

Extended abstract

This is an extended abstract of the PhD thesis entitled "Equilibrium and Nonequilibrium Thermodynamics of Planar and Curved Interfaces", by Øivind Wilhelmsen. The doctoral work was carried out at the Department of Chemistry at the Norwegian University of Science and Technology between 01.09.2012 and 31.08.2015. Professor Signe Kjelstrup served as the main supervisor and Professor Dick Bedeaux served as the co-supervisor of the work. The PhD was successfully defended the 27th of November, 2015 with Prof. D. Frenkel, Ass. Prof. E. M. Blokhuis and Prof. M. Fernandez as opponents.

Summary of the work

Interfaces can be found everywhere and their properties are of major importance to a wide variety of processes, ranging from DNA replication to weather forecasts. The PhD thesis is a fundamental study of systems with planar and curved interfaces at equilibrium and nonequilibrium.

The first part of the thesis discusses the thermodynamic stability of bubbles and droplets in systems with both finite volume and number of particles. It is shown that the macroscopic capillary approach predicts thermodynamic stability limits nearly identical to those from square gradient theory, a more rigorous mesoscopic theory. Both approaches give a stable and unstable branch of solutions, representing bubbles and droplets in the canonical ensemble. Both methods predict a minimum threshold size for stability. This minimum threshold size is used to explain how fluids can be superstabilized in nanocontainers and to derive formulas to estimate the container volume below which no droplet or bubble can form.

Finite-size effects also influence nucleation processes. A comprehensive theoretical analysis of cavitation and droplet formation in finite systems is presented next. By using general thermodynamic arguments, simple yet accurate formulas are derived to calculate the finite-size corrections for the critical size, the nucleation barrier, and the nucleation rates in the canonical ensemble. These formulas can be used to select the appropriate system size for simulations or to obtain a precise evaluation of nucleation rates of complex substances at atmospheric conditions by using a small number of molecules and correcting for finite-size effects.

Next, the curvature dependence of the surface tension is examined by evaluating the leading terms of an expansion in the total and Gaussian curvatures.

The first-order curvature correction is the Tolman length and the second-order corrections are the rigidity constants. By combining the square gradient theory with an accurate equation of state, the combined framework reproduces the surface tension and Tolman length for the shifted and truncated Lennard-Jones fluid from molecular simulations. The curvature expansion accurately describes the change in surface tension, until the radius of the bubbles and droplets become similar to the interfacial width of the planar interface at saturation. For metastabilities even closer to the spinodal limits, the curvature remains nearly constant, but the surface tension decreases due to a decreasing difference between the densities of the bubble/droplet interior and exterior. The size of droplets and bubbles in the region of constant curvature is found to be proportional to the correlation length of fluctuations in the liquid phase. The discovery of a region with constant curvature offers a new perspective on how nucleation should be described at high metastabilities.

A more applied example is examined next, when the Tolman length and rigidity constants of water are estimated. The Tolman length of water is found to be negative and weakly temperature dependent, having the relatively small value of about -0.05 nm, which is in agreement with previous estimates in the literature. Using the leading terms of the curvature expansion, the curvature dependence of the surface tension is incorporated into the framework of classical nucleation theory. The modification successfully corrects the erroneous temperature dependence of the nucleation rates given by the classical theory, thereby improving the agreement between theoretical and experimental results. Thus, the procedure offers a promising way to alleviate the problems of classical nucleation theory and obtain quantitatively accurate predictions, which hopefully is pos-

sible also for other substances. Next, the inherent properties of the temperature across interfaces are examined. Several microscopic expressions to calculate temperature in molecular simulations are evaluated, where some include configurational contributions. Their accuracy and usefulness in high- and low-density bulk systems and across vapor-liquid interfaces both at equilibrium and with a temperature gradient are investigated. It is shown that the configurational temperature is equivalent to the kinetic temperature in steady-state molecular dynamics simulations. This agreement with simulations, however, is obtained only if the discontinuity in the derivatives of the interaction potential is handled properly by using a sufficiently long truncation distance or tail-corrections.

If the entropy density is included as a variable in the square gradient theory framework, the theory suggests that the temperature has different contributions from directions parallel and perpendicular to the interface *at equilibrium*. A similar anisotropy is found in simulations by examining the configurational temperature in molecular dynamics. The results from the simulations agree qualitatively with the theory. According to the theory, the temperature anisotropy provides evidence for new entropic contributions to the tension tensor, responsible for part of the surface tension.

The last chapter of the thesis deals with the transport of heat and mass across planar and curved interfaces. The transport equations are formulated with the framework of nonequilibrium thermodynamics by using a set of interface transfer coefficients. First, the interface transfer coefficients of bubbles and droplets are investigated in both single- and two-component systems. It is verified that the coefficients obtained by combining the integral relations with results from the equilibrium square gradient model are the same as those obtained by using the nonequilibrium square gradient model, in which gradients in temperature, pressure and composition are imposed across the interface. The local heat transfer characteristics of the interfacial region (local resistivity) are found to have a large influence on the predicted curvature dependence of the interface transfer coefficients. Further, the general curvature dependence of the interface transfer coefficients are obtained by expanding the coefficients in the total and Gaussian curvatures. This provides an accurate description of heat and mass transfer across interfaces of complex nano-geometries. A method to obtain the leading terms in

the curvature expansion is presented. The method is demonstrated for an oblate spheroidal droplet (Mentos candy), a prolate spheroidal bubble (rugby ball), and a toroidal bubble (donut). Depending on the sign and magnitude of the total and Gaussian curvatures, the interfacial transfer can increase or decrease significantly. Next, the analytical expressions for the terms in the curvature expansion of the interface transfer coefficients are derived, allowing them to be calculated with higher accuracy. The magnitude and temperature-dependence of the interface transfer coefficients and the terms in the curvature expansion are discussed in detail for the truncated and shifted Lennard-Jones fluid.

The tools developed are next used to describe transfer across planar and curved water interfaces. For the complicated case of water, it is necessary to use a temperature-dependent influence parameter in the square gradient model. It is shown how this extension modifies the nonequilibrium square gradient model, and leads to thermodynamic quantities that depended on temperature gradients. The modified formulation is found to be thermodynamically consistent and to give an interface at local equilibrium, in agreement with previous work. The interface transfer coefficients and the corresponding curvature corrections are calculated for the vapor-liquid interface of water from 260 K to 550 K. A novel approach is used; this approach takes advantage of low-temperature water evaporation experiments, nonequilibrium molecular dynamics with the TIP4P/2005 model at high temperatures and square gradient theory. The framework is used to obtain new understanding of transport across the interface of coalescing nanosized water droplets, in which the resistance to heat and mass transfer was found to be significantly increased in the junction between the droplets.

The thesis presents new insight on topics heavily debated in the literature, such as the sign and relevance of the Tolman length and the rigidity constants, and deals with previously unaddressed topics, such as the inherent properties of the temperature across interfaces and the curvature dependence of the interface transfer coefficients. Several tools and techniques have been developed that can be further taken advantage of to study the properties of highly metastable fluids, the magnitude and curvature dependence of interface transfer coefficients, improve predictions from nucleation theory and design nano devices with enhanced properties.

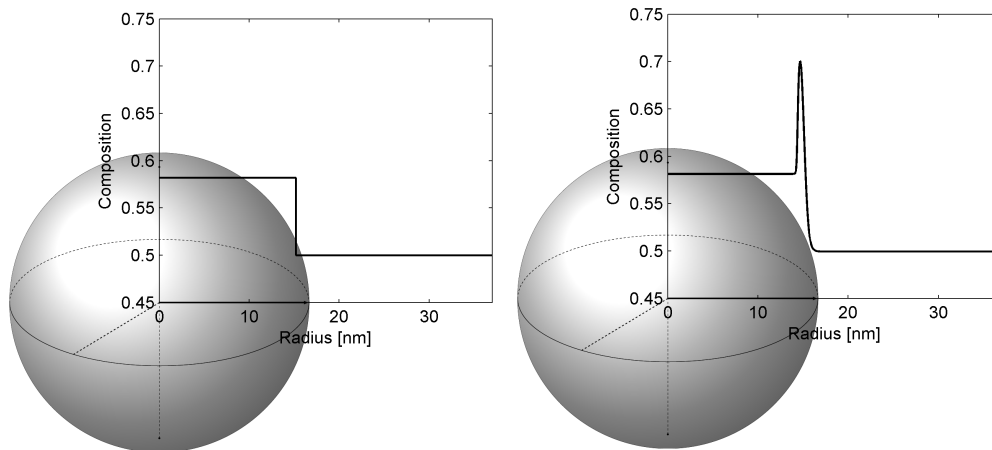


Figure 1: The composition (mass fraction) of a two-component fluid as predicted by the capillary model (left), and by the square gradient theory (right)

Problems addressed and state of the art

The narrow region between two phases, the interface-region, can be found everywhere; in a cup of coffee, on a falling raindrop or in comets passing through the solar system. It is barely a few nanometers thick, however, its properties are crucial for a wide variety of phenomena, ranging from DNA replication^[1] to volcano eruptions^[2] and weather forecasts. Interfaces are often curved, and curvature changes their properties.

The first aim of the work was to increase the general understanding of the interface region, and how curvature changes its properties. The thesis addresses topics vigorously debated in literature such as how surface tension is influenced by curvature,^[3-6] but also considered questions that have hardly been investigated, such as “How does temperature behave across interfaces?” The thesis discusses how curved interfaces influence the thermodynamic stability of bulk systems, and consider nonequilibrium-situations where heat and mass are transferred across interfaces.

Many deserve credit for their work on interfacial phenomena, yet surprisingly much remains to be learned, despite over two centuries of research. Part of the challenge lies in the nanosized thickness and highly heterogeneous nature of the interface, where properties can only be evaluated indirectly through macroscopic experiments, or through computational simulations mimicking the real world. Theories and descriptions taken for granted in bulk systems such as classical thermodynamics, differ across the interface.^[7]

Enhanced understanding of interfaces and curvature is crucial for progress in several areas in science and industry. One example is nanotechnology, envisioned as the technology of the future.^[8] The dimensions considered in nanotechnology are on the same scale as the thickness of the interface region, thereby making interfacial properties a key consideration in the design of nanodevices. The second aim of the work was to develop theory and methodology that can be used in the design of future nanodevices, for instance to more efficiently disperse heat generated in computers, or to devise new self-propelling particles, or materials with enhanced properties.

Knowledge about curved interfaces is also of importance to established industrial processes. Perhaps the most important example is nucleation, in which curved interfaces play a key role. Nucleation is the rate-limiting step of most first order phase transitions such as boiling, condensation and crystallization and starts with the formation of a nanoscopic and strongly curved embryo of the new phase.^[9] Nucleation occurs in distillation columns, multiphase heat exchangers, boilers and most process equipment involving phase-transitions. Even so, accurate quantitative predictions of this phenomenon have thus far been impossible.^[10] This brings forward the third aim of the PhD-work: to contribute to a quantitative description of nucleation processes.

A quantitative description of nucleation would enable more reliable prediction of, for instance, how components separate in a petroleum refinery, or the time needed to boil water in power plants. One could then design industrial equipment more precisely, and

thereby increase the energy efficiency as well as the economic feasibility. Even more importantly, a quantitative description of nucleation is crucial to correctly predict the outcome of potential accidents in which substances abruptly change phase, for instance in the rupture of a pipeline or tank containing a pressurized fluid. Fundamental progress on this topic may therefore contribute to enhanced safety.

Square gradient theory, also known as *diffuse-interface theory* or *phase-field theory*, has had a key role in the understanding of both equilibrium and nonequilibrium phenomena across interfaces. Examples of such phenomena are the kinetics of solid hydrate formation,^[11] nucleation processes,^[12] crystal growth^[13] and biological applications.^[14] In the thesis, it is further used to study growth of nanosized bubbles and droplets in Chapter 5.

Many scientists have contributed significantly to the development of the square gradient theory at equilibrium, to the formulation,^[15] the understanding (see^[7] and refs. therein) and application of the theory.^[16] Recent advances have facilitated the calculation of properties of interfaces also beyond equilibrium. The square gradient theory has been extended to the nonequilibrium domain for liquid-vapor interfaces,^[17] near the spinodals^[18] and for three phases in contact.^[19] The extension to the nonequilibrium domain is very useful in nanoscale systems, since the theory can predict the effect of curvature on interface transfer coefficients. The work in the PhD-thesis takes advantage of square gradient theory in all of the chapters, and contributes by this to its further development and understanding.

Square gradient theory is the first approximation to classical density functional theory for fluids. More advanced formulations use the attractive part of the interaction potential and the pair correlation function as arguments in the Helmholtz energy functional, and consider interactions over longer distances. For most fluids, however, neither the interaction potential nor the pair correlation function is available, hence restricting the applicability of this formulation. Moreover, for many properties, the square gradient theory gives results that are nearly identical to those from more advanced density functional theory formulations (see Chapter 3 in the thesis).

From a macroscopic perspective, the particle density across the interface is discontinuous, as in the capillary approach. From a mesoscopic perspective, the time average particle density profile is continuous, as in square gradient theory. Figure 1 compares the

predictions from the square gradient theory (right) and the capillary model (left), the main difference being that the square gradient theory can predict an excess of one of the components at the interface, revealed as a peak in the composition profile. Interfaces can also be studied on a microscopic level with molecular dynamics simulations, where particles interact via interaction potentials. Molecular dynamics has played a key role in understanding interfacial phenomena.^[20–22] The thesis work takes advantage of equilibrium and nonequilibrium molecular dynamics to gain further insight into the concept of temperature in Chapter 4, and into transfer of heat and mass across interfaces in Chapter 5.

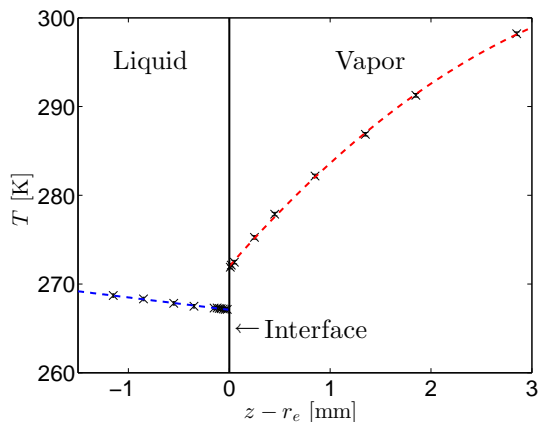


Figure 2: Temperature measurements across the vapor-liquid interface of water (crosses),^[23] document a jump in the temperature across the interface.

Interfaces away from equilibrium

Kapitza discovered in the 1940s that interfaces were considerable barriers to heat transfer, resulting in a temperature “jump” across the interface.^[24] Temperature jumps as high as 15.69 K have in recent years been documented during evaporation of water,^[23,27] where the measurements by Badam et al. are shown in Fig. 2.^[23] The interfacial barrier can be described in terms of the “interface transfer coefficients,” where the coefficient related to heat transfer is called “the Kapitza resistance.” The interface transfer coefficients have been quantified by kinetic gas theory (See^[25] and refs. therein), nonequilibrium molecular dynamics simulations^[20,22,26] and experiments^[27] for a variety of interfaces and substances. To date, few works have explored the curvature dependence of the Kapitza resistance,^[26] or other interface transfer coefficients, despite their striking importance in

nanoscience and for nucleation-processes.^[26,28] Chapter 5 in the thesis provides new insight to this by evaluating the curvature dependence of the interface transfer coefficients.

Nonequilibrium thermodynamics is a core theory to the consistent description of transport processes in systems out of global equilibrium. Onsager is regarded as the founder of the field based on his derivation of the reciprocal relations,^[29,30] where he explained the inherent symmetry on how different transport phenomena couple. In Chapter 5 in the thesis, it is shown that coupling is even more important across interfaces than in bulk systems. Nonequilibrium thermodynamics systematically defines a set of conjugate fluxes and forces that describe transport processes and how they couple. Many have contributed to the development of the field (see Chapter 1 in Ref.^[31]), and its extension to the nonlinear regime;^[32] Muschik et al.^[33] provide an excellent overview of these. The work in the thesis follows the line of research of de Groot and Mazur,^[34] and the extension to heterogeneous systems given by Kjelstrup and Bedeaux.^[31]

Interfacial curvature

Curvature quantifies the amount by which the surface of a geometric object deviates from being flat. For surfaces of three-dimensional objects, curvature can be expressed by the two principal curvatures. An equivalent description that is more commonly used is with the total and Gaussian curvatures. For simple shapes such as spheres or cylinders, the curvature depends only on their radius. For more complex forms such as the oblate spheroid (Mentos candy) and the toroid (donut), the curvature is local and changes in a more involved manner. We refer to the literature for a proper introduction to curvature and differential geometry.^[35]

Gibbs knew already in the 19th century that the excess energy of the interface depended on the curvature.^[36] The next key contribution came in 1949 by Tolman, when he introduced the first order curvature correction to the surface tension in terms of the Tolman length.^[37] Since then, there has been an ongoing vigorous discussion regarding the sign and magnitude of the Tolman length of the simple Lennard-Jones (LJ) fluid.^[3,4,6,38] The most popular approaches to obtain the Tolman length have been molecular dynamics (MD) simulations, Monte Carlo simulations and classical density functional theory. While classical density functional theory and square gradient

theory have consistently given zero or negative values,^[5,6,38] positive values have been reported from Monte Carlo and MD simulations, which evaluate the Tolman length from the pressure tensor (See^[3,4] and refs. therein). Molecular dynamics have only recently given a negative Tolman length by exploiting the curvature expansion of the Laplace relation.^[6,21,39] An agreement that the Tolman length of the LJ-fluid is negative, and that its magnitude is ~ 0.1 in units of the molecular diameter^[40] seems to be establishing in the scientific community. For most substances, neither the sign nor the magnitude of the Tolman length is known. For highly curved objects such as nanosized bubbles and droplets, it is necessary to also account for higher order contributions such as the rigidity constants.^[40] Deuling and Helfrich showed that these terms were necessary to explain the shape of, for instance, red blood cells.^[41] Chapter 3 in the thesis contributes with new insight to this discussion.

Experiments have shown that the overall thermal conductivity of nanoparticle suspensions depend on the size of the particles; resistance decreases for smaller particles.^[42] Surprisingly, nanoporous materials exhibit the opposite behavior where the resistance increases with decreasing pore size.^[43] It was hypothesized by Lervik et al. that these effects could be explained by the influence of curvature on the interface transfer coefficients.^[26] Few works have yet explored the curvature dependence of the Kapitza resistance, or other interface transfer coefficients, despite the striking importance of these properties in nanoscience.^[26,28] The thesis contains pioneering work in that respect, as the interface transfer coefficients are expanded in the total and Gaussian curvatures in Chapter 5. An exciting future work will be to figure out how these curvature effects can be exploited to design nanodevices with enhanced properties.

Nucleation processes

Nucleation is the rate-limiting step in most first order phase transitions, such as boiling, condensation and crystallization and is therefore relevant to a wide range of examples in nature and industry. The process starts with the formation of a small embryo of the new phase in the bulk of the metastable phase.^[9] Nucleation occurs only if the density fluctuations in the metastable bulk phase are large enough to overcome the activation energy of the critical embryo.

Classical Nucleation Theory (CNT) is today the most popular theory to predict nucleation

rates.^[9,44,45] Classical nucleation theory uses the framework proposed by Gibbs, assuming a discontinuous interface. However, it also assumes ideal gas and incompressible liquid and uses the surface tension of the planar interface. It succeeds in capturing the qualitative behavior, but fails to predict the correct temperature dependence of the nucleation rates, and the predicted rates often differ from measurements in unary and in multicomponent systems by several orders of magnitude.^[46] Even for the simple case of argon condensation, CNT deviates from experimental results by more than 20 orders of magnitude.^[46] Molecular dynamics and Monte Carlo simulations are important sources of information on nucleation,^[47,48] which, for complicated mixtures and realistic conditions, comes at the expense of large computational demands.^[49]

Nucleation takes place differently with a finite number of particles and a finite volume (NVT -ensemble) than at atmospheric conditions (NPT -ensemble). A main difference is that in the NVT -ensemble, there exists a stable droplet. The differences between the NVT and NPT ensembles, and the importance of finite-size effects in simulations of condensation were studied in Refs.^[50,51] Chapter 2 of the thesis builds on these works and further investigates how thermodynamic stability and nucleation differ in nanosystems with a finite number of particles and a finite volume.

One of the crudest assumptions of CNT is the so-called capillary approximation, which considers the surface of droplets or bubbles to be sharp and have the same surface tension as the planar interface. Thus, to incorporate the curvature dependence of the surface tension is expected to improve CNT-predictions, accounting for parts of the large discrepancies. Many works in the literature have attempted different routes of evaluating and including the contribution from curvature in CNT.^[40,52,53] However, accounting for these curvature effects in real systems is not an easy task. Neither the magnitude nor the sign of even the leading order corrections are known for most substances. Chapter 3 in the thesis presents important new insight to how the curvature dependence of the surface tension influences nucleation rates.

In simulations and experiments, nucleation has been carried out by using a surplus of a carrier gas, which ensures that the temperature remains constant. Nucleation, however, is a nonequilibrium process in which the growth rate is dictated by transfer of mass and energy.^[54] Holyst and Litniewski for

instance, demonstrated with large scale MD simulations of evaporating nano-droplets that the process is limited by *heat transfer*.^[55] Homogeneous nucleation with a limited volume of carrier gas was considered by Feder et al. in 1966,^[56] where they found that limited heat transfer suppressed the nucleation rate. This has been confirmed by later studies.^[57] There is also some controversy over whether liquid clusters grow at a temperature below that of the vapor,^[58] or above.^[59] Chapter 5 in the thesis presents the interface transfer coefficients of nanoscopic clusters and cavities, and a future application of these will be to address nonisothermal nucleation.

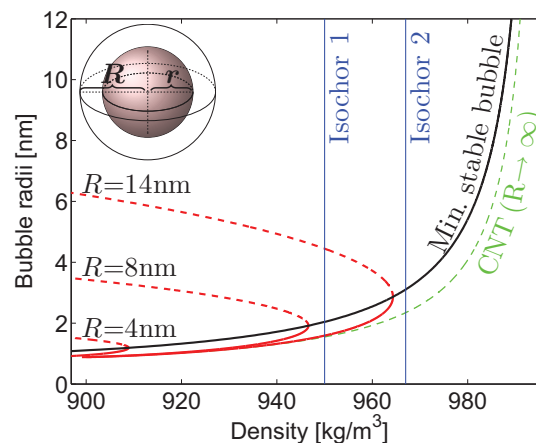


Figure 3: Stationary solutions of the modified bubble model for water cavitation at 300 K at different total densities and for different container radii. The red solid lines represent the critical bubbles and the red dashed lines the stable bubbles. The critical bubble size for a very large container ($R \rightarrow \infty$), corresponding to the standard prediction of CNT (green dashed line), two isochores (thin solid lines) and the minimum stable bubble size curve (solid line) are also indicated. The investigated system is shown as an inset in the top-left corner.

Key innovations, applications, implementations and results

The PhD thesis presents a study of the thermodynamic properties of planar and curved interfaces at equilibrium and nonequilibrium. Tools, theories and techniques such as square gradient theory, statistical mechanics, molecular dynamics and experiments have been used to gain further understanding of interfaces. The work has resulted in several findings that have contributed to the accomplishment of the first aim of the work; to increase the general understanding of interfaces and how their properties are influ-

enced by curvature. The thesis presents new insight, new theories, further development of established theories and new, important results. The bulk of the thesis (Chapters 2-5) is a collection of thirteen papers, with each paper representing a subchapter.

Chapter 2 deals with thermodynamic stability and nucleation in nanosystems. In closed nanosystems, bubbles and droplets can be stabilized and their properties can be examined, making their thermodynamic stability a natural starting point for the thesis. The chapter discusses the thermodynamic stability of multicomponent bubbles and droplets. One of the main innovations of the chapter is to demonstrate how metastable fluids can be made superstable under certain condition. Fig. 3 illustrates how liquid water can be made superstable in nanosized containers. By comparing the stationary solutions for $R = 14$ nm, 8 nm and 4 nm in Fig. 3, where R is the radius of the container, we see that the density beyond which there are no longer any stationary solution, corresponding to a situation where cavitation is impossible, shifts to lower values and hence higher metastabilities as the container becomes smaller. For instance, at a density of 967 kg/m^3 (Isochore 2), no bubbles can form in containers smaller than 14 nm. At an initial density of 950 kg/m^3 (Isochor 1), a bubble can form in a 14 nm container, but no bubbles form in containers smaller than 8 nm. The minimum stable bubble size changes with density according to the solid line in Fig. 3. In practical terms, this effect will always give a lower limit to how few particles and how small the total volume can be before nucleation becomes impossible. Superstabilization can be used in practice to study the properties of highly metastable, fluids either by experiments or by simulations in the canonical ensemble.

Chapter 3 discusses how curvature influences the surface tension by examining the leading order corrections in the Helfrich expansion:

$$\sigma(H, K) = \sigma_0 - \delta\sigma_0 H + \frac{k}{2} H^2 + \tilde{k} K + \dots,$$

where σ_0 is the surface tension of the flat surface, $H = \kappa_1 + \kappa_2$ is the total curvature, $K = \kappa_1 \kappa_2$ is the Gaussian curvature and κ_1 and κ_2 are the principal curvatures. The leading order curvature-corrections are the Tolman length δ , the bending rigidity k and the rigidity constant \tilde{k} associated with the Gaussian curvature. A main innovation of this chapter is to establish a methodology where square gradient theory combined with an accurate EoS is used to calculate the Tolman length and the rigidity constants of

a fluid. It is shown by comparison to molecular simulations, that this works very well for the truncated and shifted Lennard Jones (LJ)-fluid. While the standard CNT typically predicts the correct dependence of nucleation rates on supersaturation, it gives the wrong temperature-dependence. For substances such as water and 1-pentanol, this has been well documented,^[9,60,61] and it is also evident from comparing the red dashed lines in Fig. 4 with the experimental results.

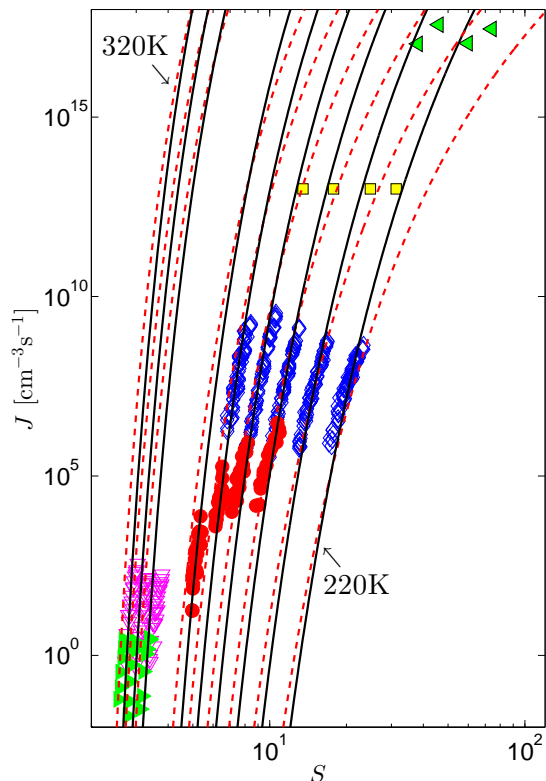


Figure 4: Experimental nucleation rates from Wölk and Strey (blue diamonds),^[60] Manka et al. (red circles),^[62] Brus et al. (pink and green triangles),^[63,64] Manka (yellow squares)^[65] and from Wyslouzil et al.^[66] for the temperatures $T(\text{K}) = \{320, 310, 300, 270, 260, 250, 240, 230, 220\}$, compared to CNT (red dashed lines) and c-CNT (solid lines).

In the thesis, the Tolman length and rigidity constants of water are estimated by using the developed methodology. The Tolman length of water is found to be negative and weakly temperature dependent, having the relatively small value of about -0.05 nm, which is in agreement with previous estimates in the literature. Using the leading terms of the curvature expansion, the curvature dependence of the surface

tension is incorporated into the framework of classical nucleation theory, which is then called c-CNT. While CNT underestimates nucleation rates at low temperatures and overestimates nucleation rates at high temperatures (see red dashed lines in Fig. 4), c-CNT (solid lines) gives results which are closer to experiments, both at low and high nucleation rates, where the magnitude of the rates spans 20 orders of magnitude. Thus, the procedure offers a promising way to alleviate the problems of classical nucleation theory and obtain quantitatively accurate predictions, which hopefully is possible also for other substances.

Chapter 4 starts by investigating the accuracy and usefulness of different microscopic expressions to calculate the temperature in molecular simulations, where some of them included configurational contributions. The standard means of determining the temperature in molecular dynamics simulations is by using the kinetic temperature. Alternatively, one can calculate the temperature exclusively from configurational information of the molecules by using the configurational temperature. The thesis evaluates the accuracy and validity of these expressions and many others for use in high- and low-density bulk simulations, and for vapor-liquid interfaces, both at equilibrium and in nonequilibrium situations. It is shown that properly defined configurational temperatures give the same results as the kinetic temperature for nonequilibrium molecular dynamics simulations of high- and low-density bulk systems (for both transient and steady-state conditions) and across interfaces, with an accuracy comparable to that in equilibrium simulations. The configurational temperature is thus found to be equivalent to the kinetic temperature in steady-state molecular dynamics simulations if the discontinuity in the interaction potential was handled properly by using a sufficiently long truncation-distance or tail-corrections.

If the entropy density is included as a variable in the square gradient theory framework, the theory suggests that the temperature has different contributions from directions parallel and perpendicular to the interface *at equilibrium*. The thesis documents a similar anisotropy in simulations, by examining the configurational temperature in molecular dynamics. The results from the simulations agree qualitatively with the theory. According to the theory, the temperature anisotropy gives evidence for new entropic contributions to the tension tensor. It is explained why the entropic contributions are likely to be responsible for part of the disagreement between the

predictions from classical square gradient theory and the temperature-dependence of the surface tension obtained from experiments. It is also shown that the temperature anisotropy could give new insight into the Kapitza resistance.

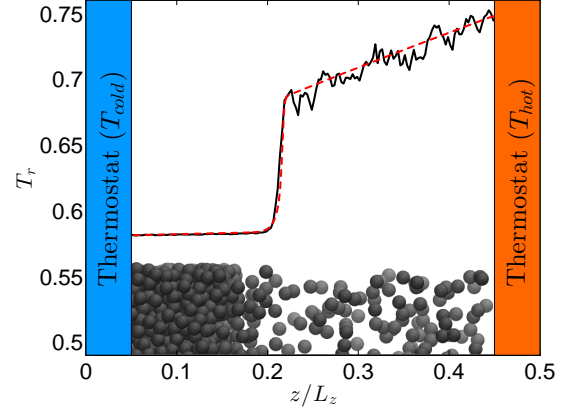


Figure 5: Temperature profile from nonequilibrium-MD (solid line) and from nonequilibrium-SGT (red dashed line), where the spheres at the bottom of the figure show where the liquid and the vapor is. The cold and the hot thermostats of the nonequilibrium-MD are also shown.

Chapter 5 deals with the nonequilibrium domain where heat and mass are transferred across interfaces. Transport across interfaces can be described with the framework of nonequilibrium thermodynamics:^[31]

$$\frac{1}{T^e} - \frac{1}{T^n} = R_{qq} J_q^e + \sum_i^{N_c} R_{qi}^e J_i,$$

$$-\left(\frac{\mu_k^e}{T^e} - \frac{\mu_k^n}{T^n}\right) + h_k^e \left(\frac{1}{T^e} - \frac{1}{T^n}\right) = R_{kq}^e J_q^e + \sum_i^{N_c} R_{ki}^e J_i,$$

where subscript “n” is used to denote either a droplet or a bubble at the center of the container, and “e” for the exterior phase. Moreover, J_q^e is the measurable heat flux, defined as $J_q^e = J_q - \sum_i^{N_c} h_i J_{d,i}$, J_i is the mass-flux of component i , $J_{d,i}$ is the diffusional mass flux, h_k is the partial molar enthalpy of component k and μ is the chemical potential. The rate of transport across the interface depends on the magnitude of the interface transfer coefficients for heat transfer, R_{qq} , mass transfer, R_{ki} and the coupling coefficients, R_{kq} .

The interface transfer coefficients of droplets and bubbles depend also on the interfacial curvature. In Chapter 5, the interface transfer coefficients are expanded in the total and Gaussian curvatures:

$$R_{ij}(H, K) = R_{ij,0} [1 + d_{ij}H + \nu_{ij}(d_{ij}H)^2 + \bar{\nu}_{ij}d_{ij}^2K], \quad (1)$$

where $i, j = \{q, \mu\}$. The length, d_{ij} gives the typical size of a droplet where curvature corrections become important and ν_{ij} and $\bar{\nu}_{ij}$ are scalars that decide the magnitude of the second order contributions.

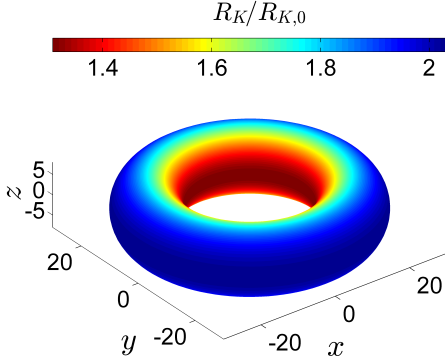


Figure 6: The interface transfer coefficient to heat transfer of a toroidal bubble of argon.

Several methods are presented in Chapter 5 to obtain the interface transfer coefficients and their leading order curvature corrections. In Chapter 5b, a method is presented to obtain the coefficients $R_{ij,0}$, d_{ij} , ν_{ij} , $\bar{\nu}_{ij}$ by combining square gradient theory and nonequilibrium molecular dynamics simulations, as depicted in Fig. 5. Equation 1 can then be directly used to describe heat and mass transfer in complex nanogeometries.

Examples of complex nanogeometries that are examined include an oblate spheroidal droplet (Mentos candy), a prolate spheroidal bubble (rugby ball), and a toroidal bubble (donut), where the interfacial resistance of a nanosized toroidal bubble is shown in Fig. 6. The linear terms in Eq. 1, d_{ij} have the same dimension as the first order curvature correction of the surface tension, the Tolman length. It is found that the linear terms, d_{ij} are more than 30 times larger in magnitude than the Tolman length. Curvature has thus a more dramatic effect on transport through interfaces than on the surface tension. Depending on the sign and magnitude of the curvature, transfer can be significantly enhanced or reduced.

The thesis presents analytical derivations expressions for d_{ij} , ν_{ij} and $\bar{\nu}_{ij}$. The curvature corrections can then be obtained even more accurately by numerically solving a set of coupled differential equations. After establishing the methodology to calculate the interface transfer coefficients for flat and curved interfaces, the tools developed are next used to pro-

vide new insight about the perhaps most important substance to mankind, water. For the complicated case of water, the square gradient theory framework had to be extended to include temperature-dependent influence parameters. The extension modifies the framework significantly and lead to thermodynamic quantities that depended on temperature gradients. The framework is confirmed to be thermodynamically consistent.

The extended framework is taken advantage of in the last chapters of the thesis to obtain the interface transfer coefficients and their curvature corrections for the vapor-liquid interface of water from 260 K to 560 K. A novel approach is used, taking advantage of water-evaporation experiments at low temperatures, nonequilibrium molecular dynamics with the TIP4P/2005-model at high temperatures, and the square gradient theory to represent the whole range. This methodology is illustrated in Fig. 7. Square gradient theory complements here the description where experiments are unavailable or simulations are currently impossible. The coefficients and their ability to describe evaporation and condensation of water using the framework of nonequilibrium thermodynamics are discussed. The coefficients can in the future be applied, both to improve the precision in weather forecasts and climate models, or to describe nano droplets of water, as shown and explained in the thesis.

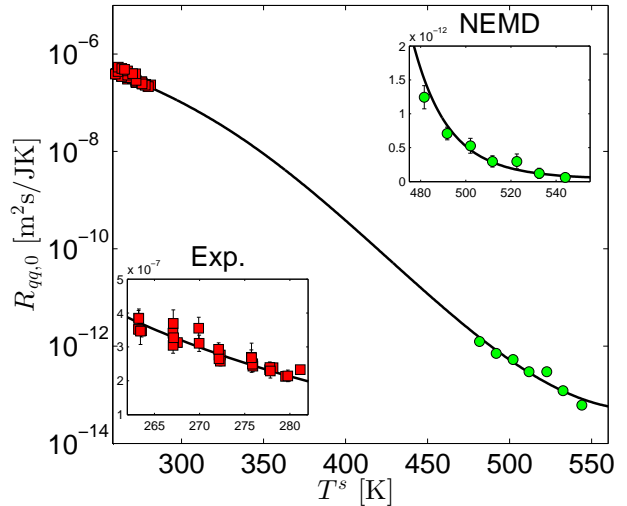


Figure 7: The interface transfer coefficient for heat transfer across the flat water-interface (top-left). The subfigures show results from experiments (red squares) and nonequilibrium-MD (green circles) including the error bars. Square gradient theory is used to bridge the results from the experiments and the simulations.

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