The total energy in a volume Ω is given by $\int_{\Omega} e_T dV$. There are multiple ways that energy can flow through the boundary of Ω . The first is simply by particles moving through the boundary together with their internal energy and this quantity (per unit time) is equal to $\oint_{\partial\Omega} e\mathbf{v} \cdot \mathbf{n} \, dS$. The second way that the energy of the volume can increase is by work done on the boundary. The work done per unit time is given by $\oint_{\partial\Omega} ((\mathbf{P} - \sigma) \cdot \mathbf{v}) \cdot \hat{\mathbf{n}} \, dS$ [10]. Finally there is an energy flux through the boundary due to temperature gradients. This flux, $\mathbf{J} = -\kappa \nabla T$, will be derived in Section 2.2.2 and contributes as $\oint_{\partial\Omega} \mathbf{J} \cdot \hat{\mathbf{n}} \, dS$. Combining all these with the proper signs one obtains

$$-\frac{\partial}{\partial t} \int_{\Omega} e_T \, dV = \oint_{\partial \Omega} e \mathbf{v} \cdot \mathbf{n} \, dS + \oint_{\partial \Omega} ((\mathbf{P} - \sigma) \cdot \mathbf{v}) \cdot \hat{\mathbf{n}} \, dS + \oint_{\partial \Omega} \mathbf{J} \cdot \hat{\mathbf{n}} \, dS,$$

which, combined with Gauss's theorem, is equivalent to

$$\int_{\Omega} \left[-\frac{\partial e_T}{\partial t} + \nabla \cdot (e_T \mathbf{v}) + \nabla \cdot ((\mathbf{P} - \sigma) \cdot \mathbf{v}) + \nabla \cdot \mathbf{J} \right] dV = 0.$$

Being true for any volume Ω this implies Equation (19).

The above derivation was done for an arbitrary stress tensor and heat flux vector. Their specific forms will be given in the next sections and are specified such that it is guaranteed that the total entropy of the system can never decrease (see Section 2.2.3) as required by the Second Law of Thermodynamics.

2.2.2 Heat flow

The heat flux is the energy flowing through a surface per unit time, per unit surface. As stated before, the heat flux vector is given by $\mathbf{J} = -\kappa \nabla T$ [11] which is also known as Fourier's law. The minus sign accounts for the fact that heat flows from hot to cold. The constant $\kappa > 0$ is the so-called thermal conductivity of the medium.

This form of the heat flux vector is only a first order approximation. In principle one could have terms proportional higher order derivatives of T as well. To see why the heat flux is proportional to derivatives of T and to get an analytical expression for κ , consider for simplicity a temperature gradient along the z-axis only, e.g. $\partial T/\partial z \neq 0$. Assume that, on average, molecules travel a distance l between collisions, i.e. l is the mean free path. Consider a molecule traveling in some direction with an angle θ with respect to the (positive) z-axis, which has traveled a distance l since its last collision, of which $l \cos \theta$ was in the z-direction. It therefore traveled from a point with temperature T_0 to a point with temperature $T_1 = T_0 + \frac{\partial T}{\partial z} l \cos \theta$ (where higher order gradient terms are neglected). The molecule started with an internal energy corresponding to a temperature T_0 , and now collides with a molecule at temperature T_1 . Let C_{molecule} be the heat capacity of a single molecule, meaning the amount of energy required to increase its temperature by 1 Kelvin. Then the molecule will bring a deficit of thermal energy to its new location equal to $C_{\text{molecule}} \frac{\partial T}{\partial z} l \cos \theta$. This energy will be deposited during the collision with the second molecule. If the number of molecules traveling through a unit area in a unit time with speed v and angle θ is given by some distribution $f(v, \theta)$, then the total heat flux will be given by

$$J_{z} = \int_{0}^{\infty} dv \int_{0}^{\pi} d\theta \left(-C_{\text{molecule}} \frac{\partial T}{\partial z} l \cos \theta \right) f(v, \theta)$$
$$= -\frac{\partial T}{\partial z} \int_{0}^{\infty} dv \int_{0}^{\pi} d\theta C_{\text{molecule}} l \cos \theta f(v, \theta)$$
$$= -\kappa \frac{\partial T}{\partial z},$$

where the exact form of $f(v, \theta)$ is irrelevant for current purposes. Experimental data [12] shows a complicated dependence of κ on both ρ and T. Often a constant κ is assumed when the density does not vary greatly. In this project, however, a system with both liquid and vapor is studied and the thermal conductivity of liquid water is significantly higher than that of vapor. Other works [6, 8] take the thermal conductivity to be linear to the density

$$\kappa = \kappa_0 \rho, \tag{21}$$

with κ_0 a constant, which seems to be a good first approximation (see for example Figure 3 of Ref [12]). For this research the above form for κ is used as well.

Note that the heat flux described in this section corresponds to heat transfer by *conduction* as the molecules transfer their energy by colliding. Another form of heat transfer is *convection*, but this type of heat transfer is already incorporated in the equations by the term $\nabla \cdot (e_T \mathbf{v})$ in Equation (19), accounting for energy being moved due to the movement of the fluid as a whole.

2.2.3 Pressure Tensor

The so-called stress tensor is a symmetric order two tensor that describes the forces (stresses) per unit area acting on the fluid. It consists of a reversible part, also referred to as the pressure tensor, and an irreversible part, also known as the dissipative stress tensor. The reversibility refers to the fact that motion due to pressure results in reversible work, whereas the dissipative stress is due to friction and results in irreversible work that increases the entropy of the system [13]. This section will derive the pressure tensor and give the form of the dissipative stress tensor.

The derivation of Equation (11) involved minimizing a functional using the Euler-Lagrange equations on the Lagrangian

$$\mathcal{L} = f(\rho, T) + \frac{M}{2} (\nabla \rho)^2 - \mu \rho.$$
(22)

The Lagrangian (22) does not explicitly depend on space or time and consequently it follows from Noether's theorem that there is a corresponding conservation law [14]. This law is of the form $\nabla \cdot \mathbf{T} = \mathbf{0}$ for a second-rank tensor \mathbf{T} given by

$$\mathbf{T} = -\mathcal{L}\,\mathbf{I} + \nabla\rho \otimes \frac{\partial \mathcal{L}}{\partial(\nabla\rho)}.\tag{23}$$

Note that the notation $\nabla \cdot \mathbf{T} = \mathbf{0}$ refers to $\sum_i \partial_i T_{ij} = 0$ (for all j) and the second term in Equation (23) is notation for $(\partial_i \rho) \frac{\partial \mathcal{L}}{\partial (\partial_j \rho)}$. Entering the Lagrangian (22) and Equation (11) into Equation 23 one finds

$$\mathbf{T} = \left(-f(\rho, T) - \frac{M}{2}(\nabla\rho)^2 + \rho \left(\frac{\partial f}{\partial\rho} - M\nabla^2\rho\right)\right)\mathbf{I} + M \nabla\rho \otimes \nabla\rho$$
$$= \left(p(\rho, T) - \frac{M}{2}(\nabla\rho)^2 - M\rho\nabla^2\rho\right)\mathbf{I} + M \nabla\rho \otimes \nabla\rho, \tag{24}$$

which turns out to be the pressure tensor [10], hereafter denoted by **P**. The conservation law $\nabla \cdot \mathbf{P} = \mathbf{0}$ represents the pressure balance or mechanical balance of the system in equilibrium. It is equivalent to Equation (11) but written in the form of a conservation law.

The full stress tensor contains a non-reversible part as well, due to the bulk and shear viscosity of a fluid in motion. When a piece of fluid flows with a higher velocity than its neighbors it will be slowed

down and vice versa. Gradients of velocity therefore induce stress and the so-called dissipative stress tensor, or viscous stress tensor, is given by

$$\sigma_{ij} = \eta (\nabla_i v_j + \nabla_j v_i) + (\zeta - 2\eta/3) (\nabla \cdot \mathbf{v}) \delta_{ij}, \tag{25}$$

where η is the shear viscosity and ζ the bulk viscosity. This is a standard form for the dissipative stress tensor for so-called Newtonian fluids, used in for example Ref. [6, 8]. It can be derived by starting from the most general form of a tensor proportional to velocity gradients and then demanding the tensor to be isotropic (for an isotropic fluid) and symmetric (conservation of angular momentum). For a derivation, see Ref. [15]. The full stress tensor is given by $\mathbf{P} - \sigma$.

The viscosity (both shear an bulk) is often taken to be a constant which is a reasonable assumption when the density does not vary greatly. The viscosity of a liquid is a lot larger than that of a gas so when studying systems with both liquid and gas phases one can not simply use a constant viscosity. Similar to the thermal conductivity, a viscosity linear to the density can be used [6, 8],

$$\eta = \eta_0 \rho, \tag{26}$$

which is what will be used in this research as well. The bulk viscosity is chosen to be equal to the shear viscosity. Note that the viscosity affects the time-dependent behavior of the system but should not influence the final stable state where $\mathbf{v} = 0$. This means that the correctness of the viscous behavior is of less importance when looking for steady state solutions.

The above derivation for a pressure tensor is only valid for an isothermal system. When extending the model to the non-isothermal case there are two options [6, 8]. The first is to add a flux of internal energy in the energy conservation equation [10, 6, 16]. The second option, used in this work, is to extend the pressure tensor with a term proportional to the temperature gradient [6, 8]. The way to derive this extra term is to demand that the total entropy of the system must be strictly increasing in time.

The total entropy is given by Equation (9). Taking the variation of this equation, assuming the variation vanishes on the boundary, one finds

$$\begin{split} \delta S &= \int_{V} d\mathbf{r} \; \left[\left(\frac{\partial(\rho s)}{\partial \rho} \right)_{e} \delta \rho + \left(\frac{\partial(\rho s)}{\partial e} \right)_{\rho} \delta e + C(\nabla^{2} \rho) \; \delta \rho \right] \\ &= \int_{V} d\mathbf{r} \; \left[-\frac{\mu}{T} \delta \rho + \frac{1}{T} \delta e + C(\nabla^{2} \rho) \; \delta \rho \right]. \end{split}$$

Here Equation (5) and Equation (6) were used to obtain the second line. To continue, it is now more convenient to use \hat{e} , defined in Equation (16), as an independent variable rather than e itself. The reason is that the integral of \hat{e} is a conserved quantity, see Equation (10), and is used in the hydrodynamic equations. Using $\delta \hat{e} = \delta e + \delta (\frac{K}{2} (\nabla \rho)^2)$ the variation of S can be rewritten as

$$\delta S = \int_{V} d\mathbf{r} \left[-\frac{\mu}{T} \delta \rho + \frac{1}{T} \delta \hat{e} - \frac{1}{T} \delta (\frac{K}{2} (\nabla \rho)^{2}) + C(\nabla^{2} \rho) \delta \rho \right]$$
$$= \int_{V} d\mathbf{r} \left[-\frac{\mu}{T} \delta \rho + \frac{1}{T} \delta \hat{e} + K \nabla \cdot (\frac{1}{T} \nabla \rho) \delta \rho + C(\nabla^{2} \rho) \delta \rho \right]$$
$$= \int_{V} d\mathbf{r} \left[-\frac{\hat{\mu}}{T} \delta \rho + \frac{1}{T} \delta \hat{e} \right],$$
(27)

where $\hat{\mu}$ is defined as

$$\hat{\mu} = \mu - KT\nabla \cdot \left(\frac{1}{T}\nabla\rho\right) - CT\nabla^{2}\rho$$
$$= \mu - T\nabla \cdot \left(\frac{M}{T}\nabla\rho\right), \tag{28}$$

with M = K + CT as before.

Using Equation (27), the derivative of S with respect to time can be computed,

$$\frac{dS}{dt} = \int_{V} d\mathbf{r} \, \left[-\frac{\hat{\mu}}{T} \frac{d\rho}{dt} + \frac{1}{T} \frac{d\hat{e}}{dt} \right]. \tag{29}$$

Plugging Equation (17) and Equation (20) into the above line yields

$$\frac{dS}{dt} = \int_{V} d\mathbf{r} \left[\frac{\hat{\mu}}{T} \nabla \cdot (\rho \mathbf{v}) - \frac{1}{T} \nabla \cdot (\hat{e} \mathbf{v}) - \frac{1}{T} \mathbf{P} : \nabla \mathbf{v} + \frac{1}{T} \sigma : \nabla \mathbf{v} + \frac{1}{T} \nabla \cdot (\kappa \nabla T) \right] \\
= \int_{V} d\mathbf{r} \left[\mathbf{v} \cdot \left(-\rho \nabla \frac{\hat{\mu}}{T} + \hat{e} \nabla \frac{1}{T} + \nabla \cdot (\frac{1}{T} \mathbf{P}) \right) + \frac{1}{T} \left(\sigma : \nabla \mathbf{v} + \nabla \cdot (\kappa \nabla T) \right) \right].$$
(30)

The quantity $\sigma : \nabla \mathbf{v}$, called the viscous heat production rate, can be written into the following form using Equation (25):

$$\begin{split} \sigma : \nabla \mathbf{v} &= \sum_{ij} \sigma_{ij} \nabla_i v_j = \sum_{ij} \left[\eta (\nabla_i v_j + \nabla_j v_i) + (\zeta - 2\eta/d) (\nabla \cdot \mathbf{v}) \delta_{ij} \right] \nabla_i v_j \\ &= \sum_{ij} \eta \left[(\nabla_i v_j) (\nabla_i v_j) + (\nabla_j v_i) (\nabla_i v_j) \right] + (\zeta - 2\eta/d) (\nabla \cdot \mathbf{v})^2 \\ &= \sum_{ij} \frac{\eta}{2} \left(\nabla_i v_j + \nabla_j v_i - \frac{2}{d} \delta_{ij} (\nabla \cdot \mathbf{v}) \right)^2 + \zeta (\nabla \cdot \mathbf{v})^2. \end{split}$$

In this form it is clear that $\sigma : \nabla \mathbf{v} \geq 0$. If there is no heat flow from the outside, so $\nabla T = 0$, then entropy can never decrease, i.e. dS/dt must be non-negative. This must hold for all velocities \mathbf{v} , in particular velocity fields that are constant in space ($\nabla_i \mathbf{v}_j = 0$), so going back to Equation (30), it follows that

$$-\rho \nabla \frac{\hat{\mu}}{T} + \hat{e} \nabla \frac{1}{T} + \nabla \cdot \left(\frac{1}{T} \mathbf{P}\right) = 0.$$
(31)

If this were non-zero, one could construct a constant velocity field so that the first term in Equation (30) becomes negative (and the others zero). This yields a requirement on the pressure tensor, taking the following form when written in components

$$\sum_{j} \nabla_{j} \left(\frac{1}{T} \mathbf{P}_{ij} \right) = \rho \nabla_{i} \frac{\hat{\mu}}{T} - \hat{e} \nabla_{i} \frac{1}{T}.$$
(32)

One can now use the Gibbs-Duhem relation $d\mu = -s dT + \frac{1}{\rho} dp$ [17] which, together with $f = \mu \rho - p = e - T\rho s$, implies the thermodynamic identity

$$d\frac{p}{T} = -e \ d\frac{1}{T} + \rho \ d\frac{\mu}{T}.$$

Using this identity together with Equation (28) and the previously found pressure tensor from Equation (24), one finds that the requirement (32) for the pressure tensor is not satisfied:

$$\sum_{j} \nabla_{j} \left(\frac{1}{T} \mathbf{P}_{ij} \right) = \rho \nabla_{i} \frac{\hat{\mu}}{T} - \hat{e} \nabla_{i} \frac{1}{T} + \nabla_{i} \left(\rho \nabla \rho \cdot \nabla \frac{M}{T} \right).$$
(33)

The full calculation can be found in Appendix C. Extending the diagonal part of the pressure tensor with $-T\rho\nabla\rho\cdot\nabla\frac{M}{T}$ makes the requirement hold and ensures an increasing entropy. The full pressure tensor is therefore given by

$$\mathbf{P} = \left(p(\rho, T) - \frac{M}{2}(\nabla\rho)^2 - M\rho\nabla^2\rho - MT\rho(\nabla\rho) \cdot \nabla\frac{1}{T}\right)\mathbf{I} + M \nabla\rho \otimes \nabla\rho.$$
(34)

2.2.4 Steady state

One of the goals of this research is to find steady state solutions with no parts of the system moving around (zero velocity). The methods introduced in Section 2.1.3 give equilibrium solutions but are not enough to handle non-uniform temperatures. In Section 2.2, the hydrodynamic equations were introduced but they are far more general, as they describe the complete time evolution of the system instead of only the steady state solutions. It seems they are too powerful and possibly too complicated for the purpose of this research. However, it turns out that numerically solving the full set of time dependent hydrodynamic equations is an easier task than only solving the time independent steady state version.

To find the equations that describe a system in steady state, simply set all time derivatives to zero. As the particles are not moving anymore, the velocity is set to zero as well. Doing this reduces Equations (17-19) to only

$$\nabla \cdot \mathbf{P} = \mathbf{0},\tag{35}$$

$$\nabla \cdot (\kappa \nabla T) = 0. \tag{36}$$

Finding a steady state solution of the system requires only finding a density profile $\rho(\mathbf{r})$ and temperature profile $T(\mathbf{r})$ satisfying the above two equations. Note that $\nabla \cdot \mathbf{P} = \mathbf{0}$ is the conservation law derived in Section 2.2.3, It is equivalent to the equilibrium equations in case of constant temperature. The second equation ($\nabla \cdot \mathbf{J} = 0$) specifies energy balance and is the steady state version of the heat equation.

Solving these equations directly can be extremely demanding numerically as will be further explained in Section 3.1. By trial and error it turns out that one needs a precision of more than 50 digits to get a convergent result out of these differential equations in one dimension. The initial values on the boundary of the system need to be known with equal precision, which is impossible as these values are not known in advance.

Instead, when solving the time dependent hydrodynamic equations (17-19) there is no need for high precision initial values as the system will stabilize by itself. When there is too much energy at a certain point, the energy will simply dissipate to the rest of the system by means of the energy conservation law. This allows for a relatively crude initial system configuration which then automatically evolves to a stable solution. This does not mean, however, that there are no numerical issues when solving the hydrodynamic equations. Other problems arise which will be discussed in Section 3.2.2 but they are of a different nature than the issues involved in solving Equations (35-36) in a direct manner.

2.2.5 Boundary conditions

Solving the system of equations introduced in the previous section requires a number of boundary conditions. First of all the system needs to be specified at all points in space at some initial time t = 0. Secondly, for all other moments in time, one needs to put a constraint on the spatial boundaries of the system. This research distinguishes two options, referred to as an *closed wall* and an *open wall*.

The *closed wall* boundary condition simply represents a solid wall in the system. For the system that was studied, the boundary representing the nanoparticle is a solid wall. The physical interpretation of one of the closed wall conditions are related to the properties of the walls. The wall material will have a certain attraction to the fluid molecules causing either a higher or lower fluid density to be energetically preferred near the wall. When a wall is in contact with both a liquid and gas this will result in a so-called contact angle between the wall and the liquid-gas interface. This is visualized in Figure 6.

In this work all contact angles were taken to be 90° which translates to the condition $\nabla_{\hat{n}}\rho = 0$ where $\nabla_{\hat{n}} = \hat{n} \cdot \nabla$ is the derivative in the direction normal to the surface. This boundary condition does



Figure 6: Visual representation of the contact angle θ of a material. The left instance shows a bubble on a surface that repels the liquid whereas the right instance shows a surface that attracts the liquid.

assume that there is a local equilibrium near the wall [8] so that the contact angle will always be relaxed to the equilibrium contact angle.

A second constraint for the closed wall is the no-slip condition, meaning the velocity vector is zero at the walls. When \hat{n} is the vector normal to the wall then $\hat{n} \cdot \mathbf{v} = 0$ means that the component of the velocity normal to the wall is zero corresponding to the fact that particles can not go through the wall (hence the name *closed wall*). The other components of the velocity vector could in principle be non-zero meaning the fluid can flow alongside the wall ('slipping'). Setting the full velocity vector to zero at the wall, referred to as the no-slip condition, means that also this is prohibited.

A constraint on the temperature can take two forms. One can either impose the temperature T itself resulting in some heat flux or impose a heat flux $\mathbf{J} = \kappa \nabla T$ resulting in some temperature. Imposing a vanishing heat flux corresponds to a fully-insulating wall (at which the fluid can vary in temperature). Note that the imposed temperature or heat flux can be time-dependent (e.g. a pulse).

Work by Laurila et al. [8] uses a zero pressure gradient $\nabla_{\hat{n}} \mathbf{P}_{ij} = 0$ as an additional boundary condition. Such a condition is impossible within the numerical framework that was used for this research (see Section 3.2), because it is a boundary condition with a higher order derivative than the equations themselves, which is not accepted by the built-in solvers of Mathematica. Furthermore it turned out that setting more boundary conditions negatively influenced the stability of the numerical computations as will be explained in Section 3.2.2, hence a zero pressure gradient boundary condition was not considered in this research.

As a summary, the boundary conditions for the closed wall are given by

$$v_i = 0 \qquad \forall i,$$

$$\nabla_{\hat{n}} \rho = 0,$$

$$T = T_{\text{wall}}, \quad \text{or} \qquad \kappa \nabla T = \mathbf{J}_{\text{wall}}.$$

The open wall boundary conditions represents a bulk fluid. The open wall is connected to an infinite bath of a fixed density and temperature. This bulk fluid is usually taken to be a fluid at coexistence density for some temperature, so $T = T_{\text{coex}}$ and $\rho = \rho_{\text{coex}}$. Laurila et al. suggest a vanishing normal

gradient of the velocity fields, $\nabla_{\hat{n}} v_i = 0$, as well as a fixed pressure $\mathbf{P}_{ij} = p_{\text{coex}} \delta_{ij}$. Since the pressure is determined by ρ and T, for consistency it is required that $p(\rho_{\text{coex}}, T_{\text{coex}}) = p_{\text{coex}}$. Note that the pressure tensor \mathbf{P}_{ij} contains derivatives of ρ , so the condition on the pressure tensor implies that both $\nabla \rho$ and $\nabla^2 \rho$ vanish at the boundary.

Numerical trial and error however showed that the numerical stability was greatly influenced by the choice of boundary conditions. Using only a condition on ρ and T gave the numerically most stable results.

The boundary conditions for the open wall are therefore given by

$$\rho = \rho_{\rm coex},$$
$$T = T_{\rm coex}.$$

Note that fluid is allowed to flow in and out through the boundary since v is not required to vanish.

3 Numerical Methods

3.1 Equilibrium

Although finding the equilibrium states (constant temperature) of the system is not the goal of this research, a considerable amount time was devoted to researching such solutions. This section will reflect on some of the issues encountered in these computations.

Solving for an equilibrium solution means finding a solution of Equation (35) or Equation (11). As they are equivalent in equilibrium, consider only Equation (11) because it is written in a simpler form. In one dimension, with Cartesian coordinate z, the equation takes the form

$$\frac{\partial f(\rho(z), T)}{\partial \rho} - M \rho''(z) - \mu = 0,$$

which is a second order differential equation in $\rho(z)$. Note that the parameter M can be scaled away by choosing an appropriate length scale (see Appendix A). An extra condition that needs to be imposed is the number of particles N, which takes the form

$$N = A \int_0^L \rho(z) \, dz,$$

for some area A. The chemical potential μ was introduced as a Lagrange multiplier for the condition of a constant number of particles. From a mathematical point of view, a solution to the differential equation is determined by N and any two conditions on ρ which do not have to be at the same point in space. They can be two values for ρ , or two values for ρ' or one of both, say $\rho(0)$ and $\rho'(L)$. In principle the value of μ will follow from these conditions. The physical interpretation of these boundary conditions are related to the properties of the walls of the system. The relationship between ρ and ρ' depends on the contact angle of the wall (see Section 2.2.5). An example set of conditions would be $N = N_0, \ \rho'(0) = \rho'(L) = 0.$

Although mathematically the system is completely determined by the above boundary conditions, numerical solving is a lot more involved.

The first problem at hand is that instead of being able to set ρ' at two separate positions (a so-called *boundary value problem*), one needs to set a value of both ρ and ρ' at *one* position (*initial value problem*). Only when both values are known at a single location can one use the differential equation to compute ρ'' at this location and subsequently calculate ρ and ρ' at some displacement Δz and continue. One possible way of 'imposing' only $\rho'(0)$ and $\rho'(L)$ is imposing $\rho'(0)$ as a normal condition and then compute the solution for many different values of $\rho(0)$ and choose the solution that gives the required value of $\rho'(L)$. This is known as the *shooting method*.

The second problem is that the parameter N can not directly be put in, and a numerical value of μ needs to be given in order to solve the equation directly. After solving the differential equation one can compute N by integrating $\rho(z)$. Similar to the first problem one can compute the solution for many different values for μ and choosing the one that gives the required N. This turns out to be difficult because N also depends on the boundary conditions for ρ and ρ' . A single value of μ can result in different values of N. Furthermore the range of valid values for μ depends on these other boundary conditions as well, and small deviations of μ can cause large changes in N.

It follows that one should set $\rho'(0)$ and then try a range of different values for both $\rho(0)$ and μ and then check the resulting value of N and $\rho'(L)$. Searching this 2 dimensional space of values is tedious as many values result in invalid (diverging) solutions and an extremely high precision is needed to compute proper solutions in the first place.

Fortunately in some cases there are analytical expression for μ . As derived in Section 2.1.3, μ follows from the common tangent construction. This construction also gives the pressure and with Equation 12 it gives a value for ρ' . Using this method the result shown earlier in Figure 5 was obtained.

Another problem unmentioned here so far, is that many initial values will result in a free energy (local) maximum instead of minimum. The variational derivative of the functional yields a differential equation that extremizes it. Depending on the set of initial conditions (ρ, ρ', μ) form three dimensional space) one will find both local minima, local maxima, and other types of extrema (similar to saddlepoints for regular functions). Finding the global minimum means finding the unique point in this three dimensional space of initial conditions.

To get an idea for the precision required for this differential equation, consider for example the solution shown in Figure 5. At the left and rightmost point of the system the derivative of ρ is almost, but not completely, zero. A derivative that is exactly zero would result in a solution with ρ being a constant. Subsequently one needs an extremely high precision to specify values that are *almost* zero. By trial and error it turns out that one needs a precision of more than 50 digits to get a usable result out of these differential equations in one dimension. The initial values on the boundary of the system need to be known with equal precision, which is only possible if one has an analytical expression for them.

3.1.1 Functional minimization

There is an alternative way to numerically solving the equilibrium problem. The differential equation originated from a free energy functional which was to be minimized. Instead of using the differential equation, one can take any density profile $\rho(z)$ and compute the total free energy by its definition in Equation (8) with a constant temperature. Note that this is also possible for functions discretized on a grid. It is then possible to apply small random variations to the density values and compute the new total free energy. Accepting only changes that decrease the energy will then lead to a (local) minimum. This method can also be applied to the entropy which does not require constant temperature as input. The total entropy, as defined in Equation (9), can be maximized by varying both the particle density ρ and energy density e resulting in a (local) maximum. Although a constant temperature is not required, the local maximum will always have constant temperature. This was derived analytically in Section 2.1.3 and the numerical computations confirmed this.

To incorporate the condition of a fixed number of particles N, one should start with an initial density profile $\rho(z)$ that satisfies this condition, and then do only moves that do not invalidate this condition. Since the integral of ρ should remain constant it means that if $\rho(z_1)$ is increased, then $\rho(z_2)$ should be decreased by the same amount (if the grid is uniform). This way the search process only visits solutions for a single value of N and therefore minimizes the free energy under that condition. Similarly when maximizing the entropy there is the condition of constant total energy U which is the integral over e(z). This means only variations of e are allowed that leave U unchanged.

To apply the method in practice with reasonable speed and accuracy a large number of gridpoints is needed near the liquid-gas interface. A finer grid, however, will result in a slower computation. A so-called adaptive mesh refinement method was applied to solve this issue. After every hundred iterations the program checks if there are points with derivatives that are too high. If so, additional gridpoints are added dynamically and when the function is sufficiently smooth the gridpoints will be removed again. Values for minimum and maximum grid spacings as well as values for the fluctuations in ρ and e were found by trial and error. An example result of this method is shown in Figure 7. The final state shown at the bottom graph is obtained without having to work with 50 digit precision or knowing initial values with that same accuracy. The result itself is not as accurate either as only the first 4 significant digits are correct, but this is more than enough for the purpose of simply finding the density profile. Note that the figure shows a *local* maximum of the entropy. To find the global optimum it is sufficient to run the same program (with the same initial configuration) a couple of times and select the result with the highest total entropy. The figure also shows that the resulting temperature profile is uniform, and that the adaptive mesh refinement method was applied yielding more gridpoints at the interfaces.



Figure 7: Example of maximizing the entropy by varying the density ρ and energy density e on a grid. The definitions of ρ_c , T_c are given in Equation (7), and the length scale $l \approx 1.0$ nm in Appendix A. The top graph shows the initial configuration. The second graph shows the state after some random exchanges and the bottom graph shows the final result, a local maximum of the entropy. The bottom graph also shows that the number of gridpoints at the liquid-gas interface is higher than at other locations.

Everything described in this section so-far was valid in equilibrium. Although a constant temperature was not a requirement for maximizing the entropy, it was a result. To describe a system with temperature gradients it is not possible to consider the free energy. Instead, as described before, the pressure conservation law $\nabla \cdot \mathbf{P} = \mathbf{0}$ with \mathbf{P} as in Equation (34) can be used. Solving this, even in one dimension, is much harder than the previous problem. As described above, the initial conditions need to be known with an extremely high precision only achievable when an analytical expression is known. Adding the temperature as an unknown makes this worse as there are more initial conditions to be set for which there are no analytical expressions. The other approach of directly extremizing a functional by random fluctuations is not applicable here as this differential equation is not directly the result of minimizing a functional.

3.2 Hydrodynamics

The system of interest is a single hot nanoparticle immersed in a bulk fluid, as sketched in Figure 1. To study this, the hydrodynamic equations (17, 18, 20) were solved for a system with spherical symmetry. The quantities ρ , e, \mathbf{v} do not depend on the angular coordinates θ , φ but only depend on the radial coordinate r. Furthermore, the vector velocity is assumed to only have a component in the radial direction. Note that this is actually a consequence of spherical symmetry². This restriction might not be physically reasonable as this does not allow vortex flow that can occur when there are high temperature gradients. However to account for these phenomena, the equations would need to be solved in three dimensions which does not only make the equations more complex but is also computationally too demanding. With only n = 1000 gridpoints per spatial dimension, going from n (spherical symmetry) to n^3 (all three dimensions) gridpoints in total would make the computation take a million times longer. Although effects like vortexes are relevant and interesting, this research is only a first step in studying these type of systems and therefore such effects are ignored for now. In Ref. [2] a similar system is studied and the same assumptions are made.

The resulting hydrodynamic equations have one spatial coordinate r and a time coordinate t. In Appendix B, these (1+1)-dimensional hydrodynamic equations are given explicitly.

Numerically solving (partial) differential equations is a field of mathematics that tries to overcome the many problems pertaining to the stability and correctness of numerical differential equations. Even within this field, solving the hydrodynamic equations is an elaborate problem on its own. An often employed technique is the so-called Characteristic Based Splitting (CBS) scheme. This is a method for improving the stability of the hydrodynamic equations by modifying the time integration step. A general solving method would treat all variables (ρ, e, \mathbf{v}) equally and compute their value from values at previous points in time. This can be done using either an explicit or implicit method, as explained later in 3.2.1. The CBS time integration step involves computing some variables in an explicit way and others in an implicit way. For example, when the next time step for the velocity is computed, the viscosity term is implicit, and the pressure term contains both an implicit and explicit part. A method like the CBS scheme was not used because it is too involved for the purpose of this research. Furthermore, the solving method used in Mathematica already switches between (fully) explicit and implicit solvers based on the stiffness of the problem (see Section 3.2.1) and this yields sufficiently accurate results as will be shown in Section 3.4.

Another often employed method is adaptive mesh refinement, also mentioned in Section 3.1. It is a general method not specifically tied to the hydrodynamic equations. This technique involves a dynamical grid, where the grid spacing is changed while the equations are solved. This allows for a fine grid spacing in regions where this is required, e.g. near the liquid-gas interface, and a coarse grid spacing in other regions so that the computation is faster. The adaptive mesh refinement technique is especially useful if the location of the interface moves through the system so that the fine grid spacing moves with it. However such a dynamic scheme is overly complicated for the purpose of this work. As it is usually known in advance where the interface will be (a rough indication at least), a static but non-uniform grid can be used. This has the same advantages as the adaptive mesh refinement technique because the computation is accurate enough near the interface and fast because the grid is coarse where allowed. In Section 3.3, more detailed specifications are given regarding the grid spacing nearby and far from the interface.

²If the vector would have a tangential component independent of the angular coordinates then the resulting vector field can not be well-defined, as parallel transport of vectors on a sphere depends on the path taken.

3.2.1 Method of lines

The numerical method of lines³ is a technique for numerically solving (coupled) partial differential equations. The spatial dimension is discretized resulting in a system of coupled one dimensional (the time dimension) ordinary differential equations. These ODEs can be solved with sophisticated general-purpose methods that are available for one dimensional ODEs as opposed to for example a simple explicit Euler scheme. The name of the technique refers to the fact that for every spatial gridpoint, the one dimensional ODE has a single curve as a solution, so that one obtains a set of curves ('lines') in time.

Discretizing the spatial direction involves putting the functions on a grid and using the finite difference method for derivatives in the spatial direction. For example, for some function u(x,t) on a grid with spacing h, the second derivative can be approximated by

$$\left. \frac{\partial^2 u}{\partial x^2} \right|_{x=x_i} \approx \frac{u(x_i+h,t) - 2u(x_i,t) + u(x_i-h,t)}{h^2}.$$

The result is a set of differential equations for a large set of functions $u_i(t) \equiv u(x_i, t)$ that only involve time derivatives. All spatial derivatives are linear combinations of other $u_j(t)$ functions so the equations are coupled to 'its neighbors' (even if the original partial differential equation is not a coupled one). The error estimate of the approximation of spatial derivatives of u can be derived from Taylor's formula. There are several options for the finite difference derivatives. One can use higher order derivatives to have smaller errors and it is possible to only use points at one side instead of a centered derivative. For example, the first derivative can be approximated by

$$\begin{aligned} \frac{\partial u}{\partial x}\Big|_{x=x_{i}} &= \frac{u(x_{i+1},t) - u(x_{i},t)}{h} + \mathcal{O}(h),\\ \frac{\partial u}{\partial x}\Big|_{x=x_{i}} &= \frac{u(x_{i+1},t) - u(x_{i-1},t)}{2h} + \mathcal{O}(h^{2}),\\ \frac{\partial u}{\partial x}\Big|_{x=x_{i}} &= \frac{3u(x_{i-4},t) - 16u(x_{i-3},t) + 36u(x_{i-2},t) - 48u(x_{i-1},t) + 25u(x_{i},t)}{12h} + \mathcal{O}(h^{4}), \end{aligned}$$

where the last example only uses points to the left of x_i which is required at boundaries of the system. Similar expressions exist for second and higher order derivatives. In this research all spatial derivatives (interior and boundary) used a 4-th order approximation, meaning the error term is proportional to h^4 . Although it is possible to do a full analysis of the accuracy and convergence of the finite difference approximations, such an analysis is outside the scope of this work and the grid size has been chosen by comparing with other works as well as by trial and error.

The system of ordinary differential equations in the time direction, can be solved using any ODE method that supports initial value problems. For this research, Wolfram Mathematica was employed which uses the so-called LSODA method in the time direction. This is a hybrid of the non-stiff Adams method and a stiff Gear backward differentiation formula method (also known as a BDF method)⁴. Imagine some differential equation dy/dt = f(t, y). The Adams method is an *explicit* multistep method which can be thought of as Eulers method but instead of computing y_{n+1} from only $f(t, y_n)$, Adams method also includes terms with y_{n-1} , y_{n-2} and so on. The method is explicit, meaning only backward differences are used. The BDF method is an *implicit* multistep method, which means the value of y_{n+1} is computed not only from y_n but also from $f(t, y_{n+1})$. This means that one has to solve a system of equations for y_{n+1} to get an explicit expression and go to the next time step. If the problem is stiff, meaning derivatives with respect to time are large, then the BDF method performs much better and

³https://reference.wolfram.com/language/tutorial/NDSolveMethodOfLines.html



Figure 8: Left: coexistence gas density ρ_g as a function of temperature T. Right: density contrast ρ_l/ρ_g between liquid and gas coexistence densities as a function of temperature T. The definitions of ρ_c, T_c are given in Appendix A.

needs fewer steps to achieve the same accuracy. For a non-stiff problem however, Adams method is faster as it does not need to solve a system of equations first. The solver in Mathematica will test the system for stiffness and switch methods when appropriate. Note that other works on hydrodynamic equations [6, 8] use the explicit or implicit Euler method (which is essentially a specific case of Adams method and the BDF method using only one step) but do this in combination with the previously discussed CBS scheme specifically tailored to the hydrodynamic equations.

3.2.2 Numerical difficulties

The main problems that were encountered are concerned with convergence (and not accuracy) of the numerical scheme. Solutions that did converge usually converged to the expected values. Using the wrong spatial grid size or time step size can result in diverging solutions. As a computer only has finite precision the numerical solution will never perfectly match the 'real' one. For example, the density at some point in the system may come out too high or low because of finite precision arithmetics. Due to the nature of hydrodynamics this does not have to be a problem at first, because a higher (lower) density would be accompanied by a higher (lower) pressure and as such the system would stabilize itself resulting in the correct density.

The simulations become more troublesome for lower temperatures for multiple reasons explained below. Note that in most experiments the liquid is at room temperature and for water, room temperature is at $T = 0.45T_c$.

The hydrodynamic equation for momentum balance (18) has a singularity at zero density. The singularity is explicit when rewriting the equation to get an expression for $\partial \mathbf{v}/\partial t$ which contains the term $(1/\rho)\nabla \cdot \mathbf{P}$. The density contrast ρ_l/ρ_g between the liquid and gas coexistence densities increases with lowering temperature. As the gas density gets closer to zero, numerical computations become more troublesome as small fluctuations have a bigger impact near a singularity. The value of the gas density itself as well as the density contrast are shown in Figure 8. The figure shows a gas coexistence density of $\rho_g \approx 0.01\rho_c$ and a density contrast of approximately 225 at $T = 0.45T_c$. The density contrast increases more rapidly at lower temperatures. For all grid spacings and time steps that were used, the density contrast did not appear to cause problems for $T \geq 0.45T_c$ where the density contrast remains smaller than 225.

Another possible issue for lower temperatures is the small interface width, combined with the density contrast. Figure 9 shows the width of the liquid-gas interface as a function of temperature. It is obtained by solving the equilibrium equation (11) with planar symmetry, yielding solutions like the



Figure 9: Liquid-gas interface width $\xi_{\text{interface}}$ (in units of the length scale $l \approx 1$ nm) as a function of temperature in planar geometry. The definition of $\xi_{\text{interface}}$ used for this plot is the distance between the points with densities $\rho_g + 0.01(\rho_l - \rho_g)$ and $\rho_g + 0.99(\rho_l - \rho_g)$, where ρ_g, ρ_l are the coexistence gas and liquid densities respectively.

one shown in Figure 5. The interface width is then defined as the distance between the points that are at 1% and 99% between the gas and coexistence densities. Doing this for a range of temperatures yields the points in Figure 9. From the figure it follows that at $T = 0.45T_c$, the density varies by a factor of 225 over a region of only 2 nanometers. Although this requires a fine grid spacing of 0.1 nm, the liquid-gas interface did not seem to be the cause of divergencies in the simulation.

Instead, the main concerns are the boundary conditions which can cause non convergent fluctuations. No problems were encountered when both walls of the system are closed, provided the grid spacing was sufficient to describe the liquid-gas interface. In some cases the second order derivatives of the density shows oscillations in the spatial direction, but these always remain smaller than 10^{-8} and do not grow in time. However, problems arise when one of boundaries of the system is supplied with the open wall boundary condition. Fluctuations in the 8-th digit are not stable near the boundary and grow until they become of the order of the density itself. The observations regarding the stability were made by trial and error of different settings. The boundary is more stable at higher temperatures, and putting more restrictions on the boundary can worsen the stability. Furthermore the grid spacing near the boundary affects the stability and, against intuition, a coarser spacing at the boundary sometimes improves results. Exploring these effects effects is beyond the scope of this work and the attention was restricted to systems with settings that were shown to work. As pointed out in Section 2.2.5, ignoring the zero density gradient condition gave a more stable result and therefore only the values of ρ and T are restricted at the open boundary. For $T \geq 0.9T_c$, a grid spacing of roughly 1 nm near the boundary proved to be the best choice and a finer grid spacing of 0.1 nm decreased the stability.

For simulations at $T = 0.45T_c$ the open boundary seemed an issue for any of the chosen grid spacings. Instead another technique was applied, where the gradients of all fields are artificially damped. The method is inspired by Ref [4], where it was applied in order to make sure that pressure waves emitted during bubble nucleation are not reflected at the open system boundary. The same technique also improves the stability of the open boundary and allows simulations at $T = 0.45T_c$. The gradient of every field is replaced by a damped version. For the density field, this means the following replacement is performed

$$\frac{\partial \rho}{\partial r} \to \epsilon(r) \frac{\partial \rho}{\partial r}$$

where $\epsilon(r)$ is a function that is 1 everywhere except in a region near the open boundary where it

smoothly transitions to a low value. Note that higher order derivatives are treated according to

$$\frac{\partial^2 \rho}{\partial r^2} \to \frac{\partial}{\partial r} \left(\epsilon(r) \frac{\partial \rho}{\partial r} \right).$$

The simulations in which this method was used had a nanoparticle radius of 10 nm (the closed wall system boundary) and an open boundary at r = 500 nm. $\epsilon(r)$ was chosen to be a hyperbolic tangent varying from 1 to 0.1 in the region $300 \le r \le 500$. The equations are therefore unmodified for $10 \le r \le 300$ and in Ref. [4] it was shown that the physics in this region is not affected by the damping layer after it.

Some simulations were done where the liquid density at the open boundary was not *on* the coexistence curve but either slightly above or below it. This was done to test if the problems at the open boundary had a physical origin, but the stability was not influenced by these changes in boundary values.

3.3 System specification

This section will give the numerical values of different properties and settings used in the simulations.

3.3.1 Physical quantities

The length scale is one that naturally arises when making the equations dimensionless. In Appendix A expressions are derived for the length and time scales. The length scale depends only on the surface tension γ , and using the value $\gamma = 70 \cdot 10^{-3}$ N/m for the water-air interface, one obtains $l \approx 1.0$ nm. Similarly the time scale is found by using the particle mass $m = 3.0 \cdot 10^{-26}$ kg, resulting in a picosecond timescale of $t_0 = 3.1$ ps. As specified in Section 2.2.2 and 2.2.3, the viscosity and thermal conductivity are chosen to be linear in the density:

$$\eta = \eta_0 \rho,$$

$$\kappa = \kappa_0 \rho.$$

The values for η_0 and κ_0 are taken from Ref [8], which uses $\eta_0 = 2.0 \cdot 10^{-7} \text{ m}^2/\text{s}$ and $\kappa_0 = 1.8 \cdot 10^{-29} \text{ Wm}^2/\text{K}$, or per unit mass $\kappa_0 = 6.0 \cdot 10^{-4} \text{ Wm}^2/(\text{kgK})$. These values are such that at room temperature and atmospheric pressure, where the water liquid density is $\rho_l \approx 1.0 \cdot 10^3 \text{ kg/m}^3$, the viscosity is $\eta = 2.0 \cdot 10^{-4}$ Pa s. Although the actual viscosity for water is closer to $\eta = 1.0 \cdot 10^{-3}$ Pa s, this approximation is sufficient for current purposes.

3.3.2 Time step

The LSODA time integration method described in Section 3.2.1 includes a technique for dynamically computing a time step that meets certain accuracy criteria. On top of this, a maximum time step can be given which was chosen depending on the problem that was being studied. When required, the time step will automatically be decreased to achieve more accuracy. When simulating bubble kinetics and nucleation, the maximum time step was chosen to be $0.005 t_0 \approx 0.015$ ps or 15 femtoseconds. During the simulation the time step was automatically decreased by more than a factor of 10 at the start of the bubble nucleation. Testing the stable size of a vapor bubble involves less chaotic behavior allowing for a larger time step. In this case the maximum time step was chosen to be equal to t_0 or sometimes even 10 t_0 when simulating behavior at longer time scales.

3.3.3 Grid

The grid used is a non-uniform grid where the spacing is based on the expected location of the liquid-gas interface. This depends on the type of behavior that is investigated.

When testing the stable size of a vapor bubble, the system is initialized in a coexisting phase with the interface at a known location expected to not move more than a few tens of nanometers. In this case the interface is not near a system boundary, and the following grid spacing was used. In a region around the expected interface location, extending 150 nm to the left and to the right, the grid spacing is 0.1 nm. At both sides surrounding this region there is another interval of 150 nm with a grid spacing of 0.5 nm. The remaining parts of the system have a grid spacing of 1.0 nm.

When simulating the kinetics of bubble nucleation, the system is initialized into only a liquid phase with no liquid-gas interface. As a heat pulse is applied, large gradients are expected at the nanoparticle boundary in both particle density, energy density and velocity. Therefore, at the first 200 nm near this boundary a fine grid spacing of 0.1 nm is used. The next 100 nm has a spacing of 0.5 nm and the remaining part of the system extending to the other boundary has a grid spacing of 1 nm.

3.3.4 Initial configuration

For simulations of bubble nucleation the system was initialized with a constant density profile equal to the coexistence liquid density. The temperature is constant and the velocity is zero. For simulations where the stable bubble size was investigated, as well as verifications of the Young-Laplace law, the initial configuration is a coexisting state. To obtain this initial configuration, the equilibrium equations (obtained using square-gradient Density Functional Theory) are solved in planar geometry, giving a density profile $\rho_{\text{planar}}(z)$ that interpolates between the liquid and gas densities. This result is used as an initial configuration for the spherical system $\rho(r, t = 0) \equiv \rho_{\text{planar}}(r)$. The temperature of the initial configuration is always taken to be a constant. As the interface was obtained in planar geometry and is therefore not stable in radial geometry, there is an initial velocity current to correct for this. The interface always relaxes quickly to one that is radially stable and satisfies the Young-Laplace law (see Section 3.4.1).

3.3.5 Equations

A slight modification of the original energy equation was used to increase stability. The energy equation is given by (20) and is an equation for $\hat{e} = e + \frac{K}{2} (\nabla \rho)^2$. However simulations were significantly more stable when $\partial \hat{e} / \partial t$ was replaced by $\partial e / \partial t$. In Ref [8] the same replacement was done although no explanation for this was given as to why this is allowed. Note that the replacement does not matter for stationary states where time derivatives vanish.

3.4 Validation of method

To verify the numerical model two tests were performed of a system with radial geometry. The first is a verification of the Young-Laplace law at uniform temperature and the second is at non-uniform temperature regarding the stability of the system when crossing the spinodal curve.

3.4.1 Young-Laplace law

As explain in Section 2.1.4, the pressure inside a vapor bubble will be higher than the pressure of its surrounding liquid, and this is quantified by the Young-Laplace law in Equation (15). The surface tension in this equation can be computed using Equation (14) by solving an equilibrium system in planar geometry.

The goal is to verify this law by measuring Δp in a spherical system and comparing it with the value for γ that was computed using the planar solution. For this, consider a spherical system of some radius $r = r_{\text{max}}$ with a vapor bubble around the origin and a liquid at the outside. The system is closed at the outer boundary so that the number of particles is conserved, and the temperature is uniform. The system used in the numerical simulations excludes a small region around the origin and has a radius ranging from r = 1 nm to $r = r_{\text{max}}$. The reason for not including the origin is because in spherical



Figure 10: Radial dependence of the pressure \mathbf{P}_{rr} defined in Eq. (34) for a vapor bubble with a radius of 50 nm at temperature $T = 0.90T_c$. The system ranges from $r_{\min} = 10$ nm to $r_{\max} = 100$ nm.

coordinates, the equations are troublesome near the origin. The equations (in spherical coordinates) contain terms like $\frac{g(r)}{r^2}$ where g(r) is an arbitrary function of r vanishing at r = 0. Mathematically speaking, all relevant quantities are properly defined in the origin and there are no real divergencies. However, even though the limit $r \to 0$ exists, an expression like this is problematic with finite precision arithmetic. The simplest solution is simply excluding such a part from the solution and solve the equations on the remaining region.

The boundary conditions for this system are the 'closed wall' conditions as described in Section 2.2.5 both at $r = r_{\min}$ and $r = r_{\max}$. The initial configuration is a coexistence of a bubble with some radius r_{initial} , obtained as described in Section 3.3.4. As the configuration is only stable in planar geometry, the system has to stabilize. Sound waves (pressure waves) propagate through the simulation domain eventually resulting in equilibrium. Figure 10 shows the relevant component of the pressure tensor \mathbf{P}_{rr} as a function of radius for both the initial configuration and the stabilized one.

In a finite system, the pressure difference Δp manifests as a liquid pressure that is lower than coexistence pressure instead of a vapor pressure that is higher than coexistence pressure. The liquid particles are used to fill up the bubble region, causing the density of the liquid region to lower (as the region is finite) resulting in a lower pressure as seen in the figure.

It should be noted that the final (stable) bubble size depends on the total size of the system. Initializing a bubble of r = 50 nm in a system with $r_{\text{max}} = 1000$ nm will result in a system with no vapor phase at all. In a large system, there is enough liquid available to fill up the relatively small region of vapor without lowering the average density by a large amount. The Young-Laplace law is not affected by this because the pressure difference depends on the interface curvature only, regardless of the total system size. The total system size can be chosen in such a way that the desired bubble size is stable.

For a definition of the pressure inside the bubble the average of \mathbf{P}_{rr} was taken over r ranging from $r = r_{\min}$ to $r = r_{bubble} - 10$ nm. The pressure outside the bubble was taken to be the average over the range $r = r_{bubble} + 10$ nm to $r = r_{\max}$. In Figure 10 for example, the pressure inside the bubble is the average up to r/l = 40 and the outside pressure is averaged starting from r/l = 60.

Using this definition the time dependence of the pressures was computed as the system approaches equilibrium, together with the difference in pressure. The results are shown in Figure 11. The difference in pressure Δp is found to stabilize faster than the pressures themselves. This result was also observed by [8] but no explanation is known.

The computation described above was done for a variety of temperatures and bubble sizes. It should be noted that the width of the interface depends on the temperature and the radius of the bubble



Figure 11: Time dependence of the pressures inside and outside a vapor bubble with a radius of 50 nm at $T = 0.90T_c$. The timescale on the horizontal axis is in picoseconds. This data in this figure is taken from the same simulation as used for Figure 10.



Figure 12: Verification of the Young-Laplace law (pressure difference Δp versus bubble radius r) at different temperatures. The lines show the Young-Laplace law $\Delta p = 2\gamma/r$ where γ is obtained from a planer solution using Equation (14). The points show the result of the numerical computation. The errors are less than 1 percent and smaller than the marker size. For bubble sizes less than r/l = 100 the system had a boundary at $r_{\rm max}/l = 100$. For the bubbles with radius r/l = 120, the system size was $r_{\rm max}/l = 150$.



Figure 13: Density and temperature profile as a function of radius for different temperatures of the nanoparticle. The system is in a metastable liquid state for temperatures $T \leq 0.936T_c$. Although the two metastable systems reached steady state, the density profile shown for $T = 0.937T_c$ has not reached a steady state yet. The system starts at $r_{\min} = 100l$ corresponding to a nanoparticle with a radius of 100 nm.

would not be properly defined if it was of the same order of magnitude as the interface width. For temperatures $T \leq 0.95T_c$, the interface width remains an order of magnitude smaller (see Figure 9) than the bubble size ensuring a properly defined bubble radius. The pressure difference Δp was recorded at t = 30.000 ps and compared to the Young-Laplace law. The changes in density due to Laplace pressure are typically only a few percent [8] and therefore this method provides a check of the accuracy of the numerical model. The results are shown in Figure 12 and show a good match between the numerical computation and the prediction. It should be noted that although the small errors (less than 1 percent), the definition of pressure contains an average so small spatial fluctuations in the density within the bubble are washed out. Even at $T = 0.5T_c$, where the density contrast ρ_l/ρ_g is large, the precision of the numerical model is well within required bounds. However, as explained in Section 3.2.2, other issues due to system boundaries arise at $0.5T_c$.

3.4.2 Spinodal crossing

An additional tool that serves as a verification of the numerical methods is the spontaneous decomposition of the system when crossing the spinodal curve.

The system considered has a radial geometry with r ranging from 100 nm to 800 nm, corresponding to a 100 nm nanoparticle. The system was initialized at $T_0 = 0.9T_c$ with liquid coexistence density $\rho(r) = \rho_{\text{coex}}$. Subsequently the temperature of the fluid at the wall $r = r_{\text{min}}$ was increased to some other temperature T_1 (while at the open boundary $r = r_{\text{max}}$ the fluid is fixed to stay at $T = T_0$). For *rapid* temperature increments this always resulted in the nucleation of a bubble. Instead, when the temperature was increased in a quasi-static manner, the system was able to stay in a metastable liquid phase.



Figure 14: The same density profiles as in Figure 13 but now plotted in a temperature-density coexistence diagram (see Figure 4. The dotted and dashed lines represent the spinodal and coexistence curves respectively. The black dot indicates the bulk density and temperature at $r = r_{\text{max}}$ and the horizontal line indicates the fixed temperature $T = 0.936T_c$ of the fluid at $r = r_{\text{min}}$.

Several examples of resulting configurations are shown in Figure 13. For a bulk temperature of $T_0 = 0.9T_c$ the computations revealed that the liquid phase was metastable up to a wall temperature of $T_1 = 0.936T_c$ and bubble nucleation always occurs at higher temperatures.

Plotting the density and temperature profile in a coexistence diagram provides additional insight. Figure 14 shows a part of the coexistence diagram together with the results shown earlier in Figure 13 although the *r*-dependency is not visible anymore. The open boundary of the system is at a fixed temperature and (coexistence) density, represented by the large point in the figure. The closed boundary at the nanoparticle, however, only puts a constraint on the temperature and not on density. This constraint is shown as a horizontal line in the figure. In the figure it can be seen that the spontaneous nucleation for a bubble corresponds to the crossing of the spinodal curve, signifying the correctness of the numerical simulations.

4 Results

This chapter presents the results of this research starting with the bubble kinetics. This involves a short heat pulse being applied to the system (from the nanoparticle) after which a bubble nucleates, grows, and finally collapses. The simulations were all done at a bulk liquid temperature of $T = 0.45T_c$, which corresponds to the room temperature of water. The same temperature was used in Ref. [4]. Although simulations are numerically more involved at this low temperature (artificial damping is required as explained at the end of Section 3.2.2), simulation closer to T_c are troublesome since the liquid-gas interface has a width that comparable to the bubble radius, making the notion of bubble ill-defined. Furthermore, the pressure and density in these bubbles are not constant, making it hard to define a bubble pressure or density. This chapter starts with an explanation of the type of heat pulse that was applied, after which several results pertaining to the temperature and pressure evolution are presented and discussed. Finally, at the end of the chapter there will be a discussion about steady-state solutions and stable bubble sizes. As opposed to bubble nucleation, these simulation are easier to perform at temperatures closer to T_c as will be explained later.

4.1 Heat pulse

The heat flux into the fluid is given by $\mathbf{J} = -\kappa \nabla T = -\kappa_0 \rho \nabla T$ evaluated at $r = r_{\min}$. The natural scale is found by using the dimensionless units in Appendix A, and one finds $\mathbf{J} = (\kappa_0 \rho_c T_c/l) \tilde{\mathbf{J}}$ where $\mathbf{J}_0 = (\kappa_0 \rho_c T_c/l) \approx 7.4 \cdot 10^{10} \text{ W/m}^2$ for water. For a nanoparticle with a radius of 10 nm, this corresponds to a power of $\mathbf{J}_0 \approx 0.9 \cdot 10^{-4} \text{ W} \approx 3.2 \cdot 10^4 k_B T_c/t_0$, where $t_0 = l \sqrt{m \rho_c/p_c} \approx 3.1 \text{ ps}$.

The heat pulse was chosen to be a single square wave pulse into the fluid. It should be noted, however, that in experiments, the *nanoparticles* are powered by a square wave laser pulse. The resulting heat flux into the fluid is quite different because of the dynamics of the heat flow from the nanoparticle into the fluid. These dynamics are outside the scope of this work so only square wave pulses of different amplitudes and lengths were considered. In simulations, the square wave was implemented as a sharp hyperbolic tangent to avoid discontinuities.

For all plots in the following section, the system ranges from $r_{\rm rmin} = 10$ nm to $r_{\rm rmax} = 500$ nm and the temperature is $T = 0.45T_c$. Unless specified otherwise, the heat pulse has an amplitude of $0.5 \, {\rm J}_0$ and is applied over a timespan of $16 t_0 \approx 50$ ps. This means the total amount of energy supplied is equal to $2.3 \cdot 10^{-15} \, {\rm J} \approx 2.6 \cdot 10^5 \, k_B T_c$. The heat pulse always starts at $t = 10t_0 \approx 31$ ps to make sure any numerical fluctuations at initialization have vanished.

4.2 Bubble radius

The simulation results clearly show the existence of a bubble, but there are several ways to define its existence and radius. As the liquid-gas interface has a finite width, the question arises of how to define the precise location of the interface and therefore the bubble radius. Gas and liquid densities can be identified by $\rho/\rho_c > 1$ for liquid and $\rho/\rho_c < 1$ for the gas phase. This suggest that the two phases are separated at the surface where $\rho/\rho_c = 1$, and one can define the bubble radius R_b to be such that $\rho(R_b) = \rho_c$. This is the definition that is used throughout this work. An alternative is to define $\rho_{\text{avg}} = (\rho_{\text{max}} + \rho_{\text{min}})/2$ and then R_b such that $\rho(R_b) = \rho_{\text{avg}}$. Here ρ_{max} and ρ_{min} are the maximum and minimum densities anywhere in the system. This definition was used in Ref. [4]. Figure 15 demonstrates the two definitions and shows their difference over time. Except for the very early stage of bubble nucleation, the difference in radii are less than 0.20 nm, allowing the possibility of comparing results with Ref. [4].

Figure 16 shows the bubble radius for different heat pulses. The total amount of energy supplied by



Figure 15: Left: The two definitions of bubble radii at a single point in time. The solid line shows a density profile $\rho(r)$ at an early stage of bubble nucleation (t = 82 ps). The bottom arrow shows the definition used in this work, $\rho(R_b) = \rho_c$, and the top arrow corresponds to the definition $\rho(R_b) = \rho_{\text{avg}}$. Right: The two radius definitions (dashed and dotted lines, left axis) as well as their difference (solid line, right axis), both as a function of time. The dashed (bottom) line corresponds to $\rho(R_b) = \rho_c$, and the dotted (top) line corresponds to $\rho(R_b) = \rho_{\text{avg}}$. The system and heat pulse are as described in Section 4.1.



Figure 16: Bubble radius R_b for four different heat pulses as a function of time. The system and is as described in Section 4.1. All pulses transfer the same total amount of energy into the system but differ in amplitude and pulse length. The lines, from top to bottom, correspond to the following pulses. dashed: amplitude 2 \mathbf{J}_0 , pulse length 4 t_0 . dotted: amplitude 1 \mathbf{J}_0 , pulse length 8 t_0 . solid: amplitude 0.5 \mathbf{J}_0 , pulse length 16 t_0 . dot-dashed: amplitude 0.4 \mathbf{J}_0 , pulse length 20 t_0 .



Figure 17: Fluid temperature (left axis) near the nanoparticle as a function of time. The temperature is in units of the critical temperature $T_c \approx 656$ K. The three different lines, from top to bottom, denote the temperature at r_{\min} , $r_{\min} + 1$ nm and at $r_{\min} + 2$ nm. The dashed gray line (right axis) denotes the radius of the bubble. The horizontal red line near the axis indicates the period over which the heat pulse was applied. The system properties are as described in Section 4.1. The left dataset is obtained using a heat pulse amplitude of 0.5 \mathbf{J}_0 and pulse length 16 t_0 . The right dataset is the same system but using a heat pulse with an amplitude of 2 \mathbf{J}_0 and length 4 t_0 . The total amount of energy transferred into the system is equal to 8 $\mathbf{J}_0 t_0$ in both cases.

the pulses is equal, and the figure shows that shorter intense pulses lead to earlier bubble nucleation and faster growth. Furthermore the short-pulse bubbles have a larger maximal radius and a longer lifetime.

4.3 Bubble temperature

The heat pulse results in a rapid increase of the temperature near the nanoparticle surface. The rate at which the temperature increases as well as the maximum temperature depends on the pulse. The time dependence of the temperature near the nanoparticle is shown in Figure 17 for two different pulses. The pulses have different lengths, but they supply the same amount of total energy to the fluid. This figure shows that shorter pulses lead to higher maximum temperatures, and earlier in Figure 16 it was shown that short pulses also lead to larger bubbles. Furthermore the figure shows that the temperature decreases more rapidly than it increases, and that the temperature at the nanoparticle boundary is substantially higher than the temperature at 1 nm into the liquid. Later it will be shown that during these temperature peaks, the notion of bubble is ill-defined as pressure and density within the bubble are not constant. Only shortly after these peaks can one speak of an actual bubble.

In Figure 18 the temperature profile is shown as a function of radius, at different times. When a nanobubble forms, the initial temperature gradient is very large (over 300 Kelvin per nanometer) as was also visible in Figure 17. At this moment, the density has crossed the critical density, so it satisfies the vapor bubble definition given earlier. However, as the figure shows, the liquid-gas interface is larger than the bubble itself. As the bubble grows larger, the interface becomes sharper and there is a region corresponding to a bulk gas phase. The graphs also shows that during bubble growth, except for the early nucleation, the highest temperatures are located near the interface. The temperature in the bubble is slightly lower but still higher than the bulk liquid temperature. At the time of maximal bubble radius, the temperature inside the bubble is relatively homogeneous and varies by roughly 20 Kelvin over the bubble radius. During collapse, when the liquid acts as an external force compressing the bubble, the temperature inside the bubble increases again.

Figure 19 shows the same profiles but displayed in a temperature-density coexistence diagram. From



Figure 18: Density (solid line, left axis) and temperature (dashed line, right axis) profiles as a function of radius at different times. The system is as described in Section 4.1 and the heat pulse has an amplitude of 0.5 J_0 and pulse length 16 t_0 . It is the same data as the solid line in Figure 16 and as in the left graph in Figure 17. The top left graph corresponds to early bubble nucleation, the top right graph is during bubble growth. The bottom left graph is at the time of maximal radius and the bottom right graph is during bubble collapse. Note that the temperature axis of the top left graph has a different scale than the others. The fluid ranges from $r_{\rm min} = 10$ nm to $r_{\rm max} = 500$ nm with a bulk temperature $T = 0.45T_c$ at $r_{\rm max}$.



Figure 19: Local thermodynamic state of the fluid on a temperature-density coexistence diagram, taken at different times. The solid gray lines denote the coexistence and spinodal curves. The smaller graphs on the right show a zoomed in version of a part of the main diagram. The four lines correspond to the four panels of Figure 18, and the line for t = 175 ps mostly falls on top of the line for t = 263 ps. The system is as described in Section 4.1 and the heat pulse has an amplitude of 0.5 \mathbf{J}_0 and pulse length 16 t_0 . The fluid ranges from $r_{\min} = 10$ nm to $r_{\max} = 500$ nm with a bulk temperature $T = 0.45T_c$ at r_{\max} .

Figure 19(b)-(c) it can be seen that, except for early bubble nucleation, the temperature gradient is localized in the liquid. Furthermore Figure 19(b) shows that the thermodynamic state of the liquid follows the coexistence curve. Both of these results are in agreement with the results presented in Ref. [4]. The figure also confirms that after bubble nucleation, the temperature is relatively homogeneous in the vapor bubble. Because of this, the vapor bubble can be considered as a single state point (within some bounds) on the coexistence diagram. This observation allows one to probe the thermodynamics of the vapor as it traces out a path on the coexistence diagram. To this end, the temporal evolution of the state of the vapor is plotted in Figure 20. The figure shows the evolution of the thermodynamic state at r_{\min} (the nanoparticle boundary) as well as the state at $r_{\min} + 1$ nm and $r_{\min} + 2$ nm. In the next section a constraint is introduced that signifies the existence of a bubble with homogeneous pressure, denoted in Figure 20(b)-(c) by the green and red dots. For most of its lifetime, the state of the vapor is between these dots. Figure 20 shows that in this region, all three lines are relatively close to each other, confirming that the thermodynamic state of the vapor is well defined.

The results displayed in Figure 20 differ from the results presented in Ref. [4]. These differences can be attributed to the fact that in Ref. [4] a different heat pulse was applied to the system, which influences the evolution of the fluid near the nanoparticle boundary. Furthermore, a different contact angle was chosen for the nanoparticle boundary condition, causing a different density near the nanoparticle.

4.4 Bubble pressure

To characterize the thermodynamic nature of the bubble growth, one can consider the *adiabatic exponent*, denoted by γ (not to be confused with the surface tension). This exponent can be used to identify whether or not the evolution of a gas adiabatic, meaning without the flow of heat. For an ideal gas, an analytic derivation of this exponent can be done, and at $T = 0.45T_c$ the density in the gas



Figure 20: Temporal evolution of the system on a temperature-density coexistence diagram. The solid line corresponds to the state at r_{\min} (the nanoparticle surface), and the dashed and dotted lines show the state at $r_{\min} + 1$ nm and $r_{\min} + 1$ nm respectively. The arrows indicate the direction of time. The smaller graphs on the right show a zoomed in version of a part of the main diagram. The green and red dots indicate the start and end of the well-defined bubble constraint (37) introduced in Section 4.4. The oscillations shown by the solid line in (c) are numerical artifacts of the boundary conditions and happen *after* the red dot. The system is as described in Section 4.1 and the heat pulse has an amplitude of 0.5 \mathbf{J}_0 and pulse length 16 t_0 . The fluid ranges from $r_{\min} = 10$ nm to $r_{\max} = 500$ nm with a bulk temperature $T = 0.45T_c$ at r_{\max} .



Figure 21: Pressure profiles P_{rr} as a function of radius for two different bubble sizes. The arrows in the plot indicate the bubble radius corresponding to that pressure profile. The system and heat pulse are as described in Section 4.1. The pressure P_{rr} is the rr component of the pressure tensor in Equation (34).

bubble is low and so the ideal gas law should be a good approximation. The surrounding liquid can be seen as an external pressure acting on the gas bubble, expanding it and compressing it. An ideal gas satisfies $PV = Nk_BT$ and hence when a system evolves isothermally it satisfies $P \sim V^{-1}$ under the assumption that N is constant. For adiabatic evolution (also with constant N) the gas satisfies the power law behavior $P \sim V^{-\gamma}$ and the adiabatic exponent is given by $\gamma = C_p/C_V$ where C_p and C_V are the heat capacities of the fluid at constant pressure and constant volume, respectively. As water is a triatomic molecule, its adiabatic exponent should be between 7/5 and 9/5. The Van der Waals model however does not incorporate the rotational degrees of freedom of molecules. The system studied here is therefore a monoatomic vapor and its expected adiabatic exponent is 5/3.

To compare the isothermal and adiabatic models to the simulations, the pressure inside the bubble is plotted versus its volume, where the volume of the nanoparticle is excluded.

Like the bubble radius, the pressure inside the gas bubble also admits multiple definitions. Note that the pressure here refers to the rr component of the pressure tensor in Equation (34). At early stages of bubble evolution the density, temperature and pressure within the bubble are not constant. Hence one can not speak of a properly defined pressure of the bubble at that stage. During the stage where the bubble radius is close to its maximum, the pressure within the bubble has stabilized, as can be seen in Figure 21. This figure clearly shows that at the earlier bubble stage, there is no well defined notion of bubble pressure. For comparison, the pressure at $r = r_{\min}$ has been plotted as a function of time as well as the pressure at $r_{\min} + 1$ nm and at $r_{\min} + 2$ nm, see Figure 22. It is clear that for times 100 ps $\leq t \leq 250$ ps the pressure is well-defined. In the same time interval the radius is also well-defined so both the pressure and volume have meaningful values. Based on this, the following constraint is now used as a definition of a *well-defined bubble*:

$$|P(r_{\min} + 2 \text{ nm}) - P(r_{\min})| < 0.001.$$
(37)

In the analysis that follows, the pressure was taken to be the average over r ranging from r_{\min} to $r_{\min} + 2$ nm to cancel out possible fluctuations.

With a properly defined pressure and radius, the relation between P and V can be investigated. Note that the volume of the gas bubble is simply $(4\pi/3)(R_b^3 - r_{\min}^3)$. Figure 23 shows a plot of $\ln P$ versus $\ln V$ and it can be concluded that neither exponent corresponds to classical expectations. For bubble growth the exponent varies between 0.5 and 1.5 depending on the simulation parameters. During collapse the pressure is almost constant and the exponent is close to zero. The plots also show that the shape of the heat pulse greatly influences the bubble evolution. For both simulations in the figure



Figure 22: Time evolution of different pressure definitions. The dotted lines, left axis, show the three pressure definitions as a function of time: P_{rr} evaluated at $r_{\min}, r_{\min} + 1$ nm and $r_{\min} + 2$ nm. The lines for $r_{\min}, r_{\min} + 1$ nm fall on top of each other, the line for $r_{\min} + 2$ nm is slightly below the other ones at times before t = 100 ps. The black (and partly gray) line, right axis, shows the difference between the pressure at $r_{\min} + 2$ nm and at r_{\min} . The well-defined bubble constraint (37) is only satisfied where the line is solid black. It is not satisfied where the line is dashed gray. The data is taken from the same simulation as shown in Figure 15 so the time values can be compared. The system and heat pulse are as described in Section 4.1.

the same amount of total heat was applied (but over a different timespan so a different pulse shape) and the pressures and maximal radii differ as well as the P - V relationship. In Ref. [4] it was also concluded that neither an exponent of 5/3 nor 1 is valid and other values were found, namely 2.6 for growth and 0.4 for collapse. The difference between those exponents and the ones found here can be attributed to the fact in Ref. [4] a different heat pulse was applied to the system.

The discrepancies between the observed exponents and the values 1 or 5/3 can be explained by looking at the total number of particles in the gas bubble. The relationships $P \sim V^{-1}$ and $P \sim V^{-\gamma}$ are valid for an ideal gas under the assumption of a constant number of particles. Although the ideal gas law is a good approximation at low densities, a constant number of particles is not applicable here. Figure 24 shows the number of particles N_b in the gas bubble as a function of time, defined by:

$$N_b = 4\pi \int_{r_{\min}}^{R_b} r^2 \rho(r) \ dr$$

The figure shows that N_b rapidly increases during the very early nucleation phase when the notion of bubble is not properly defined. During this same phase there is a small peak after which N_b decreases again. From then on there is a 'well-defined bubble' and during the remaining growth of this bubble, N_b grows more slowly. When the bubble collapses, the number of particles decreases slowly, as the gas is condensing into the liquid. It should be noted that when N_b is not constant, the concept of adiabatic evolution becomes a bit unclear. It would mean that the gas is expanding (or collapsing) while particles are moving in or out but *without* heat flowing in or out.

Since N_b is not constant, it can be more interesting to consider the average density $\rho_b = N_b/V$ in the bubble. Here V is the volume of the bubble, defined as $V = (4\pi/3)(R_b^3 - r_{\min}^3)$. The average density



Figure 23: The pressure in the bubble versus the bubble volume for two different datasets. The well-defined bubble constraint (37) is only satisfied where the line is solid black. It is not satisfied where the line is gray. Both plots show the lines $P \sim V^{-1}$ and $P \sim V^{-5/3}$ as well as a fit for the collapse of the bubble, with exponents 0 (top) and 0.13 (bottom). The top dataset is obtained using a heat pulse as described in Section 4.1. That is a pulse amplitude of 0.5 \mathbf{J}_0 and pulse length 16 t_0 . The bottom dataset is the same system but using a heat pulse with an amplitude of 2 \mathbf{J}_0 and length 4 t_0 . The total amount of energy transferred into the system is equal to 8 $\mathbf{J}_0 t_0$ in both cases.



Figure 24: The number of particles N_b inside the vapor bubble (solid black line, left axis) and the radius of the bubble (dashed blue line, right axis) as a function of time. The well-defined bubble constraint (37) is only satisfied where the line is solid black. It is not satisfied where the line is gray. The dataset on the left is obtained using a heat pulse with amplitude 0.5 \mathbf{J}_0 of length 16 t_0 and the bottom dataset using an amplitude of 2 \mathbf{J}_0 and length 4 t_0 . The total amount of energy transferred into the system is equal to 8 $\mathbf{J}_0 t_0$ in both cases.



Figure 25: The average density ρ_b (defined as N_b/V) in the vapor bubble (solid black line, left axis) and the radius of the bubble (dashed blue line, right axis) as a function of time. The density is in units of the critical density ρ_c . The well-defined bubble constraint (37) is only satisfied where the line is solid black. It is not satisfied where the line is gray. The dataset on the left is obtained using a heat pulse with amplitude 0.5 \mathbf{J}_0 of length 16 t_0 and the dataset on the right using an amplitude of 2 \mathbf{J}_0 and length 4 t_0 . The total amount of energy transferred into the system is equal to 8 $\mathbf{J}_0 t_0$ in both cases.

 ρ_b is shown in Figure 25, for the same two datasets as were shown in Figure 24. The figure shows that the density does vary (although not by a large amount) over the lifetime of the bubble.

To try and improve on the $P \sim V^{-1}$ and $P \sim V^{-\gamma}$ relationships, the pressure was plotted versus the (inverse) density ρ instead of V. This takes into account the fact that the number of particles N_b in the bubble is not constant. The relation $P \sim \rho$ is expected to hold for isothermal evolution as is clear from the ideal gas law $P = \rho k_B T$. As stated before, the concept of adiabatic evolution without a constant number of particles is somewhat ill-defined, and it is not clear if $P \sim \rho^{5/3}$ should hold. Nevertheless, the $P - \rho$ dependence was plotted and it is shown in Figure 26. Interestingly, the growth of the bubble now seems to match the adiabatic exponent 5/3 even though it is theoretically not clear whether such a power law should hold. The exponents during bubble collapse are still very low, similar to what was seen before.

4.5 Stable bubble size

As opposed to investigating the *kinetics* of bubble formation, another goal of this work is to find solutions of steady state bubbles. In the experiment where nanoparticles are solar powered and generate vapor (see Ref. [1]) the bubbles are expected to be stable as they rise to the surface of the container (whilst the nanoparticle stays inside the bubble). The nanoparticles used in this experiment have a radius of about 100 nm, significantly larger than the nanoparticles investigated for bubble kinetics which have a radius of 10 nm. In order to match more closely with the experiment, all simulations discussed in this section correspond to a nanoparticle of 100 nm, meaning the fluid ranges from $r_{\rm min} = 100$ nm to $r_{\rm max}$.

One can expect that for a constant heat flux into the fluid, a bubble of some radius can be sustained, and the amount of heat flowing into the fluid at the nanoparticle boundary is equal to the total heat flowing out of the fluid at the 'open boundary' at $r = r_{\text{max}}$. The size of such a stable radius will depend on the heat flux. Note that one can impose either the heat flux or the temperature at the boundary and the other quantity will follow. In the simulations described in this section, the temperature was imposed as a boundary condition instead of the heat flux. This choice does not influence the resulting



Figure 26: Log-log plots of the pressure P_{rr} in the bubble versus the inverse bubble density ρ_b^{-1} for four different datasets. The well-defined bubble constraint (37) is only satisfied where the line is solid black. It is not satisfied where the line is thin and gray. The plots show the lines $P \sim \rho^1$ and $P \sim \rho^{5/3}$ as well as a line with exponent 0.3 that matches the collapse of the bubble. The pulse amplitude and length are shown in the plot titles in units of \mathbf{J}_0 and t_0 respectively. The total amount of energy transferred into the system is equal to 8 $\mathbf{J}_0 t_0$ in all four cases.

steady state solutions.

Although experiments are usually performed at room temperature, corresponding to $T = 0.45T_c$, simulations are more easily performed near T_c . Simulations at $0.45T_c$ require artificial damping of derivatives at the open boundary, as was described in Section 3.2.2. For the system studied here this not acceptable, because the amount of heat flowing out of the open boundary is relevant and should not be artificially damped. All simulations referred to in this section are therefore performed at a bulk temperature of $T = 0.90T_c$.

In order to find (the size of) a stable bubble, a system was first initialized into a liquid state with constant temperature ($T = 0.90T_c$). Subsequently the temperature at the nanoparticle boundary was increased (over the timespan of few thousand picoseconds) so that a bubble nucleates and start growing. The temperatures that were considered ranged from $0.91T_c$ to $T0.94T_c$. It was quickly observed, however, that the growth of such bubbles show no sign of slowing down. At initial bubble nucleation, there is a quick bubble growth and it reaches a size of about 200 nm depending on the temperature. After this, the growth is very slow with only one nanometer per 200.000 picoseconds. Even after long simulation times of 10^7 ps = $10 \ \mu$ s, the bubble growth rate does not diminish.

In Section 3.4.2 it was shown that the crossing of the spinodal occurs at a nanoparticle temperature of $T = 0.937T_c$. Below this temperature the system remains in a liquid state, unless the temperature is increased quick enough in which case a bubble can also exist at a nanoparticle temperature of $T = 0.91T_c$. Simulation results suggested that for $T = 0.94T_c$, the radius of a stable bubble might very well be more than 2000 nm. Such large bubbles require large systems that are more complicated to simulate and take more computational time. Therefore it is advantageous to first search for smaller stable bubbles and therefore consider lower nanoparticle temperatures. The temperature at the nanoparticle was therefore taken to be $T = 0.91T_c$ and increased quickly enough to ensure the existence of a bubble.

As the bubble growth rate was too slow, it was required to start the simulation with a much larger bubble (instead of nucleating one) and let the system evolve from there. The system was initialized into a coexisting state that was obtained from equilibrium equations, as described in Section 3.3.4. Different initial bubble radii were considered, ranging from 200 nm to 2000 nm. The system size $r_{\rm max}$ was taken to be $r_{\rm max} = 1000$ nm for bubbles smaller than (or equal to) 500 nm, and $r_{\rm max} = 5000$ nm for bubbles larger than 500 nm.

Figure 27 shows the bubble radius R_b as a function of time for different starting locations of the liquid-gas interface. Note that initially all bubbles are shrinking because initially the temperature is constant everywhere so the bubble is not stable. The temperature at the nanoparticle is only increased slowly after 30 ns. Figure 27(b) shows a simulation where the bubble first shrinks (after the nanoparticle temperature is increased) and only starts growing after about 400 nanoseconds. This can be explained by considering the heat flux profiles as will be shown later. Figure 27(a)-(d) suggests that for a nanoparticle temperature of $0.91T_c$, the size of a stable bubble is lies between 250 and 300 nm. Pinpointing the exact size, however, turned out to be difficult due to the fact that the simulations are computationally demanding. The timescale on which these bubbles stabilize is several microseconds. This is orders of magnitude larger than the simulation timescale equal to $t_0 \approx 3.1$ ps, causing long simulation times and making a sweep of the parameter space infeasible. Furthermore, looking at the heat flux profiles reveals that even though the graphs in Figure 27 seem to suggest a stable radius between 250 and 300 nm, the stable bubble radius might be much larger than that, as will be explained next.

Figure 28 shows two heat flux profiles taken from the dataset corresponding to Figure 27(b), where the bubble was initialized at a radius of 250 nm. The heat flux profile shown in Figure 28(a) is taken at time t = 125 ns when the bubble is shrinking, whereas that in Figure 28(b) corresponds to a growing



Figure 27: Bubble radius R_b (in nanometers) as a function of time (in nanoseconds). The temperature of the bulk liquid at r_{max} is $T_0 = 0.90T_c$. The temperature at r_{\min} (at the nanoparticle) is $T_1 = 0.91T_c$. The different graphs show different starting positions of the liquid-gas interface (200, 250, 300 and 400 nm). The temperature at r_{\min} starts out at T_0 and is then slowly increased to T_1 , which causes the behavior near 30 ns.



Figure 28: Heat flux (solid line, left axis) and temperature (dashed line, right axis) at two different times. The dataset corresponds to what is shown in Figure 27(b). The heat flux shown here $(r^2 \mathbf{J})$ is normalized with a factor of r^2 to account for the spherical geometry: a horizontal line therefore corresponds to an equal heat influx and outflux ($\nabla \cdot \mathbf{J} = 0$). The heat flux is in units of $l^2 \mathbf{J}_0$, where $l \approx 1$ nm and \mathbf{J}_0 is given in Section 4.1. The simulated fluid ranges from $r_{\min} = 100$ nm to $r_{\max} = 5000$ nm.



Figure 29: Heat flux (solid line, left axis) and temperature (dashed line, right axis). The heat flux is normalized as in Figure 28. The arrows indicate the evolution of the heat flux profile in time. The simulated fluid ranges from $r_{\min} = 100$ nm to $r_{\max} = 5000$ nm.

bubble at t = 1250 ns. Note that since the shown heat flux contains a factor r^2 , a horizontal line corresponds to a steady state where the total amount of heat flowing out of each spherical surface is equal to the amount of heat flowing in. Furthermore, both graphs show a decreasing flux in the liquid phase, meaning energy is locally being stored, so the temperature is increasing. Figure 28(a) shows that when the bubble is shrinking, there is more energy flowing away (outwards, through the liquid) from the interface than energy flowing in from the nanoparticle. In Figure 28(b) at a much later point in time, this is reversed and more energy is delivered by the nanoparticle than there is energy leaving through the liquid phase. The direction in which the liquid-gas interface is moving is therefore related to the heat flux difference at the interface. As the figure shows, the heat flux profile in the liquid becomes flatter as time evolves. Because of this, a bubble that first seems to be only shrinking might start growing at a much later stage.

Figure 29 shows a heat flux profile taken from the simulation corresponding to Figure 27(d), where the liquid-gas interface was initialized at 400 nm. Figure 27(d) suggest that the stable bubble size is less than 400 nm as the bubble radius is only decreasing. The heat flux profile, however, indicates that the bubble might start growing again at a much later point in time. The arrows in Figure 29 indicate the evolution of the heat flux profile in time. It is, however, computationally very demanding to simulate this as it can take microseconds before the heat flux has stabilized. A definite answer to the question of the size of a stable bubble therefore remains unresolved.

5 Conclusion and outlook

In summary, this work presented a theory and analysis of the dynamics associated with vapor bubbles around nanoparticles in water. Systems with nanobubbles are relevant to recent experiments where nanoparticles are heated up by either laser pulses or solar energy. In this work the Van der Waals model was introduced together with square-gradient density functional theory, allowing the description of equilibrium systems with a liquid-gas phase transition. Then, the necessary hydrodynamic tools were presented that made the study of non-equilibrium fluids possible. These equations were solved numerically, which required some non-trivial numerical schemes. The Young-Laplace law provided a verification of the numerical correctness.

The hydrodynamical model was then applied to study the system of interest, a vapor bubble around a hot nanoparticle in liquid water. The kinetics on short timescales as well as stable bubbles on longer timescales were studied. Results include the time-dependent behavior of density, temperature and pressure profiles. Furthermore it was shown that delivering the same amount of energy with a *short* pulse yields a larger bubble and larger temperature gradient than what would be obtained by using a longer pulse. The growth of these bubbles bears resemblance to the adiabatic expansion of an ideal gas, even though the number of particles in the bubble is not conserved. Interestingly, the power law $P \sim \rho^{5/3}$ seems to hold for the bubble expansion, and exploring the theory behind this is a possible topic for future work. Determining the amount of heat required to sustain a stable bubble remains an open problem, as the relevant timescales of these phenomena are orders of magnitude larger than the hydrodynamic simulation timescale.

Systems with nanobubbles are promising tools for a variety of applications and it is therefore useful to continue the study of these systems. This work contains assumptions that are possibly over simplified and might be improved in future studies. For example, spherical symmetry is assumed which excludes the possibility of a velocity with a non-zero angular component. This means that there is no flow in the direction around the nanoparticle in which kinetic energy can be stored. Real-world systems with temperature gradients do exhibit such circular flow behavior but including such terms in the equations of motion was outside the scope of this research. It is important to analyze the possible effects this might have on the system studied here. A simulation of a three dimensional system might be too computationally demanding because of the high number of gridpoints, but the same effects are present in two dimensions. Solving the equations in two dimensions might allow one to learn about the effects that these flows have on nanobubbles and possibly extrapolate this to three dimensional systems.

Another possibility for future work is describing non-equilibrium systems by maximizing the entropy. When maximizing the entropy using square-gradient density functional theory, a direct consequence is a constant temperature. However, it might be possible to maximize the entropy under the constraint of a constant heat flux, in order to find a set of equations that describe a steady state non-equilibrium system. In principle, a maximal entropy applies only to equilibrium systems so a temperature gradient is excluded. Nevertheless, one could consider the system as being made up of several smaller subvolumes. In each of these subvolumes the temperature is approximately constant and such a volume is then in mechanical equilibrium (or steady state) with its neighbors. Adding the constraint of constant heat flux was briefly attempted by the use of an additional Lagrange multiplier. However, the resulting equations were too complex to be solved numerically, similar to the steady state equations as described in Section 3.1. Further studying of this method, however, might provide a way of using entropy maximization as a way to describe steady state systems with temperature gradients.

A Appendix: dimensionless units

The temperature, density and pressure at the critical point of the Van der Waals model in Equation (1) are given by

$$k_B T_c = \frac{8a}{27b}, \qquad \rho_c = \frac{1}{3b}, \qquad p_c = \frac{a}{27b^2}$$

The values for a, b are chosen to match the properties of water, resulting in $T_c \approx 656$ K, $\rho_c \approx 197$ kg/m³ and $p_c = 2.23 \cdot 10^7$ Pa. One can obtain a dimensionless equation of state

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

where $T, \tilde{\rho}, \tilde{p}$ are the dimensionless temperature, density and pressure defined as

$$\tilde{T} = \frac{k_B T}{k_B T_c}, \qquad \qquad \tilde{\rho} = \frac{\rho}{\rho_c}, \qquad \qquad \tilde{p} = \frac{p}{p_c}.$$

Using this equation of state, results will be valid for any value of the parameters a, b by scaling back all quantities. The other quantities introduced in Section 2.1.1 can be made dimensionless as well by defining a rescaled free energy, internal energy and entropy

$$\tilde{f} = \frac{8b}{k_B T_c} f\left(=\frac{27b^2}{a}f\right), \qquad \tilde{e} = \frac{8b}{k_B T_c}e, \qquad \tilde{s} = \frac{8}{3k_B}s.$$

scaled in such a way that they are equal to one at the critical point (in d = 3 dimensions). The quantities in Equations (2, 3, 4) become

$$\begin{split} \tilde{f}(\tilde{\rho},\tilde{T}) &= \frac{8}{3}\tilde{T}\tilde{\rho}\left(\log\left(\frac{\tilde{\rho}\;\tilde{T}^{-\frac{d}{2}}}{1-\tilde{\rho}/3}\right) + \log\left(\rho_c\Lambda_c^d\right) - 1\right) - 3\tilde{\rho}^2,\\ \tilde{e} &= \frac{d}{2}\frac{8}{3}\tilde{\rho}\tilde{T} - 3\tilde{\rho}^2,\\ \tilde{s} &= -\frac{8}{3}\left(\log\left(\frac{\tilde{\rho}\;\tilde{T}^{-\frac{d}{2}}}{1-\tilde{\rho}/3}\right) + \text{const}\right) + \frac{d}{2}\frac{8}{3}, \end{split}$$

for which $\tilde{f} = \tilde{e} - \tilde{T}\tilde{\rho}\tilde{s}$ holds.

The next step is to make the integral in Equation (8) dimensionless as well as the hydrodynamic Equations (17-19). The parameter M in front of the square-gradient term can be scaled away by introducing the appropriate length scale l. The mass m in the momentum equation can be scaled away by choosing the right time scale t_0 . Define

$$l = \sqrt{\frac{8M}{9k_B T_c b}} = \sqrt{\frac{3M}{a}} \quad (\sim 1 \text{ nm}), \qquad t_0 = \sqrt{\frac{m\rho_c}{p_c}} l = \sqrt{\frac{27mMb}{a^2}} \quad (\sim 3 \text{ ps}).$$

By using the surface tension (directly related to M) of water the value of l can be obtained which is approximately one nanometer. Together with the mass of water one obtains a timescale in the order of picoseconds. By scaling every coordinate by l ($d\mathbf{r} = l^3 d\tilde{\mathbf{r}}$) Equation (8) becomes

$$\begin{split} F[\rho(\mathbf{r})] &= \int_{V} d\mathbf{r} \, \left(f(\rho(\mathbf{r}), T(\mathbf{r})) + \frac{M}{2} (\nabla \rho(\mathbf{r}))^{2} \right) \\ &= \int_{\tilde{V}} d\tilde{\mathbf{r}} \, l^{3} \left(\frac{k_{B}T_{c}}{8b} \tilde{f}(\tilde{\rho}, T) + \frac{M}{2} \left(\frac{\rho_{c}}{l} \right)^{2} (\tilde{\nabla} \tilde{\rho}(\tilde{\mathbf{r}}))^{2} \right) \\ &= \frac{k_{B}T_{c}}{8b} l^{3} \int_{\tilde{V}} d\tilde{\mathbf{r}} \, \left(\tilde{f}(\tilde{\rho}, T) + \frac{1}{2} (\tilde{\nabla} \tilde{\rho}(\tilde{\mathbf{r}}))^{2} \right), \end{split}$$

independent of M. Using $\tilde{F} = \frac{8b}{l^3} \frac{1}{k_B T_c} F$ instead of F gives a pressure tensor $\tilde{\mathbf{P}} = \mathbf{P}/p_c$ that is independent of M as well. The term $\partial(m\rho \mathbf{v})/\partial t$ in Equation (18) can be rewritten using the time scale t_0 . Define the dimensionless velocity as $\tilde{\mathbf{v}} = (t_0/l)\mathbf{v}$, then

$$\frac{\partial(m\rho\mathbf{v})}{\partial t} = \frac{m\rho_c l}{t_0^2} \frac{\partial(\tilde{\rho}\tilde{\mathbf{v}})}{\partial \tilde{t}} = \frac{p_c}{l} \frac{\partial(\tilde{\rho}\tilde{\mathbf{v}})}{\partial \tilde{t}}.$$

The right hand side of Equation (18) has a term $\nabla \cdot \mathbf{P}$ which becomes $(p_c/l)\tilde{\nabla} \cdot \tilde{\mathbf{P}}$. The p_c/l cancels and the equation is indeed dimensionless and independent of M and m.

Equations (18,19) also contain the viscosity η in the dissipative stress tensor σ and the thermal conductivity κ . However, all 'variables have been used' and one can not use another scaling to get rid of η and κ . Values for η and κ are simply taken to be those of water, rescaled to fit in the dimensionless hydrodynamic equations.

B Appendix: radial geometry

All quantities are assumed to only depend on the radial coordinate r. For a second-rank tensor $\mathbf{A}(r)$ with components A^{i}_{j} , the r component of the vector $\nabla \cdot \mathbf{A}$ is given by

$$(\nabla \cdot \mathbf{A})_r = \partial_r A^r_{\ r} + \frac{2}{r} A^r_{\ r} - \frac{1}{r} \left(A^\theta_{\ \theta} + A^\phi_{\ \phi} \right) + \frac{\cos\theta}{\sin\theta} A^\theta_{\ r} + \partial_\theta A^\theta_{\ r} + \partial_\phi A^\phi_{\ r}. \tag{38}$$

For a tensor proportional to the identity tensor this simplifies to

$$(\nabla \cdot \lambda \mathbf{I})_r = \partial_r \lambda + \frac{2}{r} \lambda - \frac{1}{r} (\lambda + \lambda) = \partial_r \lambda.$$
(39)

For a scalar $\rho(r)$ and a radial vector $\mathbf{v}(r) = v(r)\hat{\mathbf{r}}$, gradients are given by

$$\nabla \rho = \frac{\partial \rho}{\partial r} \hat{\mathbf{r}}, \qquad \nabla^2 \rho = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho}{\partial r} \right), \qquad \nabla \cdot \mathbf{v} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 v \right).$$

The hydrodynamic equations (17-20) require explicit expressions for

 $\nabla\cdot\mathbf{P},\qquad \nabla\cdot\sigma,\qquad \nabla\cdot(\rho\mathbf{vv}),\qquad \mathbf{P}:\nabla\mathbf{v},\qquad \sigma:\nabla\mathbf{v},\qquad \nabla\cdot(\kappa\nabla T).$

The pressure tensor **P** is defined in Equation (34). The only non vanishing component in $\nabla \rho \otimes \nabla \rho$ is the rr component so the tensor is of the form

$$\mathbf{P} = X\mathbf{I} + Y \,\hat{\mathbf{r}} \otimes \hat{\mathbf{r}},$$

$$P_r^r = \underbrace{p(\rho, T) - M\rho \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho'\right) - \frac{1}{2} M(\rho')^2 - T\rho \rho' \frac{\partial}{\partial r} \frac{M}{T}}_X + \underbrace{M(\rho')^2}_Y,$$

with other components $P^{\theta}_{\theta} = X$ and $P^{\phi}_{\phi} = X$ and where $\rho' = \partial \rho / \partial r$. Entering this in Equation (38) yields

$$(\nabla \cdot \mathbf{P})_r = \partial_r (X+Y) + \frac{2}{r}Y = \partial_r X + \frac{1}{r^2}\partial_r (r^2 Y).$$

The dissipative stress tensor is defined in Equation (25). In spherical coordinates it becomes

$$\sigma_{ij} = (\zeta - 2\eta/d) (\nabla \cdot \mathbf{v}) \delta_{ij} + \eta (\nabla_i v_j + \nabla_j v_i),$$

$$\sigma = (\zeta - 2\eta/d) (\nabla \cdot \mathbf{v}) \mathbf{I} + 2\eta \mathbf{B},$$

$$B_r^r = \partial_r v, \qquad B_\theta^\theta = B_\phi^\phi = \frac{v}{r}.$$

For **B** it follows from Equation (38) that

$$(\nabla \cdot B)_r = \partial_r \partial_r v + \frac{2}{r} \partial_r v - 2\frac{v}{r^2} = \partial_r \left(\frac{1}{r^2} \partial_r (r^2 v)\right) = \partial_r \left(\nabla \cdot \mathbf{v}\right).$$

To obtain an expression for $(\nabla \cdot \sigma)_r$, Equation (39) is used is used for the part proportional to the identity tensor. This gives

$$(\nabla \cdot \sigma)_r = (\zeta + 2\eta(1 - \frac{1}{d}))\partial_r(\frac{1}{r^2}\partial_r(r^2v)).$$

The tensor $\rho \mathbf{v} \mathbf{v}$ in $\nabla \cdot (\rho \mathbf{v} \mathbf{v})$ only has an *rr* component, and by Equation (38) it follows that

$$(\nabla \cdot (\rho \mathbf{v} \mathbf{v}))_r = \frac{1}{r^2} \partial_r (r^2 \rho v v).$$

The notation $\mathbf{P} : \nabla \mathbf{v}$ refers to the double dot product of so-called dyadics⁵. In other notation it is given by $\sum_{ij} P_j^i \nabla_i v^j$. Although \mathbf{v} only has an r component and no θ, ϕ dependence, the tensor $\nabla \mathbf{v}$ also has $\phi \phi$ and $\theta \theta$ components due to curvature. With $\mathbf{v} = v(r)\hat{\mathbf{r}}$, the expressions $\mathbf{P} : \nabla \mathbf{v}$ and $\sigma : \nabla \mathbf{v}$ are given by

$$\begin{split} P^i_{\ j} \nabla_i v^j &= P^r_{\ r} \partial_r v + P^{\theta}_{\ \theta} \frac{1}{r} v + P^{\phi}_{\ \phi} \frac{1}{r} v = X \frac{1}{r^2} \partial_r (r^2 v) + Y \partial_r v, \\ \sigma^i_{\ j} \nabla_i v^j &= \sigma^r_{\ r} \partial_r v + \sigma^{\theta}_{\ \theta} \frac{1}{r} v + \sigma^{\phi}_{\ \phi} \frac{1}{r} v = (\zeta - 2\eta/d) \left(\frac{1}{r^2} \partial_r (r^2 v) \right)^2 + 2\eta \left((\partial_r v)^2 + 2\frac{v}{r^2} \right). \end{split}$$

The scalar temperature T(r) satisfies $\nabla T = \frac{\partial T}{\partial r} \hat{\mathbf{r}}$ so $\nabla \cdot (\kappa \nabla T) = \frac{1}{r^2} \partial_r (r^2 \kappa \partial_r T)$ where $\kappa = \kappa_0 \rho(r)$.

The final equations become

$$\begin{split} &\frac{\partial\rho}{\partial t} = -\frac{1}{r^2} \partial_r (r^2 \rho v), \\ &\frac{\partial\rho v}{\partial t} = -\frac{1}{r^2} \partial_r (r^2 \rho v v) - \partial_r X - \frac{1}{r^2} \partial_r (r^2 Y) + (\zeta + 2\eta(1 - \frac{1}{d})) \partial_r (\frac{1}{r^2} \partial_r (r^2 v)), \\ &\frac{\partial e}{\partial t} = -\frac{1}{r^2} \partial_r (r^2 e v) - X \frac{1}{r^2} \partial_r (r^2 v) - Y \partial_r v + (\zeta - 2\eta/d) \left(\frac{1}{r^2} \partial_r (r^2 v)\right)^2 + 2\eta \left((\partial_r v)^2 + 2\frac{v}{r^2}\right) + \kappa_0 \frac{1}{r^2} \partial_r (r^2 \rho \partial_r T) \end{split}$$

C Appendix: pressure tensor

The goal is to check if the pressure tensor

$$\mathbf{P} = \left(p(\rho, T) - \frac{M}{2} (\nabla \rho)^2 - M \rho \nabla^2 \rho \right) \mathbf{I} + M \, \nabla \rho \otimes \nabla \rho,$$

satisfies

$$\sum_{j} \nabla_{j} \left(\frac{1}{T} \mathbf{P}_{ij} \right) = \rho \nabla_{i} \frac{\hat{\mu}}{T} - \hat{e} \nabla_{i} \frac{1}{T}.$$
(40)

The most general form is given by M = K + CT with K, C constants, however, this derivation will be done for M = K (so C = 0) because it is simpler and it is the form of M used for this research.

⁵http://en.wikipedia.org/wiki/Dyadics

Computing the left hand side of (40) yields

$$\begin{split} \nabla_{j} \left(\frac{1}{T} \mathbf{P}_{ij}\right) &= \nabla_{i} \left(\frac{p}{T}\right) - M \nabla_{i} \left[\frac{1}{T} \left(\frac{1}{2} (\nabla \rho)^{2} + \rho \nabla^{2} \rho\right)\right] + M \nabla_{j} \left(\frac{1}{T} (\nabla_{i} \rho) (\nabla_{j} \rho)\right) \\ &= \nabla_{i} \left(\frac{p}{T}\right) - M \left(\frac{1}{2} (\nabla \rho)^{2} + \rho \nabla^{2} \rho\right) \nabla_{i} \left(\frac{1}{T}\right) - \frac{M}{T} \nabla_{i} \left(\frac{1}{2} (\nabla \rho)^{2} + \rho \nabla^{2} \rho\right) \\ &+ M (\nabla_{i} \rho) (\nabla_{j} \rho) \nabla_{j} \left(\frac{1}{T}\right) + \frac{M}{T} \nabla_{j} \left[(\nabla_{i} \rho) (\nabla_{j} \rho) \right] \\ &= \nabla_{i} \left(\frac{p}{T}\right) + \frac{M}{T} \left[-\nabla_{i} \left(\frac{1}{2} (\nabla \rho)^{2} + \rho \nabla^{2} \rho\right) + \nabla_{j} \left[(\nabla_{i} \rho) (\nabla_{j} \rho) \right] \right] \\ &- M \left(\frac{1}{2} (\nabla \rho)^{2} + \rho \nabla^{2} \rho\right) \nabla_{i} \left(\frac{1}{T}\right) + M (\nabla_{i} \rho) (\nabla_{j} \rho) \nabla_{j} \left(\frac{1}{T}\right). \end{split}$$

where summation over repeated indices is implied. Note that

$$\begin{aligned} -\nabla_i \left(\frac{1}{2} (\nabla \rho)^2 + \rho \nabla^2 \rho \right) + \nabla_j \left[(\nabla_i \rho) (\nabla_j \rho) \right] &= -(\nabla_j \rho) (\nabla_i \nabla_j \rho) - (\nabla_i \rho) (\nabla^2 \rho) - \rho (\nabla_i \nabla_j \nabla_j \rho) \\ &+ (\nabla_j \nabla_i \rho) (\nabla_j \rho) + (\nabla_i \rho) (\nabla^2 \rho) \\ &= -\rho (\nabla_i \nabla_j \nabla_j \rho), \end{aligned}$$

so that

$$\nabla_{j}\left(\frac{1}{T}\mathbf{P}_{ij}\right) = \nabla_{i}\left(\frac{p}{T}\right) - \frac{M}{T}\rho(\nabla_{i}\nabla_{j}\nabla_{j}\rho) - M\frac{1}{2}(\nabla\rho)^{2}\nabla_{i}\left(\frac{1}{T}\right) - M\rho(\nabla^{2}\rho)\nabla_{i}\left(\frac{1}{T}\right) + M(\nabla_{i}\rho)(\nabla_{j}\rho)\nabla_{j}\left(\frac{1}{T}\right).$$
(41)

Using Equations (16) and (28) to expand the terms at the right hand side of Equation (40) gives

$$\begin{split} \rho \nabla_i \frac{\hat{\mu}}{T} &= \rho \nabla_i \frac{\mu}{T} - M \rho \nabla_i \left[\nabla \cdot \left(\frac{1}{T} \nabla \rho \right) \right] \\ &= \rho \nabla_i \frac{\mu}{T} - M \rho \nabla_i \left[\left(\nabla_j \frac{1}{T} \right) (\nabla_j \rho) + \frac{1}{T} (\nabla^2 \rho) \right] \\ &= \rho \nabla_i \frac{\mu}{T} - M \rho \left[\left(\nabla_i \nabla_j \frac{1}{T} \right) (\nabla_j \rho) + \left(\nabla_j \frac{1}{T} \right) (\nabla_i \nabla_j \rho) + \left(\nabla_i \frac{1}{T} \right) (\nabla^2 \rho) + \frac{1}{T} (\nabla_i \nabla_j \nabla_j \rho) \right], \end{split}$$

 $\quad \text{and} \quad$

$$\hat{e}\nabla_i \frac{1}{T} = e\nabla_i \frac{1}{T} + \frac{1}{2}M(\nabla\rho)^2 \nabla_i \frac{1}{T}.$$

Note that by the Gibbs-Duhem relation,

$$d\frac{p}{T} = -e \ d\frac{1}{T} + \rho \ d\frac{\mu}{T} \qquad \Longrightarrow \qquad \nabla_i \frac{p}{T} = -e \ \nabla_i \frac{1}{T} + \rho \ \nabla_i \frac{\mu}{T}.$$

Combining these terms, it follows that

$$\nabla_{i}\frac{p}{T} = -\hat{e}\nabla_{i}\frac{1}{T} + \rho\nabla_{i}\frac{\hat{\mu}}{T} + \frac{1}{2}M(\nabla\rho)^{2}\nabla_{i}\frac{1}{T} + M\rho\left[\left(\nabla_{i}\nabla_{j}\frac{1}{T}\right)(\nabla_{j}\rho) + \left(\nabla_{j}\frac{1}{T}\right)(\nabla_{i}\nabla_{j}\rho) + \left(\nabla_{i}\frac{1}{T}\right)(\nabla^{2}\rho) + \frac{1}{T}(\nabla_{i}\nabla_{j}\nabla_{j}\rho)\right].$$

Putting this back into (41) cancels out many terms:

$$\nabla_{j} \left(\frac{1}{T} \mathbf{P}_{ij}\right) = -\hat{e} \nabla_{i} \frac{1}{T} + \rho \nabla_{i} \frac{\hat{\mu}}{T} + M(\nabla_{i}\rho)(\nabla_{j}\rho) \nabla_{j} \left(\frac{1}{T}\right) + M\rho \left[\left(\nabla_{i} \nabla_{j} \frac{1}{T}\right) (\nabla_{j}\rho) + \left(\nabla_{j} \frac{1}{T}\right) (\nabla_{i} \nabla_{j}\rho) \right].$$

The last three terms can be rewritten into a simpler form:

$$\nabla_j \left(\frac{1}{T} \mathbf{P}_{ij}\right) = \rho \nabla_i \frac{\hat{\mu}}{T} - \hat{e} \nabla_i \frac{1}{T} + M \nabla_i \left(\rho(\nabla_j \rho) \nabla_j \frac{1}{T}\right).$$
(42)

Comparing this with the constraint (40) shows that the last term should not be there. Instead it can be subtracted from the diagonal part of the pressure tensor so that

$$\nabla_j \left(\frac{1}{T} \left[\mathbf{P}_{ij} - MT \rho(\nabla_k \rho) \left(\nabla_k \frac{1}{T} \right) \delta_{ij} \right] \right) = \rho \nabla_i \frac{\hat{\mu}}{T} - \hat{e} \nabla_i \frac{1}{T}$$

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