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MOLECULAR DYNAMICS SIMULATIONS OF
HOMOGENEOUS NUCLEATION

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Academic dissertation

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Molecular Dynamics simulations of homogeneous nucleation

Jan Daniel Julin

University of Helsinki, 2011

Abstract

Nucleation is the first step in a phase transition where small nuclei of the new phase start appearing in the metastable old phase, such as the appearance of small liquid clusters in a supersaturated vapor. Nucleation is important in various industrial and natural processes, including atmospheric new particle formation: between 20 % to 80 % of atmospheric particle concentration is due to nucleation. These atmospheric aerosol particles have a significant effect both on climate and human health.

Different simulation methods are often applied when studying things that are difficult or even impossible to measure, or when trying to distinguish between the merits of various theoretical approaches. Such simulation methods include, among others, molecular dynamics and Monte Carlo simulations. In this work molecular dynamics simulations of the homogeneous nucleation of Lennard-Jones argon have been performed. Homogeneous means that the nucleation does not occur on a pre-existing surface. The simulations include runs where the starting configuration is a supersaturated vapor and the nucleation event is observed during the simulation (direct simulations), as well as simulations of a cluster in equilibrium with a surrounding vapor (indirect simulations). The latter type are a necessity when the conditions prevent the occurrence of a nucleation event in a reasonable timeframe in the direct simulations.

The effect of various temperature control schemes on the nucleation rate (the rate of appearance of clusters that are equally able to grow to macroscopic sizes and to evaporate) was studied and found to be relatively small. The method to extract the nucleation rate was also found to be of minor importance. The cluster sizes from direct and indirect simulations were used in conjunction with the nucleation theorem to calculate formation free energies for the clusters in the indirect simulations. The results agreed with density functional theory, but were higher than values from Monte Carlo simulations. The formation energies were also used to calculate surface tension for the clusters. The sizes of the clusters in the direct and indirect simulations were compared, showing that the direct simulation clusters have more atoms between the liquid-like core of the cluster and the surrounding vapor. Finally, the performance of various nucleation theories in predicting simulated nucleation rates was investigated, and the results among other things highlighted once again the inadequacy of the classical nucleation theory that is commonly employed in nucleation studies.

Keywords: homogeneous nucleation, molecular dynamics, cluster properties

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List of publications

This thesis consists of an introductory review, followed by five research articles. The papers are reproduced with permission of American Institute of Physics. In the introductory part, these papers are cited according to their roman numerals.

- I** Julin, J., Napari, I., and Vehkamäki, H. (2007). A comparative study on methodology in molecular dynamics simulation of nucleation, *J. Chem. Phys.*, **126**, 224517.
- II** Julin, J., Napari, I., Merikanto, J., and Vehkamäki, H. (2008). Equilibrium sizes and formation energies of small and large Lennard-Jones clusters from molecular dynamics. A consistent comparison to Monte Carlo simulations and density functional theories, *J. Chem. Phys.*, **129**, 234506.
- III** Napari, I., Julin, J., and Vehkamäki, H. (2009). Cluster sizes in direct and indirect molecular dynamics simulations of nucleation, *J. Chem. Phys.*, **131**, 244511.
- IV** Julin, J., Napari, I., Merikanto, J., and Vehkamäki, H. (2010). A thermodynamically consistent determination of surface tension of small Lennard-Jones clusters from simulation and theory, *J. Chem. Phys.*, **133**, 044704.
- V** Napari, I., Julin, J., and Vehkamäki, H. (2010). Performance of some nucleation theories with a non-sharp droplet-vapor interface, *J. Chem. Phys.*, **133**, 154503.

1 Introduction

A first-order phase transition begins as small embryos, or nuclei, of the new phase start appearing in the metastable old phase. This phenomenon is called nucleation. A widely relevant and perhaps the most iconic example of a nucleation process is the formation of small liquid clusters in a supersaturated vapor. One of the most important occurrences of gas-to-liquid nucleation is seen in the atmosphere, where nucleation is among the most important mechanisms behind the formation of atmospheric aerosols (Kulmala et al., 2004), which are tiny liquid or solid particles suspended in air. While part of the atmospheric particle concentration is due to direct particle emissions, current best estimates indicate that 20-80 % of atmospheric particle concentration can be attributed to nucleation from condensible gaseous species (Spracklen et al., 2008; Merikanto et al., 2009; Kazil et al., 2010). The relevant species include water, sulfuric acid, ammonia, amines and various organic acids.

Atmospheric aerosols in turn are of interest for a few reasons. Depending on the composition, they can have adverse health effects (Pöschl, 2005). Aerosols also have a significant effect on Earth's radiative balance, both by directly reflecting and absorbing solar radiation, and indirectly by serving as condensation nuclei for cloud droplets (Twomey, 1974, 1991). The properties and concentration of these aerosol particles affect the lifetime and optical properties of the clouds, and therefore the amount of radiation reflected by clouds. Overall radiative forcing is expected to have a cooling effect on the climate, but the effect is still poorly understood (IPCC, 2007).

Nucleation can be divided into two categories, heterogeneous and homogeneous. In heterogeneous nucleation the nucleation occurs on a pre-existing surface, for example the surface of an aerosol particle. In homogeneous nucleation the droplet is formed directly from the gas phase. In either case nucleation can include one or more particle species, and atmospheric nucleation usually involves two or more. What all of these cases have in common is the existence of a potential barrier that the newly formed clusters have to overcome if they are to grow to macroscopic sizes. The existence of this barrier is due to the energy cost of creating a surface between the two phases. The cluster corresponding to the top of this barrier has equal probability to either grow to macroscopic sizes or evaporate back to vapor again, and is called the critical cluster. The quantities of interest in nucleation research include the size and formation energy of the critical cluster, and perhaps most importantly their rate of appearance, called

nucleation rate.

Despite the importance of nucleation, its theoretical description is not in a particularly good shape. The most widely used theoretical description of nucleation is still the classical nucleation theory (CNT). In CNT it is assumed that the small liquid cluster can be described using the properties of a macroscopic bulk liquid. It is then perhaps not that surprising that CNT is not performing very well in predicting experimental results, with the experimental and CNT nucleation rates often differing by several orders of magnitude (see e.g. Kalikmanov et al. (2008)). With the shortcomings of CNT becoming evident, several contending theories have been proposed during the last few decades (Gránásy, 1996; Reguera and Reiss, 2004a; Kalikmanov, 2006).

As an effort to bridge the gap between experiment and theory, many computational approaches to nucleation have been employed. Quantities that are difficult or even impossible to measure experimentally can be studied with simulations, and the results can be used to validate or refute the various theoretical predictions. The atomic interactions in the microscopic clusters are most accurately described by quantum mechanics, and indeed there are ongoing computational efforts to study properties of clusters using quantum chemical calculations (Kurtén and Vehkamäki, 2008). However, the computational cost of calculating the interactions on a quantum level is huge, and thus the quantum chemical calculations are limited to relatively small systems. Larger systems can be simulated using Monte Carlo (MC) and molecular dynamics (MD) methods, where the interactions are described using classical interaction potentials. It should be noted that the interactions in MC and MD simulations could also be calculated on the fly from quantum mechanics, but this task is again computationally quite demanding especially for atmospherically relevant systems.

This thesis focuses on the application of molecular dynamics simulations to study nucleation. The basic idea in any MD simulation is to calculate the time evolution of a system of particles by solving numerically the equations of motion. When applied to nucleation the studied system is usually of two varieties, either an initial setup of supersaturated vapor which is then allowed to nucleate (Yasuoka and Matsumoto, 1998; Toxvaerd, 2001; Wedekind and Reguera, 2007; Horsch and Vrabec, 2009), or a cluster in equilibrium with a surrounding vapor (Thompson et al., 1984; Salonen et al., 2007; Horsch et al., 2008). While there are MD studies (especially of the cluster-vapor type) that involve atmospherically interesting molecular species such as sulfuric acid and water (Toivola et al., 2009) or organic acids and water (Li et al., 2010), in this work

we have focused solely on the homogeneous nucleation of Lennard-Jones (LJ) argon. Although the LJ potential does describe noble gases quite well, the main motivations behind the choice of potential is its simplicity, as well as the vast amount of existing data and ongoing work for the substance. A more complicated potential would only add extra computational costs when trying to reach the goals of this thesis, which are:

- Examine the effect various simulation technical issues, such as temperature control, have on the simulation results.
- Establish the range of validity behind the idea that the two approaches to nucleation in MD simulations, namely the actual nucleation simulations and the cluster-vapor simulations, are in fact describing the same cluster. Also attempt to combine the two approaches in order to acquire formation energies for clusters of the cluster-vapor simulations.
- Examine how reasonable it is to assume that the surface tension of a cluster can be described by the macroscopic surface tension, and examine the nature of the correction one should make to the cluster surface tension.
- Test the success of various theories in predicting MD nucleation rates and critical sizes.

2 Nucleation theories

It should be noted that all the papers of this thesis are about one-component homogeneous gas-to-liquid nucleation, and thus the following chapters are written from this point of view. Neither the theoretical approaches or simulation methods used in this thesis are limited to this specific case.

The quantities usually used to describe the level of supersaturation, that is how far from equilibrium the metastable vapor is, should be mentioned before proceeding. The level of supersaturation is given by the saturation ratio

$$S = \frac{P_v}{P_{eq}}, \quad (1)$$

where P_v is the pressure of the (supersaturated) vapor and P_{eq} the pressure of the saturated (equilibrium) vapor. Alternatively one can use for the same purpose the chemical potential difference between the supersaturated and saturated vapors $\Delta\mu = \mu - \mu_{eq}$. The saturation ratio and $\Delta\mu$ are connected by

$$\Delta\mu = k_B T \ln S, \quad (2)$$

where T is temperature and k_B is the Boltzmann constant. Throughout this thesis Eq. (2) is considered the definition of saturation ratio.

2.1 Classical nucleation theory

The classical nucleation theory was formulated in the first half of the 20th century by Volmer and Weber (1925), Farkas (1927), Becker and Döring (1935), and Zeldovich (1942). For the description of the nucleation process CNT uses equilibrium thermodynamics combined with a kinetic description of the growth and decay processes of the clusters. However, several simplifying assumptions are made: the liquid is assumed to be incompressible, and the vapor is most of the time assumed to behave like an ideal gas. The cluster is also assumed to be spherical. Finally the assumption known as the capillary approximation is made, which means that the surface tension of the clusters is assumed to be equal to the surface tension of a macroscopic planar interface.

The formation free energy (work of formation) of a cluster containing N atoms is found by a thermodynamic treatment of a cluster-vapor system using the assumptions above,

and is given by

$$W(N) = -N\Delta\mu + \gamma_\infty A = -Nk_B T \ln S + N^{2/3}\gamma_\infty(36\pi)^{1/3}\rho_l^{-2/3}, \quad (3)$$

where γ_∞ is the surface tension of a planar interface, A is the surface area of the cluster, and ρ_l is the density of the bulk liquid. From Eq. (3) we see that the formation free energy of a cluster is a combination of two terms. The first term (the “volume term”) is the free energy difference between the bulk liquid and vapor phases. The second term (the “surface term”) is the energy cost for creating an interface between the phases. The surface term is always positive and independent of the saturation ratio, while the volume term is negative when the vapor is supersaturated ($S > 1$). With the surface term proportional to $N^{2/3}$ while the volume term is proportional to N , these two terms together result in a barrier in the formation energy for supersaturated vapors, as seen in Fig. 1. The critical cluster corresponds to the top of the barrier. Obviously, the farther from equilibrium the vapor is the larger the volume term becomes, making both the barrier height (W^*) and critical size (N^*) smaller.

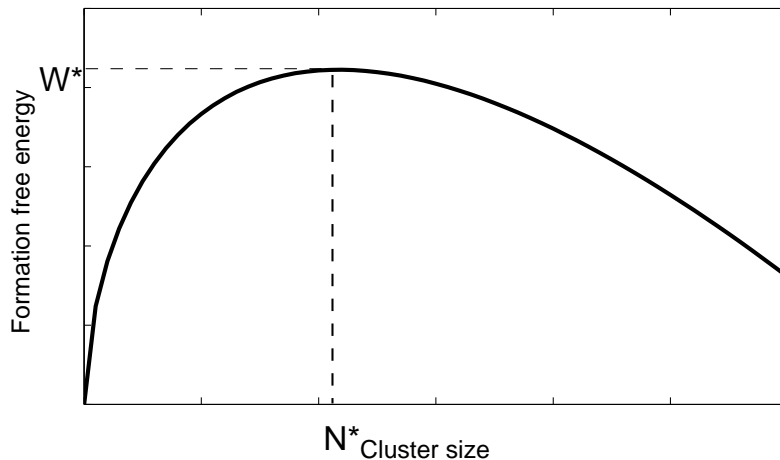


Figure 1: Critical cluster identified from the top of the nucleation barrier.

The critical size can be solved by taking the derivative of Eq. (3) with respect to N and setting it to zero, which results in

$$N^* = \frac{32\pi\gamma_\infty^3}{3\rho_l^2(\Delta\mu)^3}. \quad (4)$$

Inserting this to Eq. (3) gives for the work of formation of the critical cluster

$$W^* = \frac{16\pi\gamma_\infty^3}{3\rho_l^2(\Delta\mu)^2} = \frac{1}{2}N^*\Delta\mu. \quad (5)$$

The nucleation rate (rate of appearance of the critical clusters) requires that also cluster kinetics is considered. Once again certain assumptions are made, including that clusters grow and decay only by gaining and losing a single molecule at a time and that the cluster concentrations stay constant in time. The nucleation rate J is related to the formation free energy of the critical cluster by

$$J = K \exp\left(-\frac{W^*}{k_B T}\right), \quad (6)$$

where K is a kinetic prefactor, which is given in CNT as

$$K = \beta(n^*) C_1^e Z, \quad (7)$$

where $\beta(n^*)$ is the condensation coefficient of the critical clusters, C_1^e the equilibrium concentration of monomers and Z is the so-called Zeldovich non-equilibrium factor. If the critical size $N^* \gg 1$ the prefactor can be written as

$$K = \frac{1}{\rho_l} \left(\frac{P_v}{k_B T}\right)^2 \sqrt{\frac{2\gamma_\infty}{\pi m}}, \quad (8)$$

where m is the mass of a monomer. It should be noted that even though CNT has many shortcomings, the prefactor in the form of Eq. (8) does work quite well. This was recently seen in an MD study where nucleation rate and formation free energy were determined independently from the same simulations (Wedekind et al., 2009).

2.2 The liquid-vapor interface and surface tension

The interface between a liquid and vapor is not sharp on the microscopic level, so it is not unambiguous how the cluster radius, i.e. the location of the dividing surface between the two phases, should be defined. Perhaps the most natural choice for the location of the dividing surface is called the surface of tension. The value of surface tension depends on the choice of the dividing surface, and takes its minimum value at the surface of tension, thus making its derivatives with respect to the radius of the dividing surface zero (Rowlinson and Widom, 1989). As it turns out, having a zero first derivative for surface tension is necessary to recover the familiar macroscopic form of the Laplace equation. This then means that the physical, measurable surface tension of bulk liquid and macroscopic droplets is the surface tension at the surface of tension.

Following thermodynamic arguments already presented by Gibbs in the late 19th century (Gibbs, 1875), expressions for surface tension and the radius of a cluster in equilibrium with a supersaturated vapor are found. The surface tension with respect to the surface of tension is given by

$$\gamma_s = \left(\frac{3W^*(\Delta p)^2}{16\pi} \right)^{1/3}, \quad (9)$$

where Δp is the pressure difference between the bulk liquid and vapor phases in chemical equilibrium. The radius of the surface of tension is

$$R_s = \left(\frac{3W^*}{2\pi\Delta p} \right)^{1/3}. \quad (10)$$

It should be noted that even though the bulk liquid pressure appears in these equations, no assumption of the cluster having bulk properties has been made (Gibbs (1875), Koga et al. (1998)).

Another choice of the dividing surface is the equimolar surface, which for the one-component case means that there is no excess volume or particle number associated to the surface, implying a sharp surface. The equimolar surface is required for the surface tension to be size-independent, and is thus the choice made in CNT. The equimolar radius of a cluster is

$$R_e = \left(\frac{3N^*}{4\pi\Delta\rho} \right)^{1/3}, \quad (11)$$

where $\Delta\rho$ is the density difference between bulk liquid and vapor phases in chemical equilibrium. In general the equimolar surface and surface of tension do not coincide, but in CNT it is assumed that they do.

As the surface tension of the smallest clusters is most likely quite different from that of a planar interface, it is not surprising that the more recent theories such as those summarized in Section 2.4 tend to avoid the capillary approximation at least when the cluster size is small. However, the question of size dependence of surface tension was tackled already by Tolman (1949) in a landmark paper which presented the equation for cluster surface tension now known as the Tolman equation

$$\frac{\gamma_s}{\gamma_\infty} = \frac{R_s}{R_s + 2\delta_\infty}, \quad (12)$$

where δ_∞ is the Tolman length, defined as the difference between equimolar radius and the radius of the surface of tension at the planar limit. In the derivation of the Tolman

equation it is assumed that the difference between the two radii stays constant for different cluster sizes, and that the difference is small compared to R_s (Tolman, 1949), thus making it valid only for quite large clusters (Koga et al., 1998). However, it is generally acknowledged that Eq. (12) is the appropriate first-order (in $1/R$) correction for surface tension in the case of spherical clusters.

2.3 Nucleation theorems

The first nucleation theorem is a general relation between the formation free energy and size of the critical cluster,¹ which in its one-component form is given by

$$\left(\frac{\partial W^*}{\partial \Delta\mu}\right)_T = -N^*. \quad (13)$$

Eqs. (4) and (5) show that this clearly holds for CNT, but the nucleation theorem is more general than CNT and neither require the macroscopic assumptions such as the capillary approximation nor a spherically shaped cluster (Hill, 1962; Kashchiev, 1982; Viisanen et al., 1993; Oxtoby and Kashchiev, 1994). In fact, the nucleation theorem is not only restricted to nucleation but is applicable to inhomogeneous systems in general (Bowles et al., 2001). Eq. (13) can be cast in an alternative form

$$\frac{\partial \ln J}{\partial \ln S} \approx N^*. \quad (14)$$

While this form is not exact, the right-hand side is approximately N^* with an accuracy of one or two atoms. Eq. (14) can then be used to obtain a value for the critical size from nucleation experiments or molecular dynamics simulations.

A second nucleation theorem also exists, and in its general form the second nucleation theorem relates the derivative of the cluster formation free energy with respect to temperature with the entropy change of the cluster formation (Ford, 1996).

2.4 Other nucleation theories

As mounting experimental and simulation evidence have highlighted the shortcomings of CNT (Ford, 2004; Laaksonen and Napari, 2001; Kalikmanov et al., 2008), various

¹To be exact, the critical size in Eq. (13) is the excess particle number ΔN^* : the difference between the number of particles in the cluster and the number of vapor particles that would fit the volume occupied by the cluster. Vapor density is much smaller than liquid density, so in practice $\Delta N^* = N^*$.

theories have been developed in an attempt to replace it. Two such theories are highlighted in the following section, the diffuse interface theory (DIT) by Gránásy (1996) and the extended modified liquid drop – dynamical nucleation theory (EMLD-DNT) by Reguera and Reiss (2004a,b). These two are showcased here since they are used in **Paper V**, but they are by no means the only theories available besides CNT. One other promising candidate is the mean-field kinetic nucleation theory (MKNT) by Kalikmanov (2006), which is a semiphenomenological model where small clusters are treated with statistical mechanics and large clusters described with the capillary approximation, with an interpolation between the two.

2.4.1 Diffuse interface theory

As the name suggests, the diffuse interface theory takes into account the non-sharpness of the cluster interface, allowing for a size-dependent surface tension. Noting that the formation free energy of the clusters is expressed using the local specific enthalpy (Δh) and entropy (Δs) profiles as

$$W = \int_V (\Delta h(\mathbf{r}) - T\Delta s(\mathbf{r}))d\mathbf{r}, \quad (15)$$

DIT then replaces the actual profiles by step functions that have the same amplitude (Δh_0 and Δs_0) and integral as the original profiles. The thickness of the interface is represented by the difference between the locations of these two step functions, $R_H - R_S$. To get the DIT expressions for critical cluster size and formation free energy two assumptions are still needed: $R_H - R_S$ is assumed independent of cluster size at constant temperature, and at least the cluster center has the bulk properties. The critical formation free energy is given by

$$W^* = -\frac{4\pi}{3}(R_H - R_S)^3\Delta g_0\psi, \quad (16)$$

where $\Delta g_0 = \Delta h_0 - T\Delta s_0$, $\psi = 2(1 + q)\eta^{-3} - (3 + 2q)\eta^{-2} + \eta^{-1}$, $q = (1 - \eta)^{1/2}$, and $\eta = \Delta g_0/\Delta h_0$. DIT has been found to perform better than CNT when applied to gas-liquid nucleation of nonpolar, weakly polar, and metallic substances (Gránásy, 1996), and it has had remarkable success when compared to crystal nucleation experiments on a variety of substances (Gránásy, 1997).

2.4.2 Extended modified liquid drop - dynamical nucleation theory

The EMLD-DNT combines the extended modified liquid drop model of Reguera et al. (2003) with the dynamical nucleation theory of Schenter et al. (1999). In EMLD one considers a system in constant temperature that consists of a cluster with n molecules and $N - n$ vapor molecules confined in a spherical container with fixed volume V . The n -sized cluster within the container obeys the capillary approximation, but its size is allowed to fluctuate and it is also allowed to translate within the volume V . In EMLD-DNT the whole EMLD system (the cluster and vapor together) is considered to be the physical drop (cluster) of nucleation. A non-arbitrary choice for the volume of this N, V -cluster is required, and this is where the dynamical nucleation theory comes into play. According to DNT, the proper kinetic definition for the volume of a cluster is such that the evaporation rate is minimized (Reguera and Reiss, 2004b). This is achieved by choosing the volume that minimizes the pressure within the container. The same requirement of minimum vapor pressure is can also be argued to be the correct one by thermodynamic considerations (Talanquer and Oxtoby, 1994). With the correct volume found, the formation free energy of the N, V -cluster in an open system can then be written and the critical cluster is once again recognized from the top of the nucleation barrier.

Besides agreeing with simulation results (Reguera and Reiss, 2004b; Wedekind et al., 2007c), EMLD-DNT has also successfully predicted experimental results of n-pentanol (Zandi et al., 2006).

3 Density functional theory

Another theory often used to study nucleation is the density functional theory (DFT) (see e.g. Oxtoby and Evans (1988); Barrett (1997); Bykov and Zeng (2006); Napari and Laaksonen (2007)). However, unlike the theories in the previous section, DFT is a more general theory of fluids and is not restricted only to nucleation. DFT is a formulation of statistical physics where the free energies are functionals of the particle number density distribution $\rho(\mathbf{r})$. The classical DFT approaches are not to be confused with the quantum mechanical DFT which deals with functionals of electron densities instead. In any DFT approach to nucleation the task consists of writing down the grand potential as a functional of the density distribution, $\Omega[\rho(\mathbf{r})]$, then solving the

equilibrium density distribution by minimizing the grand potential, $\delta\Omega[\rho(\mathbf{r})]/\delta\rho(\mathbf{r}) = 0$. The formation free energy of a critical cluster is then found by subtracting the grand potential of the supersaturated vapor from the minimized grand potential. The critical size is found by integration from the equilibrium density distribution.

There are a few common ways to write the grand potential functional, with different levels of approximation (Davis, 1996). In **Papers II, IV** and **V** the perturbative approach (Zeng and Oxtoby, 1991) is used. In this method the repulsive part of the potential of interest is replaced with a hard-sphere fluid that acts as a reference system, and the attractive interactions are treated as a perturbation. The grand potential functional is written as

$$\Omega[\rho(\mathbf{r})] = \int d\mathbf{r} f_h(\rho(\mathbf{r})) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}') - \mu \int d\mathbf{r} \rho(\mathbf{r}), \quad (17)$$

where $f_h(\rho)$ is the free energy density of a hard-sphere fluid, ϕ is the interaction potential, and μ the chemical potential of the vapor. Thus the interaction potential needs to be defined, in contrast to the nucleation theories of the previous chapter. The other density functional approach that is applied in **Papers II** and **V**, the square gradient theory (SGT) (van der Waals, 1893; Cahn and Hilliard, 1958, 1959) is somewhat simpler. In SGT $\Omega[\rho(\mathbf{r})]$ is given by

$$\Omega[\rho(\mathbf{r})] = \int \left\{ f_0(\rho(\mathbf{r})) + \frac{c}{2} [\nabla\rho(\mathbf{r})]^2 - \mu\rho(\mathbf{r}) \right\} d\mathbf{r}, \quad (18)$$

where $f_0(\rho)$ is the free energy density of the uniform fluid and c is related to the direct correlation function, but in **Papers II** and **V** serves as an adjustable parameter. In SGT an interaction potential is not needed, but an equation of state is needed for $f_0(\rho)$. The choice of the equation of state can have an effect on the results (see discussion in **Paper V**).

4 Nucleation simulations

4.1 Monte Carlo simulations

Monte Carlo simulations are named after their heavy use of random numbers, and they encompass a wide variety of methods where the results are computed by stochastic

sampling. Even within nucleation studies several MC approaches exist, such as the discrete summation method of Hale and Ward (1982), or the aggregation-volume-bias MC by Chen et al. (2001) and its further developments (Chen et al., 2005). The Monte Carlo method used in this thesis (in **Papers II** and **IV**) is the growth-decay method by Merikanto et al. (2004). In the growth-decay method a single cluster is simulated and the average grand canonical growth and decay rates, \overline{G}_N and \overline{D}_N , respectively, are calculated. The formation free energy of a cluster with N atoms is given by

$$W_{N,\text{MC}} = -k_B T \sum_{N'=2}^N \ln \left(\frac{\overline{G}_{N'-1}(T, S=1)}{\overline{D}_{N'}(T, S=1)} \right) - k_B T (N-1) \ln S, \quad (19)$$

and the critical cluster is obviously identified as the one with largest formation free energy. Eq. (19) reveals a large benefit compared to MD nucleation simulations. Namely, one only needs to simulate the formation free energies for a single supersaturation, and then just use those values to calculate $W(N)$ in another supersaturation. This makes growth-decay MC very cost-effective compared to MD. Another benefit of MC is that the surface tension of the planar interface can be approximated from the cluster simulation data (Merikanto et al., 2007), although when dealing with more complex molecular species some caution is advised (Nellas et al., 2010).

However, MC lacks dynamics, and as such does not directly give information about time-dependent quantities.

4.2 Molecular dynamics simulations of nucleation

Molecular dynamics simulations mean, in a nutshell, solving numerically the classical equations of motion of an N -body system. The first MD simulations were performed by Alder and Wainwright (1957) over fifty years ago for a hard sphere system, and since then MD simulations have been successfully applied to various problems in physics as well as other fields, ranging from solid state physics to studies of polymers and biomolecules. In a classical MD simulation the interactions between the particles in the system are described with interaction potentials. The potentials, or force fields, are created by suitable parametrization of experimental data, or often also data that has been acquired by quantum chemical calculations. From these potentials the forces affecting each particle are calculated for every simulation timestep, and the equations of motion are then solved.

The potential used in all of the papers of this thesis is the Lennard-Jones (LJ) 12-6 potential

$$V(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right], \quad (20)$$

and the parameter values for argon are used for the two parameters σ and ϵ . The potential was cut and shifted, with a 5σ cutoff in **Papers I, II and IV**, and 2.5σ in **Papers III and V**. It should be noted that the choice of the cutoff distance affects the equilibrium properties of the LJ fluid, often quite drastically. Periodic boundary conditions were applied in all simulations. Finally, all results are given in the reduced LJ units, where the potential parameters σ and ϵ are taken as the units of length and energy respectively, and the mass of a single atom m is chosen as the unit of mass. The unit of time is then $\tau = \sqrt{m\sigma^2/\epsilon}$ and the unit of nucleation rate is $[J] = \sigma^{-3}\tau^{-1}$, and the unit of temperature ϵ/k_B . The benefit of choosing the LJ potential is that it is not computationally very demanding, and as such is quite ideal for studying the theoretical foundations of nucleation. Also, there exists a large amount of studies that use the LJ potential making it a benchmark of sorts. However, the LJ potential is not of academic interest only as it does describe noble gases reasonably well. Furthermore, experimental results of argon nucleation do exist (Iland et al., 2007; Sinha et al., 2010), and they can and have been compared to simulations (Kalikmanov et al., 2008).

A MD nucleation simulation is straightforward in its implementation and a quite intuitive approach to nucleation. As a starting configuration the atoms are placed in the simulation box at the desired supersaturated vapor density. The simulation is then run, and since the vapor is supersaturated it will nucleate at some point. Considering the stochastic nature of nucleation it is not known beforehand when exactly the nucleation onset will occur, only that the lower the supersaturation, the longer on average one has to wait until the onset. This means that unfortunately with lower supersaturations a lot of computational time is wasted in simulating the relatively uninteresting metastable vapor phase prior to nucleation. Necessarily a practical limit exists on how much time can be spent on a single simulation run, which means that MD nucleation simulations are limited to fairly high supersaturations with critical sizes often only few tens of atoms. As the force calculation is the most timeconsuming part of a MD run, the complexity of the potential model directly affects the achievable supersaturations.

With this computational limitation for direct nucleation simulations, an alternative method called indirect simulations is sometimes employed. In the indirect simulations a pre-existing cluster that is in equilibrium with a surrounding compact vapor phase

is simulated. The initial setup used in this thesis was such that all the atoms belong initially to the cluster, and the vapor phase is allowed to form as atoms evaporate from the cluster during the run. This initial equilibration period is relatively short. The indirect simulations enable the study of larger cluster sizes than the direct simulations, but there are some issues that place a lower limit on the achievable cluster sizes. The simulation box can not be too large or the cluster will evaporate completely, but in a too small box the periodic images of the cluster would interact with each other, and the vapor density would not obtain a constant value near the box boundary. Obviously another downside for the indirect simulations when looking from a nucleation point of view is that with the cluster existing already at the start of the simulation, the indirect simulations provide no information about the formation energies or nucleation rate. What the simulations do provide is a density profile for the cluster-vapor system, which allows the calculation of the critical size without the somewhat artificial cluster definitions such as those that will be presented in Section 4.2.1.

Finally, two auxiliary MD simulation setups are often necessary. Simulating a planar liquid-vapor interface results in values for quantities such as equilibrium vapor density, bulk liquid density and planar surface tension. Also, a partial² equation of state for the vapor phase is necessary to determine the supersaturation of the vapor. This was achieved by simulating vapor in different densities and calculating the vapor pressure from the simulations. A polynomial function was then fitted to the simulated points, and from the Gibbs-Duhem equation, $d\mu = dP/\rho$, the chemical potential can be solved (or to be exact, the chemical potential difference $\mu - \mu_{eq}$). By performing simulations in liquid densities the same procedure can be used to obtain $P(\rho)$ for the liquid phase.

4.2.1 Cluster definitions

In order to get information about critical clusters from simulations, it is obviously necessary to define how a cluster is identified in a MD simulation. One of the most widely used cluster definition is the Stillinger definition (Stillinger, 1963), in which atoms will belong to the same cluster if they are within a pre-defined cut-off distance of each other. In a LJ system the cutoff distance is usually 1.5σ or close to it, corresponding to the first minimum of the radial distribution function of the liquid. The Stillinger

²The MD simulations do not allow for a complete equation of state over the full range of densities, but instead separate pressure-density correlations for the vapor and liquid phases.

definition remains widely used in various simulation studies, including the papers of this thesis.

More recently, ten Wolde and Frenkel introduced a slightly more complex cluster definition (ten Wolde and Frenkel, 1998). In the ten Wolde-Frenkel definition, a cluster atom is required to have a minimum number of neighbors within the pre-defined cutoff distance. Since a vapor atom has less atoms in its vicinity than liquid atoms, the introduction of the neighbor requirement allows to distinguish between atoms in vapor-like and liquid-like environment and avoids the overcounting of cluster sizes due to vapor atoms passing near the clusters. If only one neighbor is required the definition reduces to the Stillinger definition. The original work of ten Wolde and Frenkel set the neighbor requirement to five atoms.

4.2.2 Temperature control

While the NVE, or microcanonical, ensemble is natural for MD simulations, constant temperature instead of energy is a more interesting scenario when it comes to nucleation. In a laboratory experiment constant temperature can be achieved with an inert carrier gas, which removes heat from the nucleating clusters through collisions. Similarly nucleating substances in the atmosphere are kept in constant temperature by the collisions with the surrounding air molecules. While it is perfectly possible to add a carrier gas species to a MD simulation, adding more atoms which have to considerably outnumber the nucleating atoms is going to increase the simulation time significantly. As a computationally cheaper alternative it is more common to couple the system to a thermostat to produce a NVT, or canonical, ensemble.

There are several thermostating methods available. The simplest method is to scale the velocities of each of the atoms so that the total kinetic energy of the system is equal to the average kinetic energy at the target temperature. However, this rather crude method prevents natural temperature fluctuations. A softer way to achieve thermostating is the Berendsen thermostat (Berendsen et al., 1984), where the velocity of each atom is scaled towards the desired value less abruptly, by a factor

$$\lambda = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_0}{T} - 1 \right) \right]^{\frac{1}{2}}, \quad (21)$$

where Δt is the timestep of the simulation and the τ parameter determines the strength

of the coupling. With $\tau = \Delta t$ the thermostat is reduced to simple velocity scaling. The Berendsen thermostat is used in most of the MD simulations of this thesis.

Even before the Berendsen thermostat an alternative thermostat was proposed by Andersen (1980). When using the Andersen thermostat a number of particles are randomly selected to be given new velocities drawn from a Maxwell-Boltzmann distribution corresponding to the target temperature. The probability for a given particle to receive a new velocity is $\nu\Delta t$, where the parameter ν describes the collision frequency of the atoms with an imaginary heat bath. While **Paper I** shows that the Andersen thermostat fares better in keeping the temperature of the nucleating cluster in check, the main problem with the thermostat is that the random new velocities introduce abrupt changes to the trajectories.

An apparent peculiarity with thermostating compared to the realistic carrier gas situation is that for larger clusters carrier gas atoms would only collide with atoms that are on the surface of the clusters. In **Paper I** the issue was investigated by performing runs where only the monomers were thermostatted. The nucleation rates were only slightly changed compared to full thermostating (see Table 1), implying that any elaborate thermostating scheme that mimics carrier gas by only affecting the surface of a large cluster is not required.

Based on the results of **Paper I** where the Berendsen and Andersen thermostats were compared, and on the results in the concurrent work by Wedekind et al. (2007a) where the direct velocity scaling, Nosé-Hoover thermostat (Hoover, 1985) (in which an additional degree of freedom which controls the temperature is introduced to the system) and carrier gas were compared, it is safe to say that the choice of a thermostat is not a critical issue in a MD nucleation simulation. The effect a thermostat has on

Table 1: Nucleation rates obtained by different methods (see Sec. 4.2.3) and thermostats. $T = 0.70$, $\rho_v = 0.023$ and potential cutoff is 5σ .

	Yasuoka-Matsumoto	Direct observation
Andersen	$2.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$
Berendsen	$1.3 \cdot 10^{-7}$	$0.5 \cdot 10^{-7}$
Andersen to free	$1.5 \cdot 10^{-7}$	$0.4 \cdot 10^{-7}$
Berendsen to free	$1.3 \cdot 10^{-7}$	$0.4 \cdot 10^{-7}$

nucleation rate is small compared to other error sources. However, in future simulation work it could be preferable to apply the recent and state-of-the-art thermostat by Bussi et al. (2007). The Bussi thermostat is a stochastic extension of the Berendsen thermostat, where a random force is added so that the proper sampling of the canonical ensemble is ensured. It was also shown to be more ergodic than the Nosé-Hoover thermostat.

4.2.3 Nucleation rate

There exists currently two prominent methods to obtain the nucleation rate from a MD simulation. The older of the two is the method of Yasuoka and Matsumoto (1998), where the number of clusters exceeding a pre-defined threshold size are counted and plotted as a function of time. Assuming that the threshold size is properly chosen so that it exceeds the critical size, the Yasuoka-Matsumoto plots will show a linear slope that is independent of the threshold size. The nucleation rate is then obtained by dividing the slope by the volume of the simulation box. An important benefit of the Yasuoka-Matsumoto method is that only a handful of runs is required to obtain the nucleation rate. However, the threshold sizes must be chosen prior to the run, requiring an educated guess as to what the critical size might be. Also, the method only gives at best a rough estimate for the critical size.

The more recent method to obtain nucleation rate is the mean-first passage time (MFPT) method introduced by Wedekind et al. (2007b). Starting from the Fokker-Planck equation, they arrived at a simple expression for the average time $\tau(N)$ it takes for a cluster of N atoms to be first observed in a simulation run

$$\tau(N) = \frac{\tau_J}{2} [1 + \operatorname{erf}(b(N - N^*))] \quad (22)$$

where $\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x e^{-t^2} dt$ is the error function and nucleation rate is connected to the parameter τ_J by $J = 1/(V\tau_J)$. It is straightforward to keep track of when a cluster of a given size appears for the first time in a MD simulation run, but as the nucleation onset can vary greatly from one run to another, several runs at the same conditions must be performed to achieve sufficient statistics. With the mean first passage times acquired, Eq. (22) can then be fitted to the data, and the fitting parameters (τ_J, N^*, b) provide the nucleation rate, critical size and even the Zeldovich factor by $Z = b/\sqrt{\pi}$. Naturally the critical size depends on the cluster definition used to get the MFPT data,

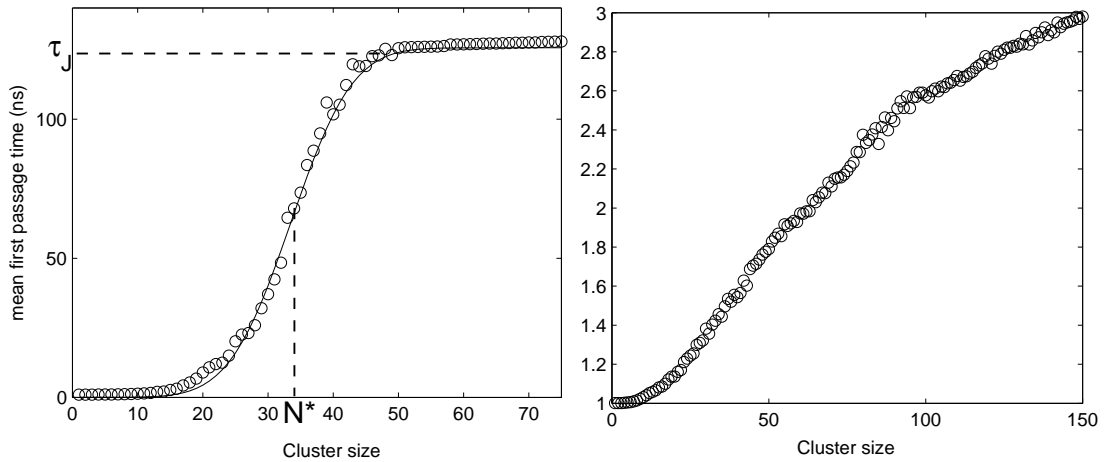


Figure 2: Left: Simulated mean first passage times with sufficiently low supersaturation that Eq. (22) can be fitted. Right: Mean first passage times in a high supersaturation situation where nucleation and growth happen on similar timescales, making the MFPT analysis impossible.

but luckily it turns out that the nucleation rate is mostly unchanged by the choice of a cluster definition (see Wedekind and Reguera (2007) and **Paper IV**). This means that a critical size that is independent from the cluster definition can be determined using the nucleation theorem, Eq. (14).

The MFPT method suffers from the drawback that strictly speaking Eq. (22) only works when the nucleation barrier is sufficiently high. For lower nucleation barriers nucleation and growth happen on similar timescales, and the MFPT plot has no longer the sigmoidal shape of Eq. (22) (see Fig. 2), which makes the fitting procedure questionable or even impossible. This means that, in contrast to the Yasuoka-Matsumoto method, the MFPT method has a limit on how high supersaturations it can be applied to. However, for the vapors in the nucleation simulations of the papers of this thesis the nucleation and growth can still be distinguished and the MFPT method can be applied. **Paper I** uses the Yasuoka-Matsumoto method as the manuscript was already submitted before the MFPT method was first introduced.

In **Paper I** the nucleation rate is also estimated by following the size of the largest cluster as the simulation proceeds, and recognizing the time of nucleation onset from when the largest size begins to grow beyond the largest cluster sizes of the metastable

vapor (the direct observation method, see Table 1). The nucleation rate is then simply the inverse of average onset time multiplied by the box volume. When compared to MFPT this method requires same amount of computational effort and results in practically the same value of nucleation rate (Chkonia et al., 2009), while giving only a rough estimate for the critical size and no information on the Zeldovich factor. Thus the introduction of MFPT has rendered the direct observation method practically obsolete.

All three of the methods have been shown to result in similar nucleation rates at least in the case of gas-liquid nucleation in LJ systems (Chkonia et al., 2009). However for certain systems discrepancies between the Yasuoka-Matsumoto and MFPT rates up to one order of magnitude have been reported (Römer and Kraska, 2007).

4.3 The clusters in direct and indirect simulations

The assumption behind the idea of using the indirect cluster-vapor equilibrium simulations to study nucleation is that this stable equilibrium cluster has the same properties as the critical cluster corresponding to the same supersaturation, since the critical cluster with its equal probability to grow or evaporate is considered to be in an unstable equilibrium on top of the nucleation barrier. However, as noted earlier, in the indirect simulations the cluster is already present at the beginning of the simulation run, meaning that one does not observe its formation and can therefore not extract its formation free energy or the nucleation rate from the simulation. But since the cluster size and supersaturation of the surrounding vapor can be obtained from the indirect simulations, the formation energy of the clusters can then be calculated by integrating the nucleation theorem, Eq. (13), provided that there is some point with known formation free energy acting as a reference point. Such a point can be acquired from the direct nucleation simulations. In **Paper II** direct nucleation simulations were performed in four different supersaturations, and the nucleation theorem in its approximative form, Eq. (14), was used to calculate a critical size from the simulated nucleation rates. Additionally, a number of indirect simulations were performed for different cluster sizes. When plotting the cluster sizes as a function of $(\Delta\mu)^{-3}$, which according to CNT should result in a straight line, it was seen that the cluster size from the nucleation simulations indeed agreed with a linear fit made to the equilibrium simulations (see Fig. 3). Formation energies for the larger clusters could then be calculated.

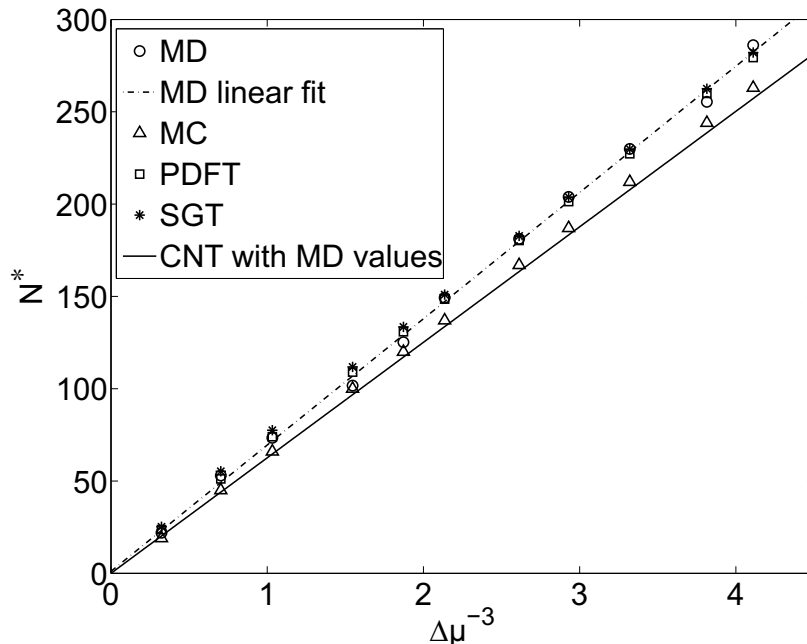


Figure 3: Critical sizes from MD, MC and both perturbative DFT and SGT. The smallest MD size corresponds to direct simulations. $T = 0.662$, potential cutoff at 5σ .

The four different direct nucleation simulation conditions resulted in only a single point in the above method where the slope of an $\ln J(\ln S)$ -plot provided only a single value for the critical size. In the later papers we used a slightly different approach, namely we made a linear fit to the simulated $\ln J$ as a function of $(\ln S)^{-2}$, which with Eq. (14) leads to a linear dependence between critical size and $(\Delta\mu)^{-3}$. It lends some confidence to the results of **Paper II** that this procedure leads to roughly same slope as the linear fit to the equilibrium simulation cluster sizes.

However, some doubt to the idea that the critical clusters of the direct nucleation simulations and the equilibrium clusters of the indirect simulations are commensurate was cast by **Paper III**. Now the potential cutoff was reduced from the 5σ of the previous paper to 2.5σ . The shorter cutoff made it possible to perform both types of simulations in same vapor conditions, as now smaller box sizes in the indirect simulations are allowed, and at the same time the decreased time spent on force calculations allowed for larger critical sizes in the direct simulations. In order to get a picture of the cluster structure ten Wolde-Frenkel cluster definitions with different neighbor requirements were used. The results are shown in Fig. (4), and as can be seen there are some

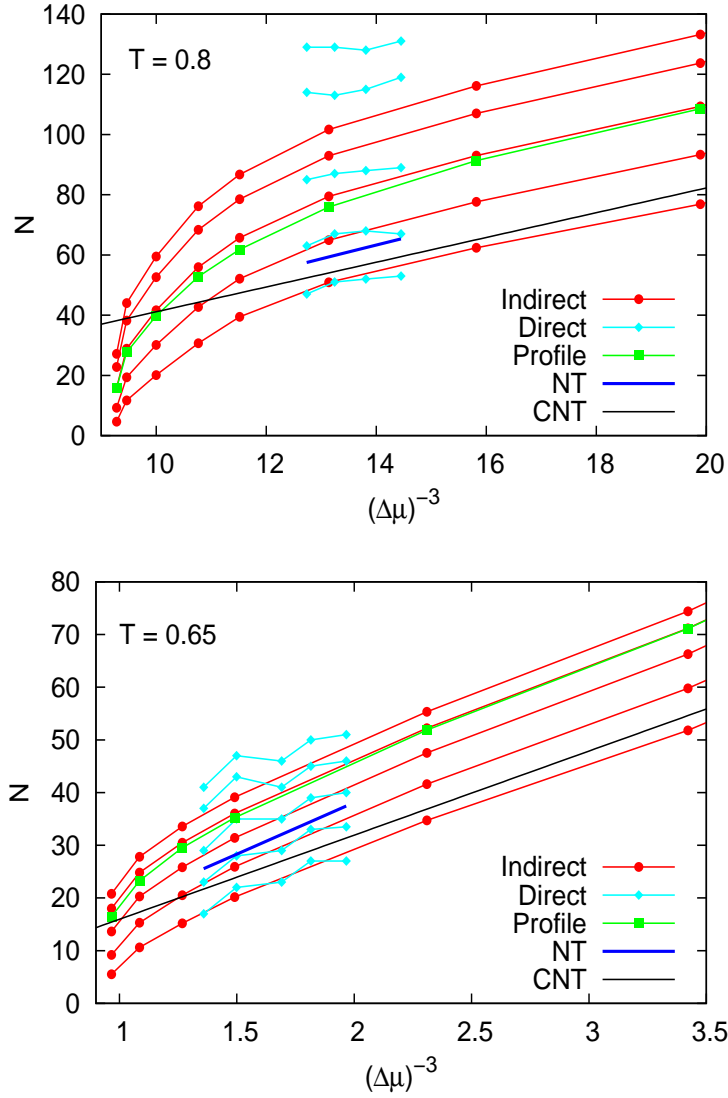


Figure 4: Cluster sizes from direct and indirect simulations with 2.5σ cutoff. The cluster definitions used are the ten Wolde-Frenkel clusters with 1-5 neighbor requirement, the five neighbor case being the smallest size. NT is the nucleation theorem size, and profile is from the density profile of the indirect simulations.

differences between the cluster sizes from the two simulation methods.

If a more strict requirement of four or five neighbors is used, the cluster sizes are quite similar in both methods. When less neighbors are required, the direct simulation sizes are larger, even considerably so at the higher temperature. This suggest that while

the clusters seem to have a liquid-like core that has the same size in both simulation types, the critical cluster of the direct nucleation simulations has more loosely connected atoms in the vicinity of this core. Another result seen in the figure, and a quite confusing one, is that the sizes obtained from the density profile of the equilibrium clusters is actually larger than the nucleation theorem sizes of the nucleation simulations, which is opposed to what the ten Wolde-Frenkel clusters tell us.

Nonetheless, the cluster sizes from the two methods seem to be getting closer to each other as the temperature gets lower. The temperature in **Paper II** is close to the triple point of the 5σ -cut LJ fluid. Thus the cluster sizes from the indirect simulations should serve as reasonable estimates for critical sizes in the conditions of **Paper II**.

4.4 The surface tension of clusters and the Tolman length

MD simulations provide the necessary quantities to calculate cluster surface tension and the radii of the two dividing surfaces from Eqs. (9-11). In **Paper IV** the simulation based values for these quantities were calculated. It turns out that the simulation based cluster surface tensions were within 5 % of the planar value even for clusters

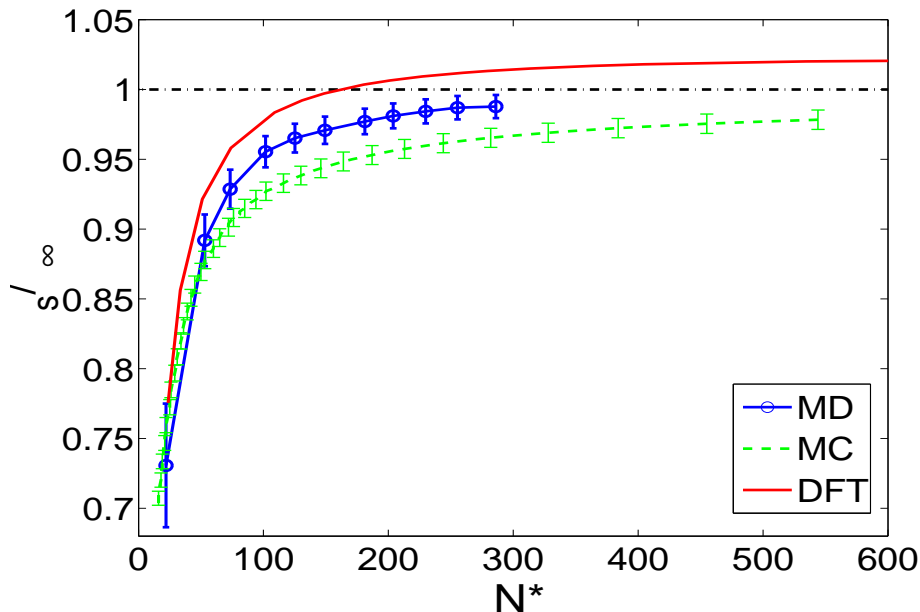


Figure 5: Cluster surface tension from different methods. $T = 0.662$, cutoff 5σ .

containing as few as one hundred atoms (see Fig. 5). For smaller clusters than that, however, the planar surface tension becomes an increasingly poor estimate as the cluster size decreases. Unfortunately, a nucleation experiment would typically have conditions where the critical size is in this size range.

In **Paper IV** estimates for the Tolman length were acquired by extrapolating the difference between the surface of tension and equimolar surface to the planar limit, and the resulting value was negative for each of the methods (MD, MC and DFT). DFT has long predicted that the Tolman length is negative (Talanquer and Oxtoby, 1995; Barrett, 2006; van Giessen and Blokhuis, 2009), but simulations of a planar liquid-vapor interface have resulted a positive value (Lei et al., 2005; van Giessen and Blokhuis, 2002; ten Wolde and Frenkel, 1998). However, besides **Paper IV**, various different methods to extract the Tolman length from cluster simulation data have appeared recently (van Giessen and Blokhuis, 2009; Sampayo et al., 2010; Block et al., 2010), all of which have resulted in a negative Tolman length.

4.5 Comparison of theories to MD results

As seen in **Paper IV**, the cluster surface tension is drastically different from the planar

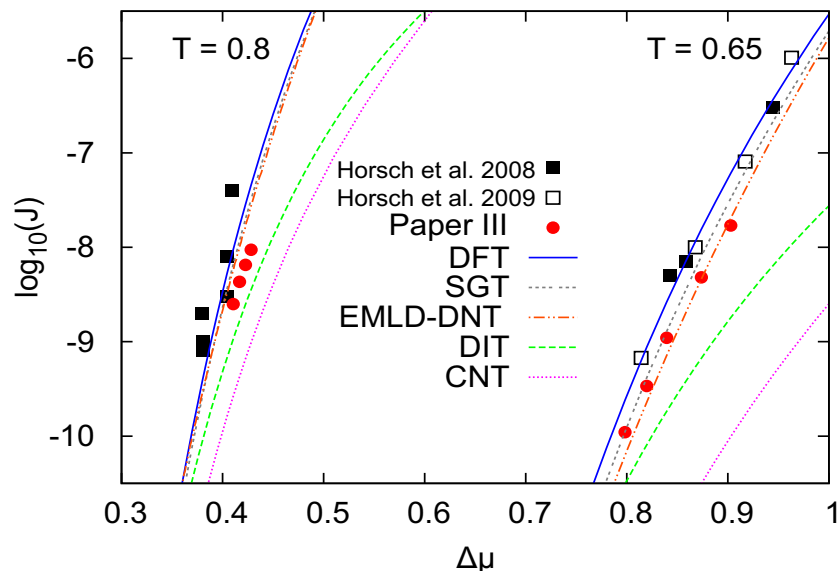


Figure 6: Comparison between simulated and theoretical nucleation rates. 2.5σ cutoff.

value when the cluster has only few tens of atoms. This happens to be the size range of the critical sizes that are achievable in direct nucleation simulations. One might then expect that if the predictions of nucleation theories were compared to MD simulation results, CNT with its capillary approximation would not be among the best choices. This is indeed the case, as **Paper V**, and Fig. 6, show. The different MD datasets are from **Paper III** and from works by Horsch et al. (2008), and Horsch and Vrabc (2009). DFT, SGT and EMLD-DNT predict the MD nucleation rates well, and DIT underestimates them, though not by as much as CNT. To the credit of CNT it should be noted that it fares better than DIT in predicting the critical sizes, and at higher temperatures the CNT nucleation rate is notably closer to the simulated ones than in lower temperatures. This reflects the known erroneous temperature dependence of CNT.

5 Review of papers

Paper I compares the temperature regulation of the Berendsen and Andersen thermostats and their effect on nucleation rate. We also considered variants of the thermostats where only the monomers in the vapor are thermostatted. The nucleation rates obtained through the Yasuoka-Matsumoto and direct observation methods are compared for each of the thermostats. Furthermore, results on velocity distributions of small clusters and cluster size distributions are reported. The choice of a thermostat and method to calculate nucleation rate are not found to be a critical issue when trying to calculate the nucleation rate from simulations.

Paper II combines direct nucleation simulations and indirect simulations of a cluster-vapor equilibrium. Using the cluster sizes from these two molecular dynamics approaches the nucleation theorem is integrated, resulting in formation free energies also for the clusters of the indirect simulations. The results are compared to Monte Carlo simulations and density functional and square gradient theory calculations. While DFT and SGT are found to agree well with the molecular dynamics results, the Monte Carlo simulations result in smaller critical sizes and formation free energies than MD.

Paper III studies the cluster structure in direct and indirect molecular dynamics simulations by employing the ten Wolde-Frenkel cluster definition with various neighbor requirements. It is found that while the more strict requirements of four or five neigh-

bors result in similar sizes for the two methods, the critical clusters from the direct simulations are larger than the equilibrium clusters of the indirect simulations when less neighbors are required. The difference between the two becomes larger when the temperature is higher.

Paper IV studies the surface tension of clusters. The surface tension is calculated via a rigorous thermodynamic route using molecular dynamics and Monte Carlo simulation data as input. Density functional theory results are also presented. The surface tension is found to be within 5% of the planar value even for clusters as small as hundred atoms. The Tolman length is also estimated by extrapolating the difference between the equimolar radius and the radius of the surface tension to planar limit. All three methods indicate a small negative value.

Paper V compares the predictions of various theories to molecular dynamics simulation data. The MD nucleation rates are best predicted by density functional and square gradient theories along with the extended liquid drop model-dynamical nucleation theory. The diffuse interface theory also fares better than the classical nucleation theory. Critical sizes are also compared.

Author's contribution

I am alone responsible for the summary of this thesis. I have also written majority of **Papers I and II**, about half of **Paper III**, all of **Paper IV** and minor parts of **Paper V**. With the exception of those indirect simulations presented in **Paper III**, I have performed all of the original molecular dynamics simulations included in this thesis and analyzed the MD simulation data. The molecular dynamics simulations have been performed using a code developed in-house, and I am responsible for programming most of the features implemented during the recent years. Besides the MD values, I have also calculated the MC values for surface tension and the two radii of dividing surfaces in **Paper IV** from existing MC formation free energy data.

6 Conclusions

In the work presented in this thesis molecular dynamics simulations are used to study homogeneous nucleation in Lennard-Jones vapors. The simulation setups included both the direct simulations of nucleation from a supersaturated vapors and the indirect simulations of a cluster in equilibrium with a surrounding vapor.

Various thermostatting schemes were employed to study their effect on nucleation rates. While the nucleation rates from different thermostats could differ by up to a factor of two, this can still be considered an acceptable agreement as the nucleation rates between theoretical, experimental and simulation values often differ by several orders of magnitude. While one should consider the correct or best choice of thermostat to be the one that best samples the canonical ensemble, it is safe to conclude that the choice of thermostat is not a critical issue when simulating the nucleation rate. In this work the method by which the nucleation rate is extracted from the simulation was also found to have a only a minor effect on the resulting nucleation rate, but there is some evidence that this conclusion can not be generalized to all substances.

Attempts to compare and combine the direct and indirect approaches were also presented in this work. The critical clusters of the direct nucleation simulations and the equilibrium clusters of the indirect simulations in the same vapor are generally considered to be of same size, but by applying ten Wolde-Frenkel cluster definitions with various neighbor conditions it was found that this may not be the case. While the clusters in both simulation types have liquid-like cores of the same size, the critical cluster of the nucleation simulations has more atoms surrounding this core than the equilibrium cluster has. This can be considered as an indication that the critical cluster has a more fragmented structure than the equilibrium cluster. On the other hand, the result can be interpreted alternatively so that if the stricter ten Wolde-Frenkel definitions are proper descriptions of liquid clusters, the clusters in the two simulation methods are actually of the same size, and it is the vapor in the vicinity of the clusters that differs between the two. Further away the vapor densities are of course the same in both methods.

In any case, the differences between the two approaches become smaller at lower temperatures, so if the temperature is close to the triple point the direct and indirect cluster sizes should be approximately the same regardless of the cluster definition. Performing both kinds of simulations close to the triple point temperature and combining critical

sizes from the two methods, formation free energies were calculated for the clusters in the indirect simulations with the aid of the nucleation theorem. The resulting values agreed well both with density functional theory and square gradient theory calculations, but Monte Carlo simulations resulted in lower formation free energies. The same was true for critical sizes, where Monte Carlo resulted in noticeably lower values. The origin of this difference remains unknown.

The formation energies from MD and MC were used further to calculate surface tensions for the clusters, and these values were compared to DFT predictions. Despite the considerable differences between the resulting values, all methods indicated that the surface tension is still quite close to the planar value when the cluster size is only one hundred atoms, lending some credibility to the capillary approximation of CNT. However, when the cluster size is below one hundred atoms the surface tension is quite different from the planar value. This is unfortunate considering that the clusters of interest in nucleation experiments, atmospheric particle formation, and usually also MD nucleation simulations consist of far fewer molecules than a hundred. The Tolman length was also approximated by an interpolation procedure, resulting in negative values for all the methods. This is surprising in light of previous simulation work where a positive Tolman length has been obtained through simulations of a planar liquid-vapor interface. However, a number of papers have been published recently where a negative Tolman length has been obtained from cluster simulation data by various means. A definitive conclusion on the sign is still pending.

Finally, a number of different theories were compared to molecular dynamics results. DFT and SGT are once again in good agreement with the simulated nucleation rates and critical sizes. However, with DFT requiring an interaction potential it is not very easily applicable to a variety of substances. Considering the three simple, nucleation specific theories (EMLD-DNT, DIT, CNT), EMLD-DNT is clearly the superior one when it comes to predicting nucleation rates, with very good agreement with the simulation results. Unfortunately this agreement does not carry on to the critical sizes. All of the theories represent an improvement to CNT when predicting the nucleation rates, with DIT performing somewhat worse than the rest.

The capability of MD nucleation simulations to provide the nucleation rate directly as a simulation result makes the approach unique among the various computational methods employed to study nucleation. As such, even with the relatively simple interaction potentials that are currently viable for them, the direct simulations will continue

to act as an important test for both existing and future nucleation theories and the assumptions made in them. However, there is probably also some interest in applying MD to atmospherically relevant molecular species. In order to describe the chemical reactions taking place in the atmospherically interesting clusters it is necessary to move beyond the classical force fields and rather describe the interactions on a quantum level. But the computational capacity needed to perform a nucleation simulation using an *ab initio* approach is beyond the current level of hardware and it is unlikely that this will change in the near future. So just as was the case with classical MD a few decades ago, the first steps into studying nucleation with *ab initio* MD will be taken with indirect approaches. Based on the results of this thesis two things should be kept in mind when setting up such simulations. First, the choice of cluster definition should be done carefully, and second, the simulations should be performed at temperatures not much above the triple point to ensure that the simulation gives a reasonable picture of the properties of clusters in nucleating vapors.

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