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MONTE CARLO SIMULATIONS OF MOLECULAR  
CLUSTERS IN NUCLEATION

JOONAS MERIKANTO

Division of Atmospheric Sciences  
Department of Physical Sciences  
Faculty of Science  
University of Helsinki  
Helsinki, Finland

Academic dissertation

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## Nomenclature

Functions:

$A$	surface area
$\alpha$	evaporation coefficient
$b$	cluster integral in Mayer theory
$\beta$	condensation coefficient
$D(T)$	correction factor in McGraw-Laaksonen theory
$\bar{D}$	average grand canonical decay rate
$F$	Helmholtz free energy
$f$	number of degrees of freedom
$\bar{G}$	average grand canonical growth rate
$h$	Planck's constant
$\Delta h$	enthalpy of vaporisation
$\mathcal{H}$	Hamiltonian
$I$	net flux of molecules over any cluster size
$J$	nucleation rate
$k$	Boltzmann constant
$K$	kinetic prefactor in nucleation rate
$K_i$	parameter in Dillmann-Meier theory
$\kappa$	isothermal compressibility of liquid
$\Lambda$	de Broglie wavelength
$m$	mass
$\mu$	chemical potential
$n$	number of molecules in a cluster
$N$	number density (concentration) ( $\mathcal{N}/\mathcal{V}$ )
$\mathcal{N}$	number of molecules
$\mathcal{N}_{\text{tot}}$	total number of clusters
$\mathcal{N}_n$	number of clusters with $n$ molecules
$\mathbf{P}$	momentum coordinate
$p$	pressure
$\Phi_n$	instability of a cluster
$Q$	partition function of the system
$Q_{\mathcal{N}}$	configurational integral of the full system
$q$	configuration integral of a cluster
$\mathbf{r}$	position coordinate
$R$	replacement free energy
$\mathbf{R}$	configuration
$r$	radius of nucleating cluster
$\rho_l$	density of bulk liquid
$\sigma_{\infty}$	planar surface tension

$\sigma_n$	size dependent surface tension
$S$	saturation ratio
$\Delta S$	entropy increase
$T$	temperature
$t$	time
$\tau$	parameter in Dillmann-Meier theory
$U$	potential energy
$V$	volume of the system
$v$	volume occupied by a molecule in liquid
$\Delta W$	work of cluster formation
$Z$	Zeldovich non-equilibrium factor
$z$	fugacity

Subscripts, superscripts and acronyms:

1	monomer
*	critical value
CNT	classical nucleation theory
DFT	density functional theory
DM	Dillmann-Meier theory
eq	equilibrium value
EMLD	extended modified liquid drop model
$i$	configuration or index for a cluster size
LD	liquid drop model
$\lambda$	molecules in the same cluster
$\lambda\mu$	molecules between different clusters
MC	Monte Carlo
MD	Molecular dynamics
ML	McGraw-Laaksonen theory
$n$	value corresponding to the cluster of $n$ molecules
SC – CNT	self-consistent classical nucleation theory
RKK	Reiss-Kegel-Katz theory
RR	Reguera-Ruby theory

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## List of publications

This thesis consists of an introductory review, followed by five research articles. The papers are reproduced with the kind permission of the journals concerned.

- I J. Merikanto, H. Vehkamäki, and E. Zapadinsky, “Monte Carlo simulations of critical cluster sizes and nucleation rates of water”, (2004), *J. Chem. Phys.* **121**, 914.
- II J. Merikanto, H. Vehkamäki, and E. Zapadinsky, “Analysis of nucleation ability of cluster configurations with Monte Carlo simulations of argon”, (2006), *J. Chem. Phys.* **125**, 084503.
- III A. Lauri, J. Merikanto, E. Zapadinsky, and H. Vehkamäki, “Comparison of Monte Carlo simulation methods for the calculation of the nucleation barrier of argon”, (2006), *Atm. Res.* **82**, 489.
- IV J. Merikanto, E. Zapadinsky, A. Lauri, and H. Vehkamäki, “Origin of the failure of classical nucleation theory: incorrect description of the smallest clusters”, (2007), *Phys. Rev. Letters* **98**, 145702.
- V J. Merikanto, E. Zapadinsky, A. Lauri, I. Napari, and H. Vehkamäki, “Connection between the virial equation of state and physical clusters in a low density vapor”, (2007), *J. Chem. Phys.* **127**, 104303.

# 1 Introduction

A better understanding of the limiting step in a first order phase transition, the nucleation process, is of major importance to a variety of scientific fields ranging from atmospheric sciences to nanotechnology and even to cosmology. This is due to the fact that in most phase transitions the new phase is separated from the mother phase by an energetic barrier. This barrier is crossed in a process called nucleation. In nucleation an unlikely density fluctuation occurs in the mother phase, forming a seed for the new phase. A large enough fluctuation will start growing spontaneously, and a new phase is formed. The probability for such a fluctuation to take place, at some given conditions and at a some given time, is related to the height of the free energy barrier separating the two phases. Therefore, the theoretics of first order phase transitions, and hence nucleation, is deeply related to the calculation of the height of the nucleation free energy barrier and the size of the critical fluctuation, known as the critical cluster size, for which the growth becomes favourable.

In the past few decades, studies of atmospheric nucleation processes have gained a whole new impetus when it was realised that a significant proportion of atmospheric aerosols is produced by nucleation (see e.g the review of Kulmala et al. (2004)). Indeed, such nucleation events may be responsible for producing between 30% to 50% of all aerosol particles (Spracklen et al., 2006). The aerosol particles cool the climate by enhancing cloud formation and scattering and absorbing the incoming solar radiation. These particles have a significant yet largely unquantified role in the global climate change (Intergovernmental Panel on Climate Change, 2007).

In atmospheric sciences, as well as in other fields, the theoretical treatment of nucleation is mostly based on a theory known as the Classical Nucleation Theory. The Classical Nucleation Theory can be applied relatively easily for nucleation calculations. Its description of molecular level nucleation processes is based purely on the use of macroscopic thermodynamic parameters that are usually known. However, in the case of vapour-to-liquid nucleation, which is the most important nucleation route in atmospheric particle formation, the Classical Nucleation Theory is known to have only a limited success in predicting the rate at which nucleation takes place at the given conditions. This has prompted theoreticians to study nucleation on a molecular level. This kind of study is most effectively carried out by using molecular simulations.

Nucleation can be either homogeneous and heterogeneous. Homogeneous nucleation occurs without any contact with a surface, whereas in heterogeneous nucleation the new phase is formed on top of a surface. Furthermore, nucleation can take place in a one-component system, or it can involve several components — in the atmosphere, multicomponent nucleation is typical and unary homogeneous nucleation never takes place. Nevertheless, this thesis applies molecular Monte Carlo simulations to study unary homogeneous nucleation. The main focus of this thesis is not, however, to use

simulations to model atmospheric nucleation, but to study the strengths and weaknesses of existing nucleation theories with relatively simple systems. Thus, the author hopes that by contributing to the search for a better theory of nucleation, the results of this thesis will also bear significance in practical applications such as in atmospheric nucleation studies. The main objectives of this thesis are:

- To build a new molecular Monte Carlo simulation method for the calculation of the cluster work of formation and the nucleation barrier, and to validate it with a comparison to other existing methods;
- To study how the nucleation barrier depends on the characteristic properties of the clusters, such as their volume and interaction energy;
- To see if the molecular Monte Carlo simulations can explain the observed differences between the laboratory measured unary homogeneous nucleation rates and Classical Nucleation Theory (CNT) predictions;
- To see whether the CNT expression for the critical cluster size is correct;
- To explain why the CNT prediction for the nucleation barrier is erroneous;
- To calculate corrections to CNT predictions for the nucleation barrier height with simulations, and within the framework of a more general theory of imperfect vapour.

The thesis consists of an introduction, presenting the nucleation kinetics and the statistical mechanical description of the imperfect vapour, followed by a review of the simulation methods used for the nucleation studies. The main results from the five research articles constituting the body of this thesis are briefly reviewed at the end of the introduction, followed by the research articles themselves.

## 2 Nucleation kinetics

### 2.1 A kinetic expression for the nucleation rate

Consider a vapour that has just been either compressed isothermally or expanded adiabatically to a supersaturated state. First, there is a short period when the distribution of molecular clusters in the vapour adjusts itself to a new state in a series of molecular collision processes. This transition state is considered to be very short, and it is difficult to analyse such a state. Rather old and crude approximations by Farley (1952) indicate that the transition will take only some tens of microseconds — a time that is short compared to the compression or expansion times in nucleation measurements.

Assuming that molecular clusters in the vapour grow and decay only by gaining and losing monomers, the change in the concentration of  $n$ -clusters  $N_n$  with respect to time  $t$  can be expressed with a birth-death equation

$$\frac{\partial N_n}{\partial t} = \beta_{n-1}N_{n-1} + \alpha_{n+1}N_{n+1} - \beta_n N_n - \alpha_n N_n = I_{n-1} - I_n, \quad (1)$$

where  $\beta_n$  and  $\alpha_n$  are the monomer condensation and evaporation rates for an  $n$ -cluster, respectively. The following cases can be identified: If  $\partial N_n/\partial t$  is not zero, the system is in a transition state. This is called the *unbalanced non-steady state* case. If  $\partial N_n/\partial t$  is zero, the net flux  $I = \beta_n N_n - \alpha_{n+1} N_{n+1}$  will be constant and has the same value for all  $n$ . This constant  $I$  can either be zero, which occurs only when the vapour is in *undersaturated* or *saturated equilibrium state*, or nonzero, when the system is said to be in an *unbalanced (supersaturated) steady state*. The unbalanced steady state case is the one in which the system is undergoing nucleation at a constant rate. This is only possible when the nucleation itself does not significantly change the vapour properties, *i.e.*, the pool of monomers is so large that nucleation does not reduce the monomer concentration significantly, and there is no significant heating of the system from the latent heat release during the formation of clusters. The theoretical treatment of nucleation usually assumes that this is indeed the situation. Although the unbalanced steady state is the one corresponding to nucleation, the saturated equilibrium state is needed for calculations due to reasons given below.

If there is no net flux  $I$  in the system, the rate of each process is equal the rate of its counter process. Then we can write a so-called detailed balance equation

$$\beta_n^{\text{eq}} N_n^{\text{eq}} = \alpha_{n+1}^{\text{eq}} N_{n+1}^{\text{eq}}, \quad (2)$$

where the superscripts (eq) mark the equilibrium values. If we assume that the decay rate of clusters is not altered by variations in the vapour density, the decay rate can be expressed as

$$\alpha_{n+1} = \alpha_{n+1}^{\text{eq}} = \beta_n^{\text{eq}} \frac{N_n^{\text{eq}}}{N_{n+1}^{\text{eq}}}, \quad (3)$$

where  $N^{\text{eq}}$  is the equilibrium distribution of clusters in a saturated vapour. In a nucleating vapour there is a constant flux  $I$  through the system, and the balance equation transforms to

$$\beta_n N_n = \alpha_{n+1} N_{n+1} + I. \quad (4)$$

Using the above expression with Eq. (3) yields

$$\begin{aligned} I &= \beta_n N_n - \beta_n^{\text{eq}} N_n^{\text{eq}} \frac{N_{n+1}}{N_{n+1}^{\text{eq}}} \\ &= \beta_n^{\text{eq}} N_n^{\text{eq}} \left( \frac{\beta_n N_n}{\beta_n^{\text{eq}} N_n^{\text{eq}}} - \frac{N_{n+1}}{N_{n+1}^{\text{eq}}} \right). \end{aligned} \quad (5)$$

Now, let's define a saturation ratio in terms the relative proportion of monomer concentrations in the supersaturated and equilibrium vapours,

$$S = \frac{N_1}{N_1^{\text{eq}}} = \frac{\beta_n}{\beta_n^{\text{eq}}}, \quad (6)$$

where the last equality follows from a somewhat poorly justified assumption that at constant temperature, the condensation rate  $\beta_n$  is directly proportional to the monomer concentration. Then Eq. (5) can be written as

$$\begin{aligned} I &= \beta_n^{\text{eq}} N_n^{\text{eq}} \left( S \frac{N_n}{N_n^{\text{eq}}} - \frac{N_{n+1}}{N_{n+1}^{\text{eq}}} \right) \\ &= \beta_n^{\text{eq}} N_n^{\text{eq}} S^{n+1} \left( \frac{N_n}{S^n N_n^{\text{eq}}} - \frac{N_{n+1}}{S^{n+1} N_{n+1}^{\text{eq}}} \right) \\ &= S \beta_n^{\text{eq}} N_n^{\text{eq}} S^n \left( \frac{N_n}{S^n N_n^{\text{eq}}} - \frac{N_{n+1}}{S^{n+1} N_{n+1}^{\text{eq}}} \right) \\ &= \beta_n N_n^{\text{eq}} S^n \left( \frac{N_n}{S^n N_n^{\text{eq}}} - \frac{N_{n+1}}{S^{n+1} N_{n+1}^{\text{eq}}} \right). \end{aligned} \quad (7)$$

Using the last expression form of Eq. (7), we can write the following set of equations

$$\frac{I}{S \beta_1 N_1^{\text{eq}}} = \frac{N_1}{S N_1^{\text{eq}}} - \frac{N_2}{S^2 N_2^{\text{eq}}} = 1 - \frac{N_2}{S^2 N_2^{\text{eq}}} \quad (8)$$

$$\frac{I}{S^2 \beta_2 N_2^{\text{eq}}} = \frac{N_2}{S^2 N_2^{\text{eq}}} - \frac{N_3}{S^3 N_3^{\text{eq}}} \quad (9)$$

$$\dots$$

$$\frac{I}{S^n \beta_n N_n^{\text{eq}}} = \frac{N_n}{S^n N_n^{\text{eq}}} - \frac{N_{n+1}}{S^{n+1} N_{n+1}^{\text{eq}}}. \quad (10)$$

From Eq. (8) it follows that

$$N_2 = S^2 N_2^{\text{eq}} - I \frac{S^2 N_2^{\text{eq}}}{S \beta_1 N_1^{\text{eq}}}. \quad (11)$$

Inserting the above expression into Eq. (9) gives, after some rearranging

$$N_3 = S^3 N_3^{\text{eq}} - I \left( \frac{S^3 N_3^{\text{eq}}}{S^2 \beta_2 N_2^{\text{eq}}} - \frac{S^3 N_3^{\text{eq}}}{S \beta_1 N_1^{\text{eq}}} \right), \quad (12)$$

and continuing in the same manner we find

$$N_n = S^n N_n^{\text{eq}} \left( 1 - I \sum_{i=1}^{n-1} \frac{1}{S^i \beta_i N_i^{\text{eq}}} \right), \quad (13)$$

The  $S^n N_n^{\text{eq}}$  term on the right hand side is often called as the *balanced steady state* concentration (also known as the *supersaturated equilibrium* concentration). We now assume that

$$\lim_{n \rightarrow \infty} \frac{N_n}{S^n N_n^{\text{eq}}} = 0, \quad (14)$$

which will be confirmed by Figure 1. Then, we obtain an expression for the nucleation rate  $J$ , being equal to the flux  $I$  over any cluster size,

$$J = I = \left[ \sum_{i=1}^{\infty} \frac{1}{S^i \beta_i N_i^{\text{eq}}} \right]^{-1}. \quad (15)$$

It is quite remarkable that all signs of the true concentration of  $n$ -clusters in the nucleating vapour,  $N_n$ , have disappeared, and that the rate can be expressed solely by using the equilibrium concentration of clusters in the saturated vapour,  $N_n^{\text{eq}}$ .

## 2.2 The balanced and unbalanced steady state concentrations

Let's now study the difference between the *balanced steady state* concentration  $S^n N_n^{\text{eq}}$  and the *unbalanced steady state* concentration  $N_n$ . A general relation between the monomer and  $n$ -cluster concentrations in equilibrium vapour is given by

$$N_n^{\text{eq}} = N_1^{\text{eq}} \exp \left( -\frac{\Delta W_n^{\text{eq}}}{kT} \right), \quad (16)$$

where  $\Delta W_n^{\text{eq}}$  describes the work of cluster formation in equilibrium vapour. To calculate the nucleation rate, we will use the classical nucleation theory expressions for  $\Delta W_n$  and  $\beta_n$  given in Section 4.1, and carry out a test calculation for water at 300 K and a saturation ratio of 5. Different distributions are plotted in Figure 1. The unbalanced steady state concentration  $N_n$  decreases with the cluster size, while the balanced steady state concentration  $S^n N_n^{\text{eq}}$  has a minimum at the so-called critical cluster size denoted  $n^*$ . For the critical cluster containing 37 molecules  $N_{n^*}/(S^{n^*} N_{n^*}^{\text{eq}}) = 0.54$ . By looking at Eq. (13), one can indeed state approximately that  $N_{n^*}/(S^{n^*} N_{n^*}^{\text{eq}}) \approx 0.5$ , if  $1/(S^i \beta_i N_i^{\text{eq}})$  is approximately symmetric around  $n^*$ , and  $\lim_{n \rightarrow \infty} N_n = 0$ .

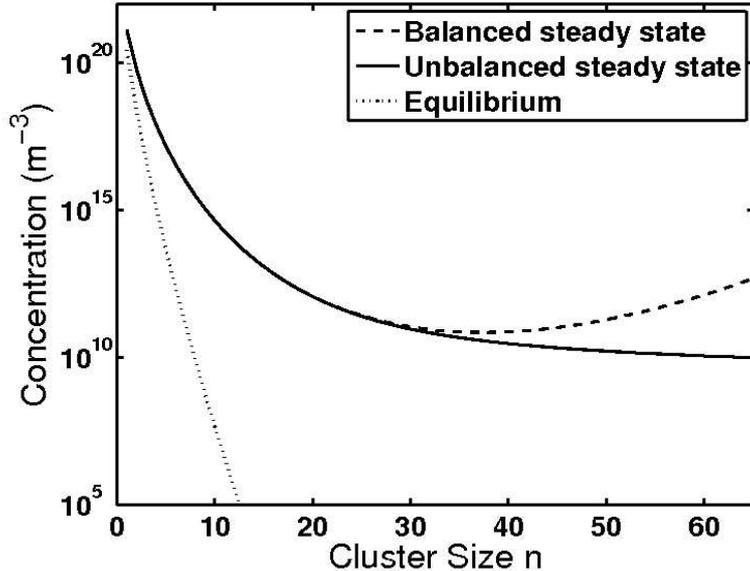


Figure 1: The balanced steady state, unbalanced steady state and equilibrium distribution of water clusters at 300 K. The steady state cases are plotted for saturation ratio 5, and the equilibrium distribution is the cluster distribution at saturation ratio 1.

### 3 Statistical mechanics of imperfect vapour

Like the kinetic considerations presented in the previous chapter, statistical mechanics offers a general and rigorous treatment of imperfect vapour and nucleation. We will restrict the analysis to the situation where the imperfect gas can be described with classical statistical mechanics, and neglect the quantum effects. This restriction poses no significant drawbacks as long as the temperature is sufficiently high and the density of the system is sufficiently low.

The Hamiltonian of a system of  $\mathcal{N}$  identical molecules of mass  $m$  is written by

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^{\mathcal{N}} \mathbf{P}_i^2 + U(\mathbf{r}_1, \dots, \mathbf{r}_{\mathcal{N}}), \quad (17)$$

where  $\mathbf{P}_i$  is the momentum of molecule  $i$  and  $U$  is the total interaction energy between the  $\mathcal{N}$  molecules. The partition function of this system is then given by

$$Q = \frac{1}{\mathcal{N}! h^f} \int \cdots \int \exp\left(\frac{-\mathcal{H}}{kT}\right) d\mathbf{r}_1 \cdots d\mathbf{r}_{\mathcal{N}} d\mathbf{P}_1 \cdots d\mathbf{P}_{\mathcal{N}}, \quad (18)$$

where  $h$  is the Planck's constant,  $f$  is the number of degrees of freedom of the complete system equal to  $3\mathcal{N}$ , and  $\mathcal{N}!$  accounts for the actual indistinguishability of the particles.

The integration is taken over the whole phase space. The Helmholtz free energy  $F$  and the pressure  $p$  of the system are related to the partition function as

$$F = -kT \ln Q, \quad (19)$$

$$p = - \left( \frac{\partial F}{\partial V} \right)_T, \quad (20)$$

The integration over momenta in Eq. (18) is straightforward (Abraham, 1974), and the partition function can be expressed as

$$Q = (2\pi mkT/h^2)^{3N/2} Q_N, \quad (21)$$

where  $Q_N$  is the classical configurational integral

$$Q_N = \frac{1}{\mathcal{N}!} \int_V \cdots \int_V \exp \left( \frac{-U(\mathbf{r}_1, \cdots, \mathbf{r}_N)}{kT} \right) d\mathbf{r}_1 \cdots d\mathbf{r}_N. \quad (22)$$

The problem then reduces to the evaluation of the above configurational integral. However, it is usually an impossible task to calculate  $Q_N$  analytically, and computational methods must be applied to deal with this problem. Next, we discuss approaches for the evaluation of this integral to calculate for example the pressure of the system.

### 3.1 The mathematical clusters of Mayer

Mayer (1937) showed that the configuration integral  $Q_N$  of Eq. (22) can be developed into a series, which results in (Sonntag and van Wylen, 1966)

$$\frac{pV}{kT} = \ln \left[ 1 + \sum_{N \geq 1} Q_N z^N \right] = \sum_{n \geq 1} V b_n z^n \quad (23)$$

where  $z = \Lambda^{-3} \exp(\mu/kT)$  is the fugacity of a vapour with chemical potential  $\mu$ , and  $b_n$  is called the cluster integral

$$\begin{aligned} b_1 &= \frac{Q_1}{V} \\ b_2 &= \frac{Q_2 - Q_1^2}{2!V} \\ b_3 &= \frac{Q_3 - 3Q_1Q_2 + 2Q_1^3}{3!V} \\ &\dots \end{aligned} \quad (24)$$

Developing the full configurational integral into series makes its approximate solution possible, since contributions from interactions between groups of two molecules, three

molecules, and so on, can be calculated separately. Mayer interpreted that these interactions between different molecular groups describe clusters in the vapour, with their total number density given by

$$N_{\text{tot}} = N_1 + N_2 + N_3 + \dots = \sum_{n=1}^{\infty} b_n z^n, \quad (25)$$

The equation of state for an imperfect vapour can then be described by a virial series

$$\begin{aligned} \frac{pV}{\mathcal{N}kT} &= 1 + (-b^2) \left(\frac{\mathcal{N}}{V}\right) + (4b^2 + 2b_3) \left(\frac{\mathcal{N}}{V}\right)^2 + \dots \\ &= 1 + \frac{B_2}{V^2} + \frac{B_3}{V^3} + \dots, \end{aligned} \quad (26)$$

where  $B_n$  are called the virial coefficients. the Mayer treatment of the imperfect vapour is rigorous, but seems to apply only to saturated vapour or vapour below its saturation point due to divergence of the virial series in supersaturated vapour (Mason and Spurling, 1969). However, a similar problem also applies to statistical mechanics descriptions of imperfect vapour in general; Eqs. (19) and (20) apply to equilibrium systems only, not supersaturated (Ford, 1997). One then needs to transform the concentration of mathematical Mayer clusters in equilibrium vapour to the balanced steady state concentration in the supersaturated vapour, which should further be modified to unbalanced steady state concentration in a nucleating vapour in order to make the virial series converge. There are other problems, however, why the Mayer clusters are not convenient for describing nucleation. First, the high order virial coefficients can not be measured accurately in experiments. Likewise, the high order cluster integrals are extremely tedious to calculate even with the most modern computer simulations. Second, the mathematical description of cluster in vapour does not offer a satisfying picture of a cluster as a physical object, which would representing a clear density fluctuation in vapour. Next, we will discuss how the physical clusters can be treated with statistical mechanics.

### 3.2 The physical clusters of Frenkel-Band-Bilj

A physical picture of clusters in vapour was developed, shortly after Mayer's description of the imperfect vapour, independently by Bilj (1938), Frenkel (1939), and Band (1939a,b). These approaches are less rigorous than the Mayer approach, since they describe the vapour as a collection of physical clusters which do not interact with each other. However, the concentration of these physical non-interacting clusters is far more simple to calculate than the concentration of mathematical Mayer clusters. The Mayer approach and Frenkel-Band-Bilj approach are compatible when the clusters can be considered as relatively compact objects separated by large spatial distances from

each other with no long-range interactions. Mathematically, this can be expressed by writing the total interaction energy as

$$U = \sum_{\lambda} U_{\lambda}(\mathbf{r}_{1_{\lambda}}, \dots, \mathbf{r}_{n_{\lambda}}) + \sum_{\lambda < \mu} U_{\lambda\mu}(\mathbf{r}_{1_{\lambda}}, \dots, \mathbf{r}_{n_{\lambda}}, \mathbf{r}_{1_{\mu}}, \dots, \mathbf{r}_{n_{\mu}}), \quad (27)$$

where  $U_{\lambda}$  describes the interactions between the molecules in the same cluster and  $U_{\lambda\mu}$  describes interactions between molecules in different clusters, and arguing that the  $U_{\lambda\mu}$  terms can be neglected. Furthermore, the finite volume of clusters is neglected. Then, the configuration integral can be written in a simple form (Abraham, 1974)

$$Q_{\mathcal{N}} = \sum_{\mathcal{N}_n} \prod_n \frac{[q(n)]^{\mathcal{N}_n}}{\mathcal{N}_n!}, \quad (28)$$

where  $\mathcal{N}_n$  now describes the number of physical  $n$ -clusters, satisfying the constraint

$$\sum_n n\mathcal{N}_n = \mathcal{N}, \quad (29)$$

and  $q(n)$  is the configuration integral for these clusters,

$$q(n) = \frac{1}{n!} \int_{\text{cluster}} \dots \int \exp \left[ \frac{-U_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)}{kT} \right] d\mathbf{r}_1 \dots d\mathbf{r}_n. \quad (30)$$

The most probable set of values  $\mathcal{N}_n$  is the one that maximizes the term in the summation of Eq. (28). This leads to the law of mass action (Abraham, 1974)

$$\frac{\mathcal{N}_n}{q(n)} = \left[ \frac{\mathcal{N}_1}{q(1)} \right]^n. \quad (31)$$

The law of mass action shown above used with statistical thermodynamics allows one to express the distribution of physical clusters in the vapour as (Saltz, 1994)

$$N_n = N_1 \exp \left( -\frac{\Delta W_n}{kT} \right), \quad (32)$$

where  $\Delta W_n$  is the work of  $n$ -cluster formation relative to a monomer (also called the intensive cluster free energy (Bowles et al., 2000)), given by

$$\Delta W_n = -kT \ln \left[ \frac{q(n)}{V} N_{1,\text{eq}}^{n-1} \right] - (n-1)kT \ln S. \quad (33)$$

where the saturation ratio is defined as  $S = N_1/N_{1,\text{eq}}$  and  $N_{1,\text{eq}}$  is the saturated number density of monomers. An expression for the cluster distribution of the same form as Eq. (25),

$$N_{\text{tot}} = N_1 + N_2 + N_3 \dots = N_1 \sum_n \exp \left( -\frac{\Delta W_n}{kT} \right). \quad (34)$$

In a vapour where cluster-cluster interactions can be neglected the cluster integrals  $b_n$  are connected to the work of cluster formation as (**Paper V**)

$$b_n = \frac{\exp\left(-\frac{\Delta W_n}{kT}\right)}{N_1^{n-1}}. \quad (35)$$

## 4 Nucleation theories

The first considerations of the laws that govern nucleation phenomena were presented by Thomson (1870, 1871) (later Lord Kelvin), followed by the work of Gibbs (1906) on thermodynamics of curved surfaces during 1876-1878. The theory that is nowadays known as the classical nucleation theory (CNT) then evolved from the joint works by Volmer and Weber (1925), Farkas (1927), Becker and Döring (1935), Zeldovich (1942), and Frenkel (1946).

Although the first experimental vapour-liquid nucleation measurements date back to Wilson (1897), proper experimental testing of CNT was difficult at the time when the theory was constructed. Early experiments gave encouraging results (Volmer and Flood, 1934), and, besides few exceptions, the CNT was mostly supported by the experiments in the following decades. For example, Katz (1970) showed that the CNT predictions for the onset pressures of homogeneous nucleation of n-alkanes were accurately reproduced in experiments. Later, when more sophisticated measurements of nucleation rates as functions of saturation ratio could be carried out, it became evident that CNT doesn't provide a sufficient theoretical framework capable of fully explaining the experimental results for example for homogeneous nucleation of water (Wölk and Strey, 2001). Also, the extent of the failure of CNT appears to depend on the measured vapour; sometimes, like in case of homogeneous nucleation of argon, the failure of CNT is very large indeed (Fladerer and Strey, 2006).

Due to the failure of CNT in predicting experimental nucleation rates, and due to a number of problematic assumptions CNT uses in its description of the nucleating clusters, a large number of modifications of CNT as well as alternative theoretical descriptions of has been published (Reiss et al., 1968; Fisher, 1967; Dillmann and Meier, 1989; Girshick and Chiu, 1990; Kalikmanov and van Dongen, 1993; McGraw and Laaksonen, 1996; Reiss et al., 1997; Reguera and Reiss, 2004). Below, we will review the classical nucleation theory, and then discuss the extension to the classical theory.

## 4.1 The classical nucleation theory

If the sum given by Eq. (15) is approximated with an integral, it can be rather easily shown (Vehkamäki, 2006) that expression for the nucleation rate  $J$  can be written as the product of three terms

$$J = \beta_{n^*} N^* Z, \quad (36)$$

where  $\beta_{n^*}$  is the condensation rate for the critical cluster, representing a cluster in a quasi-stable equilibrium with the surrounding supersaturated vapour.  $N^*$  is the balanced steady state concentration of critical clusters in a supersaturated vapour, and  $Z$  is called the Zeldovich non-equilibrium factor. The condensation rate  $\beta_{n^*}$  is given by the kinetic gas theory as

$$\beta_{n^*} = N_1 \frac{3}{4\pi} \left( \frac{6kT}{n^*m} + \frac{6kT}{m} \right)^{1/2} \left[ n^* v^{1/3} + v^{1/3} \right]^2, \quad (37)$$

where  $k$  is the Boltzmann constant, and  $T$  is the temperature,  $v$  is the volume of a single molecule in a bulk liquid, and  $m$  is the molecular mass. The equilibrium concentration of critical clusters in a supersaturated vapour,  $N^*$ , is not the real concentration of critical clusters; the true steady state concentration is modified by the nucleation flux. However, the nucleation rate can be calculated with the means of the equilibrium concentration (McDonald, 1963), given in CNT by

$$N_n = N_{\text{tot}} \exp\left(-\frac{\Delta W^*}{kT}\right), \quad (38)$$

where  $N_{\text{tot}}$  is the density of the supersaturated vapour obtained from  $N_{\text{tot}} = p/kT$ . The work of formation of the critical cluster,  $\Delta W^*$ , is obtained with the liquid drop (LD) model, which treats the tiny molecular clusters as small bits of bulk liquid. This model gives a general expression for the formation work of clusters in a supersaturated vapour as

$$\begin{aligned} \Delta W_{n,\text{LD}} &= A_n \gamma_\infty + n \Delta \mu \\ &= A_n \gamma_\infty - nkT \ln S \end{aligned} \quad (39)$$

where  $A_n$  is the spherical surface area of a droplet with a bulk liquid density,  $\gamma_\infty$  is the planar surface tension, and  $\Delta \mu = \mu_l(p) - \mu_v(p)$  is the difference of the chemical potentials of the liquid (l) and vapour phases (v), both taken in the ambient vapour pressure. Using the ideal gas expression of  $p_1 = p_1^{\text{eq}} \exp(-\Delta \mu/kT)$  results in the latter expression for  $\Delta W_n$ , where  $S$  is the saturation ratio of the vapour given by (Katz et al., 1966; Saltz, 1994)

$$S = \frac{p_1}{p_1^{\text{eq}}}. \quad (40)$$

The saturation ratio is often approximated as

$$S \approx \frac{p}{p^{\text{eq}}} = \frac{N_1 + N_2 + N_3 + \dots}{N_1^{\text{eq}} + N_2^{\text{eq}} + N_3^{\text{eq}} + \dots}, \quad (41)$$

or as

$$S \approx \frac{\rho}{\rho^{\text{eq}}} = \frac{N_1 + 2N_2 + 3N_3 + \dots}{N_1^{\text{eq}} + 2N_2^{\text{eq}} + 3N_3^{\text{eq}} + \dots}, \quad (42)$$

but it should be noted that these approximation are only valid when nearly all molecules in vapour exist as monomers.

The first term in Eq. (39), with  $A_n \propto n^{2/3}$ , dominates at small cluster sizes and  $\Delta W_n$  increases with  $n$ . At larger cluster sizes, the second term proportional to the volume of the cluster,  $V_n \propto n$ , begins to dominate and  $\Delta W_n$  decreases. The size dependence of the work of cluster formation can be viewed as the competition between the surface term and the volume term. The maximum of  $\Delta W_n$  is reached at the critical cluster size  $n^*$  — before this size the droplets tend to evaporate back to vapour, but after this size their growth is more probable. The number of molecules in the critical cluster is obtained by taking a derivative of  $\Delta W_n$  with respect to  $n$  and solving the resulting equation for  $n$ ,

$$n^* = \frac{32\pi\gamma_\infty^3}{3\rho_l^2(kT \ln S)^3}, \quad (43)$$

where  $\rho_l = 1/v$  is the density of the bulk liquid. Likewise, the radius of the critical cluster turns out to be

$$r^* = \frac{2\gamma_\infty}{\rho_l kT \ln S}. \quad (44)$$

The work of formation of the critical cluster can be expressed as

$$\Delta W_{\text{LD}}^* = \frac{4}{3}\pi r^{*2}\gamma_\infty. \quad (45)$$

The Zeldovich factor  $Z$  in Eq. (36) corrects for the use of equilibrium distribution of Eq. (38) instead of the true distribution in nucleating vapour, and takes into account the backward flux resulting from the evaporation of overcritical clusters. It is given by

$$\begin{aligned} Z &= \left( \frac{\Delta W^*}{3\pi kT n^{*2}} \right)^{1/2} \\ &= \frac{\gamma_\infty^{1/2} v}{2\pi r^{*2} (kT)^{1/2}}. \end{aligned} \quad (46)$$

Usually, the Zeldovich factor is between  $Z = 0.01 - 0.1$ . For the case described in Figure 1, the Zeldovich factor is  $Z = 0.048$  whereas the ratio of unbalanced and balanced steady state concentrations is  $N_{n^*}/S^{n^*} N_{n^*}^{\text{eq}} = 0.54$ .

There is a difference in  $S$ -dependence in equations Eq. (34) and Eq. (39) describing the work of cluster formation. As noted already by Courtney (1961), there should be a further factor of  $1/S$  multiplying the right hand side of Eq. (39). Including the  $1/S$  prefactor inside the exponent, results in a same  $S$ -dependence in equations Eq. (34)

and Eq. (39). Furthermore, by approximating  $N_v = N_1$  the classical counterpart for the cluster distribution of Eq. (32) is given by

$$\begin{aligned}
N_n &= \frac{N_{\text{tot}}}{S} \exp\left(-\frac{\Delta W_{n,\text{LD}}}{kT}\right) \\
&= N_{\text{tot}} \exp\left(-\frac{\Delta W_{n,\text{LD}} + kT \ln S}{kT}\right) \\
&\approx N_1 \exp\left(-\frac{A_n \gamma_\infty - (n-1)kT \ln S}{kT}\right). \tag{47}
\end{aligned}$$

Classical nucleation theory provides an expression for the rate of nucleation under conditions where the concentration of each cluster size remains constant. Thus, the system is assumed to remain in a pseudo-steady state; there is a constant nucleation flux from the system, which is, however, so small that the nucleation process itself does not change the vapour concentration.

## 4.2 Extensions to the classical nucleation theory

The liquid drop model is based on the capillary approximation, where macroscopic thermodynamic arguments are applied in the description of small molecular clusters. The model assigns a planar surface tension to the droplets, and ignores its possible dependence on the size of the droplet. Furthermore, the clusters are considered as perfectly spherical incompressible objects with a constant bulk liquid density profile and a sharp interface. Besides these rather crude approximations, there has been a long-lived controversy about how the translational and rotational degrees of freedom of the clusters, neglected by the liquid drop model, should be accounted for.

### 4.2.1 Reiss-Kegel-Katz theory

The problem related to the missing degrees of freedom was already pointed out by Frenkel (1946). However, Lothe and Pound (1962) presented a first detailed analysis of how the calculated nucleation rates are affected if the missing degrees are accounted for. The correction term arising from their analysis increases the nucleation rates approximately by a factor of  $10^{17}$ , which is large enough to destroy any reasonable agreement between the theoretical predictions and measured nucleation rates. The debate about this paradoxical correction term went on for decades, until finally Reiss et al. (1997) showed that the molecular length scale applied by Lothe and Pound, which was used for dividing the phase space in the calculation of the cluster partition function, was erroneous. Due to the capillary approximation, the proper length scale is not the molecular length scale, but proportional to the cube root of the volume

fluctuation of the cluster, and therefore to its compressibility. The cluster work of formation according to the Reiss-Kegel-Katz (RKK) theory is

$$\Delta W_{n,\text{RKK}} = \Delta W_{n,\text{LD}} - kT \ln R + kT \ln S, \quad (48)$$

where  $R$  is the so-called replacement free energy, given in RKK theory as

$$R = \frac{1}{N_v^{\text{eq}} \sqrt{kT \kappa v n}} \quad (49)$$

where  $N_v^{\text{eq}}$  is the number density of the saturated vapour and  $\kappa$  is the isothermal compressibility of the liquid. This correction term enhances the nucleation rate only approximately by a factor  $10^4$ . The RKK theory also results in a natural appearance of the  $1/S$  prefactor to the the cluster size distribution of Eq. (38) if the last term of Eq. (48) is taken out of the exponent.

#### 4.2.2 Non-equilibrium correction by Reguera and Ruby

Reguera and Ruby (2001) noted that the Reiss-Kegel-Katz term is purely an equilibrium correction. By considering the non-equilibrium translational and rotational effects, Reguera and Ruby (RR) introduced a further additional term,

$$\Delta W_{n,\text{RR}} = \Delta W_{n,\text{RKK}} + 4kT \ln n. \quad (50)$$

The corrections by Reiss, Kegel and Katz, and by Reguera and Ruby, are typically of a similar magnitude but to opposite directions. Importantly, both depend on the size of the cluster.

#### 4.2.3 Self-consistent classical nucleation theory

The liquid drop model assigns a finite work of formation for a monomer. Girshick and Chiu (1990) argued that this fact should be corrected for by removing the value of the monomer formation work from the formation work of all clusters. Then, by including the  $1/S$  term in the exponential,

$$\Delta W_{n,\text{SC-CNT}} = \Delta W_{n,\text{LD}} - A_1 \gamma_\infty + kT \ln S. \quad (51)$$

Then, the cluster distribution is given by

$$\begin{aligned} N_n &= N_{\text{tot}} \exp \left( -\frac{(A_n - A_1) \gamma_\infty - (n-1)kT \ln S}{kT} \right) \\ &\approx N_1 \exp \left( -\frac{(A_n - A_1) \gamma_\infty - (n-1)kT \ln S}{kT} \right). \end{aligned} \quad (52)$$

Counterarguments by Reiss et al. (1998) and Reguera et al. (2003) point out that the monomer droplet described by the liquid drop model is intrinsically different from a vapour monomer. Therefore, the liquid drop model does not need to be self-consistent. In the writer's opinion the paper by Saltz (1994) resolves this issue; there is no inconsistency in the classical theory as long as the prefactor in Eq. (38) is treated systematically. By using a explicit thermodynamic arguments, Saltz (1994) showed that by using the liquid drop model, one can either write

$$N_n = N_{\text{tot}} \exp \left( -\frac{(A_n)\gamma_\infty - (n-1)kT \ln S}{kT} \right), \quad (53)$$

or

$$N_n = N_1 \exp \left( -\frac{(A_n - A_1)\gamma_\infty - (n-1)kT \ln S}{kT} \right). \quad (54)$$

According to Saltz, the root of the apparent inconsistency in CNT is the ideal gas approximation applied with the liquid drop model. Equating  $N_{\text{tot}} = N_1$  is actually equivalent to assuming that  $\Delta W_1 = 0$ .

#### 4.2.4 Dillmann and Meier approach

The problems involving the correct calculation of the degrees of freedom with a model droplet led to the construction of phenomenological theories of nucleation. Probably the most successful of these type of approaches was the one proposed by Dillmann and Meier (1991), based on the Fisher (1967) droplet model. Dillmann and Meier wrote an expression for the droplet work of formation as

$$\Delta W_{n,\text{DM}} = K_i A_n \gamma_\infty - nkT \ln S + \tau kT \ln n - kT \ln q_0 V + kT \ln \mathcal{N}_{\text{tot}},$$

where  $K_i$  is a function describing the deviation of the surface energy of the cluster from that of a the macroscopic liquid droplet, and parameters  $\tau$  and  $q_0$  arise from translational, rotational and vibrational degrees of freedom as well as from configurational contributions. In the classical theory,  $K_1 = 1$ ,  $\tau = 0$  and  $q_0 = p/kT = \mathcal{N}_c/V$ . In the Dillmann and Meier approach all these parameters are adjusted by using the knowledge of the critical properties of vapour and the second virial coefficient. A relatively good agreement was obtained with the calculated values of nucleation rates and experimental results with several different vapours. Later on, Kalikmanov and van Dongen (1995) used this approach with the Tolman (1949) expression for the size dependent surface tension.

However, Ford et al. (1993) and Laaksonen et al. (1994) pointed out that in the original Dillmann-Meier theory the virial equation is applied after using the ideal gas approximation. A correctly derived theory is no longer in as satisfactory agreement with the observed nucleation rates as the original theory.

### 4.2.5 McGraw-Laaksonen scaling theory

By considering the restrictions that the nucleation theorem of Kashchiev (1982) imposes on the form of the work of formation of the critical cluster  $\Delta W^*$ , McGraw and Laaksonen (1996) derived an expression

$$\Delta W^* = \Delta W_{\text{LD}}^* - D(T), \quad (55)$$

where  $D(T)$  is a function of temperature only, and not of the cluster size. Their DFT calculations with Lennard-Jones system showed the validity of this scaling relation. In a subsequent paper, McGraw and Laaksonen (1997) gave an expression for the size dependent surface tension  $\gamma_n$  as

$$\gamma_n = \gamma_\infty - \frac{D(T)}{A_n}. \quad (56)$$

Therefore, the work of formation of droplets in vapour can be written according to McGraw-Laaksonen approach as

$$\Delta W_{n,\text{ML}} = A_n \gamma_n - nkT \ln S, \quad (57)$$

where  $\gamma_n$  is given by Eq. (56). It is interesting to note that while the Tolman (1949) expression for the size dependence of the surface tension is proportional to  $1/r$ , where  $r$  is the cluster radius,  $\gamma_n$  by McGraw and Laaksonen is proportional to  $1/r^2$ . McGraw and Laaksonen theory merely proposes a correction to the liquid drop expression for the formation free energy, and does not contradict with RKK theory, for example.

Talanquer (1997) has proposed a phenomenological approach to determine the unknown value of function  $D(T)$ , based on the well known fact that the liquid drop model fails in predicting zero nucleation work at the spinodal. Therefore,  $\Delta W_{\text{LD}}^*$  at spinodal should be equal to  $D(T)$ . An alternative but related method for finding the value of  $D(T)$  have been put forward by Kashchiev (2003), and limitations of these approaches have been discussed by Wilemski and Jin-Song Li (2004).

### 4.2.6 Dynamical nucleation theory

One of the latest refreshingly different views to study the nucleation process is offered by the dynamical nucleation theory (Schenter et al., 1999b,a; Kathmann et al., 1999; Schenter et al., 2002; Kathmann et al., 2004). The theory is based on the nucleation kinetics on the molecular level. In the classical kinetic approach, the evaporation rate of the clusters is determined from the condensation rate by applying a detailed balance condition of Eq. (2). The dynamical nucleation theory uses an inverse approach. The evaporation rate constant is determined from the derivative of the Helmholtz free

energy with respect to cluster radius. The radius of the cluster is found by using a variational transition-state theory (Schenter et al., 1999a) to locate a spherical dividing surface, which minimizes the reactive (evaporation) flux from the cluster. Then, the work of cluster formation is calculated for clusters having a volume which corresponds to the dividing surface, and the equilibrium cluster distribution is obtained. The condensation rate constant is then found by using the detailed balance condition of Eq. (2) (Kathmann et al., 1999).

#### 4.2.7 Extended modified liquid drop model

An interesting new model of the physical cluster is offered by the 'extended modified liquid drop model' (EMLD) (Reguera et al., 2003; Reguera and Reiss, 2003), which seemingly has more predictive power concerning the phase behaviour than the original liquid drop model, but still uses purely macroscopic thermodynamic parameters. EMLD model describes a small canonical system of  $\mathcal{N}$  molecules confined inside a spherical container. When the system is dense enough, a liquid drop forms inside this container, and the drop can maintain a relatively stable size. The drop can move freely inside the container and these translational contributions can be properly included into the model. The calculated pressure-volume isotherms from the EMLD model can predict, unlike CNT, the location of the spinodal. The combination of EMLD model with the dynamical nucleation theory provides a very successful prediction for the work of formation of the critical cluster (Reguera and Reiss, 2004).

### 4.3 Nucleation theorems

Nucleation theorems (Kashchiev, 1982; Oxtoby and Kashchiev, 1994; Ford, 1997; Bowles et al., 2000) describe how the work of formation of the critical cluster depends on the saturation ratio and temperature. These relations can be obtained from general statistical mechanic considerations, and are independent of the classical nucleation theory. Therefore, nucleation theorems can be used to obtain valuable information of the properties of the critical cluster from experimental data. Also, a proper theoretical expression for the nucleation rate should be compatible with the nucleation theorems.

In the case of one-component homogeneous nucleation, the first nucleation theorem for the work of cluster formation as defined according to Eq. (34) states that (Bowles et al., 2000)

$$\left(\frac{\partial \Delta W^*}{\partial \ln S}\right)_T = \Delta n^* - 1, \quad (58)$$

The second nucleation theorem (Ford, 1996) is given by

$$\left(\frac{\partial \Delta W^*}{\partial T}\right)_S = \Delta S^*, \quad (59)$$

where  $\Delta S^*$  is the entropy increase due to initial cluster formation. If the nucleation theorems are applied to describe how the nucleation rate  $J = K \exp(-\Delta W^*/kT)$  depends on the saturation ratio and temperature, the contribution from the prefactor  $K$  must be taken into account. If the classical prefactor of  $K = \beta_n Z N_1$  is employed, the first nucleation theorem gives

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_T = \Delta n^* + 1, \quad (60)$$

and the second nucleation theorem

$$\left(\frac{\partial \ln J}{\partial T}\right)_S = \frac{(\Delta h)^2 - kT + \Delta U^*}{kT^2}, \quad (61)$$

where  $\Delta h$  is the enthalpy of vaporization and  $\Delta U^*$  is the difference between the energy of the cluster and the energy that the molecules of the cluster would have in pure equilibrium liquid.

## 5 Nucleation Simulations

Due to the shortcomings of CNT and its extensions, there is a growing interest to study vapour-liquid nucleation at the molecular level. This type of studies rely on the aid of molecular computer simulations. They can be divided into four main categories, listed here in the order of increasing computational complexity:

- classical density functional theory (DFT) calculations;
- Monte Carlo (MC) simulations;
- Molecular Dynamics (MD) simulations;
- quantum chemical calculations of molecular clusters.

In this section we give a short revision of these methods and their applications, especially focusing on the Monte Carlo approach. First, however, we will briefly discuss how clusters have been defined in the literature.

## 5.1 Cluster definitions

Any molecular based nucleation calculation requires a definition of a cluster. Unfortunately nature does not provide an automatic definition of which molecular configurations form a single physical cluster, and one is forced to introduce an artificial definition instead. In the literature the clusters have been defined in various ways, either based on their bonding energy (Hill, 1956), volume (Lee et al., 1974), cluster dynamics (Harris and Ford, 2003), minimization of the evaporative flux (Scenter et al., 1999b), connectivity (Stillinger, 1963) or in a combination of connectivity and volume (Schaaf et al., 1999). A good review about cluster definitions and problems related to them is given by Senger et al. (1999). In all the five research articles of this thesis, the clusters have been defined according to the Stillinger definition based on connectivity between cluster molecules. It states that a cluster molecule cannot be separated by more than a Stillinger distance from another cluster molecule, and that a cluster is formed by a single network of connected molecules. The Stillinger distance is a free parameter that can be selected rather arbitrarily. In **Paper V** we will select the Stillinger distance by using the virial coefficients of the virial equation of state.

## 5.2 Density functional theory approach

The calculations based on density functional theory (DFT) approach, pioneered by Oxtoby and Evans (1988), aim to evaluate the density profile and the free energy barrier associated with the critical cluster. A good review of the density functional method is given by Oxtoby (1992). Here, we note that all molecular interactions are modelled in mean field sense; the modelling of the different cluster configurations is completely avoided. This makes the calculations economic, and enables one to study a large range of critical cluster sizes. To name a few applications, the DFT calculations have been used in studies of vapour-liquid nucleation of Lennard-Jones fluid (Talanquer and Oxtoby, 1994; McGraw and Laaksonen, 1996, 1997), of associating fluids (Talanquer and Oxtoby, 2001), of two-component mixtures (Talanquer and Oxtoby, 1996; Napari et al., 2000), and in studies of bubble nucleation (Oxtoby and Evans, 1988; Shen and Debenedetti, 2001). DFT calculations have also been able to show why CNT fails in case of surface active compounds Napari and Laaksonen (1999, 2000). Whereas calculations with one or two dimensional molecules have been successfully carried out, DFT calculations with three dimensional molecules are extremely difficult due to computational complexity.

### 5.3 Molecular dynamics simulation

Molecular dynamics (MD) simulations typically apply classical interaction potentials for the modelling of molecular interactions in the system of interest. MD simulations are focused on modelling nucleation processes directly by simulating the actual movement of particles in the system. This is done by solving the Newton's equation of motion for each particle between short time intervals. MD simulations can, in principle, solve the nucleation rate directly by calculating the rate of critical cluster formation in the system. However, the long computing times for the systems with realistic vapour densities have made this practically a challenging task. Recently, results from several promising simulations of direct nucleation have been published, including the simulations of the homogeneous nucleation of Lennard-Jones particles (Toxvaerd, 2001; Laasonen et al., 2000; Yasuoka and Matsumoto, 1998a), the heterogeneous nucleation of Lennard-Jones particles at a structureless solid surface (Toxvaerd, 2002), the Lennard-Jonesium nucleation in the presence of carrier gas (Toxvaerd, 2003), and the homogeneous nucleation of water (Yasuoka and Matsumoto, 1998b). The statistical accuracy for the nucleation rate gained from these simulations is often poor, but recently proposed analysis methods and studies of the importance of finite size effect in MD simulations are likely to improve this situation (Wedekind et al., 2006, 2007). Whereas direct calculations of nucleation rates have been considered time consuming and practically demanding, MD simulations studying a single cluster in vapour have provided an interesting method to study nucleation kinetics. These kind of simulations have been applied to study cluster decay rates (Harris and Ford, 2003; Ford and Harris, 2004), cluster lifetimes (Barrett, 2002; Napari and Vehkamäki, 2004), kinetic evaporation and condensation coefficients (Schaaf et al., 2001), and dimer evaporation (Napari and Vehkamäki, 2004).

### 5.4 Quantum chemical calculations

Quantum chemical calculations are the newest molecular simulation method applied in the nucleation studies. They aim to provide an approximate solution of the Schrödinger equation for a molecular cluster configuration. Typically, only minimum energy configurations are studied. The free energy, and hence the nucleation barrier, can be calculated from the interaction energy and the entropy of the configuration. The main difference between quantum chemical calculations and Monte Carlo simulations is the following: Monte Carlo simulations can provide a very accurate calculation for the nucleation barrier height by studying the full configurational space of clusters, but using very simplified interaction potential models. On the other hand, quantum chemical calculations aim to describe the interactions as accurately as possible, but are limited in their statistical description of cluster configuration space. Quantum chemical calculations are most suitable for studies of nucleation of complex molecules, such as those found in the atmosphere. The focus in recent quantum chemical calculations

or nucleation has been the role of sulphuric acid in atmospheric nucleation processes (Ianni and Bandy, 1999; Re et al., 1999; Kurtén et al., 2006). In principle, quantum chemical calculations could be applied in connection with Monte Carlo or Molecular Dynamics simulations, but computationally these type of calculations are still impossible to carry out in practice.

## 5.5 Monte Carlo (MC) simulations

Like the molecular dynamics simulations, also Monte Carlo (MC) simulations typically apply classical interaction potential models in nucleation studies. MC simulations are probabilistic in nature. Rather than simulating the actual movement of molecules, the focus is on efficient sampling of allowed phase space. The method is based on a stochastic process applying random numbers, which, by moving molecules in the system, generates a Boltzmann-weighted chain of configurations for a given system. The Monte Carlo moves can be translations (canonical, microcanonical and isobaric-isothermal ensembles) or also include creations and annihilations of molecules (grand canonical ensemble). This type of sampling allows the accurate and efficient calculation of thermodynamically important quantities such as the free energy barrier associated with the critical cluster formation. However, Monte Carlo calculations can not provide any information about the real time dependence of the processes; it is the price that must be paid for the efficient sampling of the configurational phase space.

### 5.5.1 History of Monte Carlo nucleation simulations

The history of Monte Carlo simulations dates back to 1949, when Metropolis and Ulam (1949) described the original Monte Carlo method, which introduced means to approximate numerical solutions to a variety of mathematical problems analytically too complicated to solve. In 1953, N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth and A. H. Teller and E. Teller (Metropolis et al., 1953) published an article entitled 'Equation of state calculations by fast computing machines'.

First uses of MC method for the study of phase transitions, to our knowledge, were carried out by Hansen and Verlet (1969) with a system of particles interacting through a Lennard-Jones potential, and by Norman and Filinov (1969) with a similar system. More famous are the first molecular Monte Carlo simulations of water by Barker and Watts in 1969. They were able to calculate the energy, specific heat and radial distribution functions with a sufficiently good comparison to experimental values to show that this new *a priori* technique was promising for the study of molecular phenomena.

Four years later, in 1973, a classic Monte Carlo simulation of nucleation was carried out by Lee et al. (1973). They evaluated the cluster Helmholtz free energies and radial

density distributions with a simulation of Lennard-Jones argon atoms in a canonical ensemble, where temperature, the volume of the system and the number of particles in the system are kept constant. Shortly after, Rowley et al. (1975) described a grand canonical Monte Carlo calculation method to study the vapour-liquid transition of Lennard-Jones particles. In a grand canonical ensemble the temperature, the volume, and the chemical potential of the system are kept fixed. The next year Bennett (1976) described an often used free energy calculation technique.

In 1981, Garcia and Torroja carried out an MC simulation with Lennard-Jones argon vapour. Based on theoretical framework of Barker and Watts (1969), they calculated the work of formation barrier separating the two phases. The nucleation rate was calculated from the height of the free energy barrier. A first comparison between simulation results and experimental nucleation rates was presented. A qualitative agreement was found, although the experimental results themselves were somewhat controversial in quality. The first heterogeneous nucleation Monte Carlo simulation was made by Ward et al. (1982) with water monolayer clusters nucleating on hexagonal AgI substrate. A subsequent paper followed next year, where calculations of critical cluster sizes were carried out (Ward et al., 1983).

In the beginning of 1990's, the concerns about climate change, the formulation of the nucleation theorem (Viisanen et al., 1993; Kashchiev, 1982; Oxtoby and Kashchiev, 1994; Ford, 1996), new extensions to the classical nucleation theory (Dillmann and Meier, 1989; Kalikmanov and van Dongen, 1993) and the sophisticated experimental techniques to obtain the nucleation rate (Viisanen et al., 1993; Looijmans et al., 1995) all gave a new impetus to nucleation studies. With the possibilities offered by the ever increasing computational capabilities, the Monte Carlo simulations have gained a whole new status as an important tool for the studies of nucleation on a molecular level.

### 5.5.2 Recent findings of Monte Carlo nucleation simulations

Monte Carlo simulations have been applied recently for several purposes in nucleation studies. They have been used to either confirm or deny the validity of CNT, to compare simulation results with experimentally observed nucleation behaviour, to study systems of interest where the experiments are challenging, and to support new theoretical frameworks. Below, we highlight some of the recent findings of Monte Carlo nucleation simulations.

The nucleation of clusters of spins in the Ising system has been studied extensively in the literature (Binder, 1976; Rikvold et al., 1994). The validity of CNT for the 3-dimensional Ising model has been confirmed with MC simulations by Acharyya and Stauffer (1998), Wonzak et al. (2000), and by Schmelzer and P. (2001). These simulations show that CNT gives accurate results for the work of formation of the critical

cluster for this model, and that the simulated cluster number distribution and lifetimes also agreed with CNT. Application of the nucleation theorems (Kashchiev, 1982; Ford, 1996) with Ising model was also shown to be in agreement with the literature values in an MC simulation by Vehkamäki and Ford (1999).

MC simulations with Lennard-Jonesium, often representing argon, have on many occasions served as a test ground for new MC methods. ten Wolde and Frenkel (1998) showed with MC simulations of Lennard-Jonesium that the dependence of the size of the critical on supersaturation cluster given by CNT is in excellent agreement with the nucleation theorem. A constant offset of the height of the nucleation barrier from the CNT values suggested the validity of the McGraw-Laaksonen scaling law (McGraw and Laaksonen, 1996, 1997). In a subsequent paper ten Wolde et al. (1999) showed that the calculated nucleation rates with the scaling law compared with Molecular Dynamics calculations lead to a kinetic prefactor of a factor 10 larger than predicted by CNT. ten Wolde et al. (1999) argued that the collisions of vapour molecules on the cluster must then be diffusive, rather than ballistic as assumed by Eq. (37). Chen et al. (2001) compared the simulated work of formation of Lennard-Jonesium with the predicted values given by CNT applied with the simulated surface tension and saturation vapour pressure. They observed that CNT predicts the critical cluster sizes accurately, but again the nucleation barrier height exhibited a constant offset from CNT values as predicted by McGraw-Laaksonen scaling law (McGraw and Laaksonen, 1996, 1997) CNT also had wrong temperature dependence for nucleation rate. Later, the Chen and Tsai (2002) obtained similar results for  $n$ -alkanes.

Nucleation of water has been studied widely both experimentally and with computer simulations. The experiments show that CNT gives a good description of the magnitude of nucleation rate, but seems to underestimate the temperature dependence of the rate (Wölk and Strey, 2001). Hale and DiMattio (2000) calculated the free energy differences of small water droplets using the discrete summation method. They showed that the results with TIP4P (Jorgensen et al., 1983) water potential model reproduce a scaled form for the nucleation rate theoretically presented by Hale (1986), which gives the temperature dependence for the nucleation rate that corresponds to experiments. Kusaka et al. (1998b) simulated water nucleation under several values of supersaturation with the SPC/E (Berendsen et al., 1987) water model. The purpose of the simulation was mainly to demonstrate the validity of a new type of grand canonical Monte Carlo simulation method for the calculation of the equilibrium cluster distribution and free energy barrier. Gao et al. (1999) used the same method to show that a uniform electric field enhances the nucleation rate of water if the chemical potential of the saturated vapour is fixed, and lowers the nucleation rate if the saturation ratio or vapour pressure is fixed. A corresponding behaviour was observed by Oh et al. (1998) in a simulation with a dipolar Stockmayer fluid.

Nucleation of Stockmayer fluid has been studied also by ten Wolde et al. (1999). Their simulations indicated that the nucleation of liquid drops was preceded by the formation

of chains, which collapsed to form liquid clusters only after they have reached a certain size. CNT was noted to both underestimate the size of the critical cluster and the height of the nucleation barrier.

Experiments with thermal diffusion cloud chamber show that both the type and density of the carrier gas have an effect on the nucleation rate (Heist et al., 1994, 1995; Brus et al., 2006; Hyvärinen et al., 2006). On the other hand, this effect has not been observed in expansion chambers, suggesting that the carrier gas effect is possibly an artefact related to imperfect modeling of the operation of a diffusion chamber. However, even with a careful focus on the operational aspects of diffusion chambers the carrier gas seems to have an effect on the measured nucleation rates (Bertelsmann and Heist, 1998; Ferguson et al., 2001; Ferguson and Heist, 2001). First theoretical treatments have not been capable of explaining the apparent magnitude of the effect (Oxtoby and Laaksonen, 1995; Ford, 1992; Kashchiev, 1996). The role played by carrier gas has been studied with Monte Carlo simulations by Novikov (1997) and by Oh and Zeng (2001). V. M. Novikov carried out an MC simulation, where the trajectories of vapour molecules colliding with the cluster were analyzed for the cases of methanol, ethanol and propanol nucleation, the carrier gas being either hydrogen or helium. It was found that at higher carrier gas densities nucleation rate is reduced, an effect caused by the interaction between the carrier gas and vapour molecules. This result was in line with the diffusion cloud chamber experiments. Oh and Zeng performed a Monte Carlo study of formation of water clusters in the presence of a nitrogen carrier gas. At 240 K they found that the barrier height to nucleation increased with the carrier-gas pressure, but little effect was seen at 298 K.

It is well known that ions can enhance the nucleation processes. Monte Carlo simulations of ion-induced nucleation have been carried out by Kusaka and Oxtoby (2000), and by Oh et al. (2001). I. Kusaka and D. W. Oxtoby simulated water nucleation around a hydronium ion, and calculated the work of formation, enthalpy and entropy of cluster sizes containing up to 25 water molecules at 200 K and 300 K. The results for the calculated quantities produced the experimental trends. K. J. Oh and X. C. Zeng studied water and methanol nucleation induced by cations and anions with and without an external electric field. They showed that anions are better nucleators of water droplets, and that for methanol cations are better nucleators. Their results indicated that the sign preference arising from the asymmetry between water-anion and water-cation interaction is present also when no external electric field is applied.

Two-component nucleation systems have been studied to some extent with MC simulations. Yoo et al. (2001) carried out a two-component nucleation simulation with a partially miscible system, bearing a similarity to a water-alcohol system. They could observe mutual enhancement of nucleation, which has been observed experimentally for the case of water-alcohol nucleation. Reguera et al. (2003) have used Monte Carlo simulation results of two-component nucleation of argon and krypton as a reference for the comparison between existing two-component nucleation models. They showed that

the 'extended modified liquid drop model' (Reguera and Reiss, 2003) can accurately predict nucleation behaviour observed in the simulation.

The sulphuric acid-water system plays an important role as a candidate for an atmospheric nucleation pathway. However, the construction of accurate force fields for this system is a challenging task, and it is likely that the simulation results greatly vary with the applied potential model. Only two nucleation Monte Carlo simulations of this system has been carried out, a grand canonical MC simulation by Kusaka et al. (1998a), and a canonical simulation by Kathmann and Hale (2001). Kusaka's results indicated that the rate-limiting step of new particle formation for a condition typical of vapour-liquid nucleation is a two-component collision of two hydrated sulphuric acid molecules, and that dissociation of the  $\text{H}_2\text{SO}_4$  molecule plays a key role in stabilizing the resulting cluster. Kathmann and Hale developed a potential model for the sulphuric acid-water system, and used it for a calculation of the free energy differences of clusters containing up to 15 sulphuric acid molecules. They calculated the model dependent surface tensions and partial vapour pressures, and also presented a method to calculate concentrations of water-sulphuric acid clusters having water to sulphuric acid molecular ratios of 1 and 4 at 298 K.

Heterogeneous nucleation has been studied with MC by Zapadinsky et al. (1994), who calculated ice cluster energies on a substrate with an ice-like structure. Calculations of the Helmholtz free energy of ice clusters on a coherent substrate followed soon after (Zapadinsky and Kulmala, 1995). It was seen that the additional free energy related to a non-ideal matching of ice and substrate lattices increased with number of molecules, contrary to previous predictions. Hale and DiMattio (1996) carried out similar calculations with a different water potential and substrate, gaining slightly different form for the free energy increase with the lattice mismatch. More recently, Zapadinsky et al. (2005) developed a new molecular approach to heterogeneous nucleation and gave a revised expression for the work of cluster formation. The derivation required defining a fictitious plane, which separates the volume with effective cluster-substrate interaction from volume with negligible cluster-substrate interaction. Monte Carlo simulations with Lennard-Jones argon were used to determine the near independence of the results for a large range of fictitious plane locations. In a subsequent paper by Lauri et al. (2006), CNT predictions for the heterogeneous nucleation rate, based on homogeneous nucleation rate and the contact angle between the cluster and the substrate, were shown to fail due to erroneous prediction of the homogeneous nucleation rate by CNT.

## 6 Review of Papers

All five research articles of this thesis focus on analysing the work of formation of non-interacting droplets in 1-component vapour. The analysis is carried out with Monte Carlo simulations of molecular clusters, where the interactions are described with classical molecular models. The studied vapours consist of Lennard-Jones argon clusters and water clusters modelled with various interaction potentials. In our simulations, the clusters are always defined according to Stillinger (1963) cluster definition.

In **Paper I**, we present a new Monte Carlo method for the calculation of the cluster work of formation. In our approach, we simulate single clusters containing a fixed number of molecules at constant temperature  $T$  and surrounding vapour density  $N$ . The clusters are located at the centre of a large container having a constant volume  $V$ . We carry out fictitious grand canonical insertions and removals of single molecules to and from the cluster. We show that the work of cluster formation can then be calculated from the average probability of the cluster growth and decay as

$$\Delta W_n = -kT \sum_{n'=2}^n \ln \frac{\overline{G}_{n'-1}}{\overline{D}_{n'}}, \quad (62)$$

where  $\overline{G}_n$  is the average growth probability and  $\overline{D}_n$  is the average decay probability of an  $n$ -cluster. The averages have been taken over all configurations as well as over the locations of the inserted or removed molecules. These calculations are applied to study nucleation of water. We compare our calculated values for the nucleation rate with the experimental results at corresponding vapour pressures, and see that the experimental temperature dependence of the nucleation rate agrees well with the temperature dependence of our calculated rates. Our simulated rates are, however, several orders of magnitude larger than the experimental rates. The deviation between our calculated rates and the experimental rates depends strongly on the applied interaction potential. We see that a polarizable interaction potential for water molecules is not any better in producing the experimental nucleation rates than the unpolarizable ones.

In **Paper II**, we apply the result that the average growth and decay probabilities are connected to the kinetic condensation rate  $\beta_n$  and evaporation rate  $\alpha_n$

$$\frac{\overline{G}_{n-1}}{\overline{D}_n} = \frac{\beta_{n-1}}{\alpha_n}. \quad (63)$$

By considering the properties of grand canonical growth and decay rates, we show that the instability of a single cluster configuration,  $\Phi_n(\{\mathbf{R}_i\})$ , describing whether the cluster is more probable to grow than to decay, can be described by

$$\Phi_n(\{\mathbf{R}_i\}) = \frac{D_n(\{\mathbf{R}_i\})}{G_n(\{\mathbf{R}_i\})}. \quad (64)$$

If  $\Phi_n(\{\mathbf{R}_i\}) < 1$ , the probability that the configuration  $(\{\mathbf{R}_i\})$  grows to size  $n + 1$  is greater than the probability of  $(\{\mathbf{R}_i\})$  decaying to size  $n - 1$ . We apply this expression to calculate the stabilities of different argon cluster configurations, classified according to their interaction energy or volume. We show that it is always possible to locate a single limiting radius for a cluster, such that configurations having this radius have the same average stability as the full set of cluster configurations. By noting that it is possible that the nucleation process itself introduces a small perturbation to cluster configurations, we carry out a test calculation of the effects of such a perturbation. We note that even very small perturbations can increase the work of cluster formation dramatically.

**Paper III** present a second method for the calculation of the cluster work of formation, using the overlapping distribution method together with discrete summation method. We show that there is an additional term in the calculation of work of formation with the discrete summation method, that has been missing in the previous applications using this method. We compare the results from the two methods for argon clusters with results from other existing methods and show that all these different Monte Carlo approaches give nearly identical results when applied at the same conditions. Some more development to the Monte Carlo method based on calculations of grand canonical growth and decay rates is also presented.

In **Paper IV**, we compare the simulated values for the works of adding a monomer,  $\delta\Delta W_n$ , to Lennard-Jones and water clusters as functions of cluster size to the values given by the liquid drop model. We see that the liquid drop model, when used with interaction potential specific values of surface tension and saturation vapour pressure, is able to predict  $\delta\Delta W_n$  accurately for clusters larger than some threshold size. The threshold cluster contains between 8 and 50 molecules, depending on the interaction potential and temperature; for water the observed threshold cluster size is significantly smaller than for the Lennard-Jones potential. However, the magnitude of the total work of formation given by the liquid drop model is erroneous, and differs from the simulation based values by a constant for clusters larger than the threshold size. Our results are in line with the McGraw-Laaksonen scaling theory, which proposes such a constant offset for the work of formation of the critical cluster. Our results indicate that the liquid drop model gives an accurate description of the size of the critical cluster. Simulations with three different water potentials all give an offset of a similar magnitude from the liquid drop values. The deviation in the results for different water potentials seen in **Paper I** results from the different model specific saturation vapour densities and planar surface tensions given by the water interaction potentials. We calculate the size dependence of the surface tension of Lennard-Jones clusters, and compare our calculations to Tolman theory and to an expression presented by McGraw and Laaksonen. Our results agree with McGraw and Laaksonen expression for cluster larger than the threshold size. A comparison with the experimental nucleation rates reveals why the classical nucleation theory succeeds fairly well in its prediction for

water nucleation, and fails drastically in its prediction for argon nucleation.

In **Paper V** we compare the work of formation of the non-interacting physical clusters and the work of formation of mathematical Mayer clusters. This analysis is carried out for Lennard-Jones and SPC/E water clusters containing up to six molecules; the first six virial coefficients for these interaction potentials are known from literature. We show how the work of formation of Mayer clusters can be calculated from this data. Then, we study how the distance parameter used in the Stillinger (1963) cluster definition affects the calculated values of the work of physical cluster formation. In the region where the cluster-cluster interactions can be approximated as negligible, the work of formation of Mayer clusters and the work of formation of physical clusters match to each other at unique values of the Stillinger distance parameter, depending on the interaction potential. This relation holds up to temperatures close to the critical temperature. At high temperatures the cluster-cluster interactions become significant, and the non-interacting cluster theory is no longer valid. The main result of **Paper V**, and the whole thesis, is the following: At moderate temperatures the change in cluster work of formation with respect to cluster size is given accurately by the liquid drop model for clusters larger than some threshold size. At small cluster sizes, the deviations from the liquid drop model predictions are directly related to the virial coefficients. Figure 2 shows this observed behaviour in case of water clusters.

If the virial coefficients up to the order equalling the threshold cluster size would be available from experiments, the McGraw-Laaksonen scaling factor  $D(T)$  could be calculated accurately. The work of cluster formation obtained from the virial coefficients is free from Lothe-Pound paradox since the partition function in Eq. (18) is integrated over all degrees of freedom. Therefore,  $D(T)$  is the only correction needed to modify the classical expression for the nucleation rate as long as the  $1/S$  factor is also included, and the excluded volume work, cluster-cluster interactions and non-equilibrium corrections can be neglected. However, experimental data for high order virial coefficients is not available as for most substances only the second virial coefficient is known. Then, one can approximate  $D(T)$  as the difference in the work of dimer formation obtained from the second virial coefficient (see **Paper V**) and the work of dimer formation obtained from the liquid drop model.

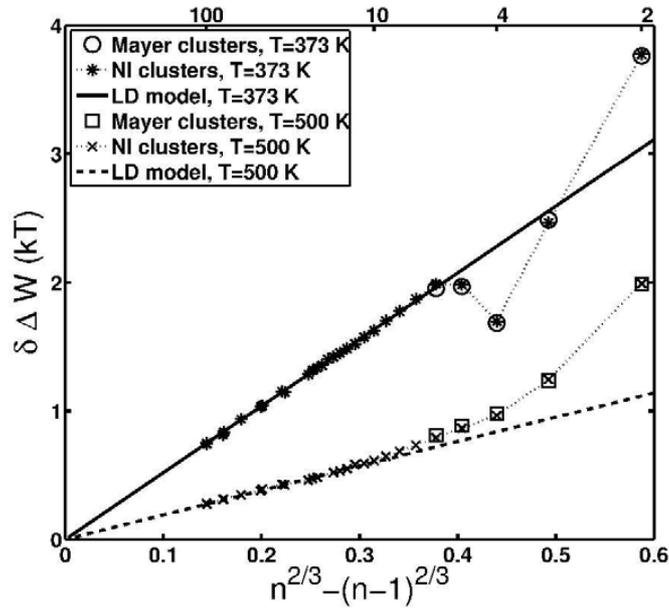


Figure 2: The work of adding a monomer to the SPC/E water cluster,  $\delta \Delta W_n$ , with respect to the change in spherical surface area of the cluster,  $n^{2/3} - (n - 1)^{2/3}$ . Results from our simulations with non-interacting clusters (NI) are compared to results obtained from literature values of virial coefficients for Mayer mathematical clusters, and to values given by the liquid drop (LD) model. The top horizontal axis describes the cluster size  $n$ .

## 7 Conclusions

The five research articles in this thesis present new Monte Carlo methods for the calculation of the work of formation of a molecular cluster in a vapour, comparisons between laboratory nucleation measurements and simulation results, and new insight to the theory of nucleation. Below, we itemize the main contributions of the papers concerning each of these topics.

### **New Monte Carlo methods:**

- We have developed a new and efficient Monte Carlo method for the calculations of work of formation of molecular clusters in vapour in **Paper I**. The method simulates the growth and decay of of a single molecular cluster in a supersaturated vapour.
- In **Paper III**, we revise the theoretical treatment of a second Monte Carlo method known as the discrete summation method, and show that previous applications of this method have neglected a term giving a significant contribution to the work of cluster formation.
- In **Paper III** we compare the results obtained with the revised discrete summation method, the results obtained with the method presented in **Paper I**, and literature values reported for other Monte Carlo methods. We show that all methods produce nearly identical results for the work of formation of Lennard-Jones argon clusters.
- **Paper V** presents a new method for the calculation of the equilibrium vapour density, surface tension size dependence and planar surface tension directly from cluster simulations. These are calculations do not require any cut-off of the interaction potential, and give accurate results with efficient sampling.

### **Comparison to laboratory experiments of nucleation:**

- In **Paper I**, we calculate the nucleation barrier for water with three different interaction potential models. We see that the obtained nucleation barriers depend strongly on the applied interaction potential model. All applied interaction potentials largely overpredict the laboratory measured nucleation rates for water. However, the temperature dependence of the simulation based nucleation rates corresponds to the experimental temperature dependence.
- In **Paper IV**, we compare the work of cluster formation of the model potentials to the CNT predictions for the same potentials. We see that for water clusters, the difference between the CNT predictions is almost independent of the applied

interaction potential. By calculating correction factors to CNT predictions for the nucleation barriers of argon and water, we show that the corrected predictions produce nucleation rates that are in good comparison with experiments.

### Contribution to nucleation theory:

- In **Paper II**, we show that the nucleation ability of different cluster configurations depends sensitively on volume and interaction energy of the configurations. Any small perturbations to the equilibrium distribution of configurations, such that may be caused by the nucleation process, increase the work of cluster formation significantly.
- In **Paper IV**, we show that the work of adding a monomer to a cluster in equilibrium vapour is accurately described by the liquid drop model applied by the CNT, once the clusters are larger than some threshold size. The threshold cluster sizes contain only a few or some tens of molecules depending on the interaction potential and temperature. However, the error made in modelling the smallest of clusters as liquid drops results in an erroneous absolute value for the cluster work of formation throughout the size range.
- The results of **Paper IV** indicate that CNT predicts the size of the critical cluster correctly. Also, since the liquid drop model gives the work of adding a monomer to larger clusters correctly, there is no indication of a size dependent replacement free energy as predicted by Reiss et al. (1997).
- In **Paper IV**, we also develop a new expression for the size dependence of the cluster surface tension in equimolar surface. The size dependence of the surface tension of argon clusters is presented in **Paper IV**, and for water clusters in **Paper V**.
- **Paper V** shows that the deviation between the simulation results and the liquid drop values for small cluster sizes are accurately modelled by the low order virial coefficients at modest temperatures and vapour densities, or in other words, in the validity range of the non-interacting cluster theory by Frenkel, Band and Bilj.
- **Paper V** shows that high order virial coefficients can be calculated analytically when the non-interacting cluster approximation is valid.

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