

UNIVERSITY OF HELSINKI

**ON THE HOMOGENEOUS AND
HETEROGENEOUS
NUCLEATION OF SOME
ORGANIC COMPOUNDS**

by

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Academic dissertation

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“The most exciting phrase to hear in science, the one that heralds the most discoveries, is not Eureka! (I found it!) but ‘That’s funny...’ ”

Isaac Asimov

UNIVERSITY OF HELSINKI

Abstract

On the homogeneous and heterogeneous nucleation of some organic compounds

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The conversion of a metastable phase into a thermodynamically stable phase takes place via the formation of clusters. Clusters of different sizes are formed spontaneously within the metastable mother phase, but only those larger than a certain size, called the critical size, will end up growing into a new phase. There are two types of nucleation: homogeneous, where the clusters appear in a uniform phase, and heterogeneous, when pre-existing surfaces are available and clusters form on them. The nucleation of aerosol particles from gas-phase molecules is connected not only with inorganic compounds, but also with nonvolatile organic substances found in atmosphere. The question is which ones of the myriad of organic species have the right properties and are able to participate in nucleation phenomena.

This thesis discusses both homogeneous and heterogeneous nucleation, having as theoretical tool the classical nucleation theory (CNT) based on thermodynamics. Different classes of organics are investigated. The members of the first class are four dicarboxylic acids (succinic, glutaric, malonic and adipic). They can be found in both the gas and particulate phases, and represent good candidates for the aerosol formation due to their low vapor pressure and solubility. Their influence on the nucleation process has not been largely investigated in the literature and it is not fully established. The accuracy of the CNT predictions for binary water-dicarboxylic acid systems depends significantly on the good knowledge of the thermophysical properties of the organics and their aqueous solutions. A large part of the thesis is dedicated to this issue. We have shown that homogeneous and heterogeneous nucleation of succinic, glutaric and malonic acids in combination with water is unlikely to happen in atmospheric conditions. However, it seems that adipic acid could participate in the nucleation process in conditions occurring in the upper troposphere. The second class of organics is represented by *n*-nonane and *n*-propanol. Their thermophysical properties are well established, and experiments on these substances have been performed. The experimental data of binary homogeneous and heterogeneous nucleation have been compared with the theoretical predictions. Although the *n*-nonane - *n*-propanol mixture is far from being ideal, CNT seems to behave fairly well, especially when calculating the cluster composition. In the case of heterogeneous nucleation, it has been found that better characterization of the substrate - liquid interaction by means of line tension and microscopic contact angle leads to a significant improvement of the CNT prediction. Unfortunately, this can not be achieved without well defined experimental data.

Keywords: homogeneous nucleation, heterogeneous nucleation, organics, classical nucleation theory

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Abbreviations

CNT	C lassical N ucleation T heory
AA	A dipic A cid
GA	G lutaric A cid
MA	M alonic A cid
SA	S uccinic A cid
RH	R elative H umidity
UNIFAC	U NIversal F unctional A ctivity C oefficient
VLE	V apor L iquid E quilibrium

Symbols

β	impinging rate
ΔG	free energy of formation
F	equilibrium concentrations of monomers
H	enthalpy
γ	activity coefficient
g^E	molar excess Gibbs energy
I	nucleation rate
m	cosine of the contact angle
M	molecular mass
μ	chemical potential
N	number concentration
\mathcal{N}^{ads}	number of molecules adsorbed
n	number of molecules
P	nucleation probability
Pch	parachor
P_i	ambient partial pressure of species i
$P_{s,i}$	equilibrium vapor pressure of species i above a flat solution surface
Φ	correction factor for the geometric mean
r	radius of the cluster
R	radius of the seed particle
R_{AV}	average growth rate
ρ	density
S	saturation ratio
σ	interfacial tension
T	temperature
\mathcal{T}	residence time
τ	line tension
θ	contact angle
v	partial molar volume
V	volume
W	work of adhesion or cohesion
x	mole fraction
X	size parameter
Z	Zeldovich factor

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List of Publications

This thesis consists of an introductory review, followed by six research articles. The papers are reproduced with the kind permission of the journals concerned. Please note that in the first three articles I appear under my maiden name Gaman.

1. A.I. Gaman, M. Kulmala, H. Vehkamäki, I. Napari, M. Mircea, M.C. Facchini and A. Laaksonen, "Binary homogeneous nucleation in water-succinic acid and water-glutaric acid systems" (2004), J. Chem. Phys. 120, 282-291
2. A.I. Gaman, I. Napari, P.M. Winkler, H. Vehkamäki, P.E. Wagner, R. Strey, Y. Viisanen and M. Kulmala, "Homogeneous nucleation of *n*-nonane and *n*-propanol mixtures: a comparison of classical nucleation theory and experiments" (2005), J. Chem. Phys. 123:244502
3. A.P. Hyvärinen, H. Lihavainen, A.I. Gaman, L. Vairila, H. Ojala, M. Kulmala and Y. Viisanen, "Surface tensions and densities of oxalic, malonic, succinic, maleic, malic and cis-pinonic acids" (2006), J. Chem. Eng. Data 51(1): 255-260
4. A.I. Hienola, P.M. Winkler, P.E. Wagner, H. Vehkamäki, A. Lauri and M. Kulmala, "Estimation of line tension and contact angle from heterogeneous nucleation experimental data" (2007), J. Chem. Phys. 126:094705
5. P.M. Winkler, A.I. Hienola, G. Steiner, A. Vrtala, G.P. Reischl, M. Kulmala and P.E. Wagner, "Effects of seed particle size and composition on heterogeneous nucleation of *n*-nonane" (2008), Accepted for publication in Atmos. Res.
6. A.I. Hienola, H. Vehkamäki, I. Riipinen and M. Kulmala, "Homogeneous vs. heterogeneous nucleation in water-dicarboxylic acid systems" (2008), Submitted to Atm. Chem. Phys. D.

Mamei...

Chapter 1

Introduction

Climate, weather, cloud formation, visibility, radiation budget, atmospheric chemistry, and human health have a common influencing factor: the aerosol. By definition, aerosol refers to all the airborne liquid droplets, solid particles and the combination of these together with the carrier gas. The aerosol particles extend over a large range of sizes (from one nanometer to tens of micrometers [Kulmala et al. (2004b)]) and over a considerable range of number concentrations, depending on the location (urban or remote natural surroundings, marine or continental, free troposphere or boundary layer) and on time (season and time of the day) [Raes et al. (2000); Pöschl (2005)].

Depending on their source, two groups of aerosols are defined: primary aerosols, directly ejected in the atmosphere by natural or anthropogenic processes (volcano activity, deflation, wave breaking, fossil fuel burning, biomass burning, pollen etc.) and secondary aerosols, formed in the atmosphere by gas to particle conversion. The precursor gases (presumably sulphur compounds, and some organics) become particles by phase transformation: nucleation and condensation. Nucleation is the onset of a phase transition in a microscopic region, such as the formation of liquid droplets in saturated vapor or the creation of gaseous bubbles in a saturated liquid.

A significant fraction (about 30%) of the total number of particles present in the atmosphere is formed originally by nucleation from the gas phase [Spracklen et al. (2006)]. However, the vapors involved in the nucleation mechanism still remain unknown [Kulmala et al. (2006)].

We can define two types of nucleation: homogeneous and heterogeneous. Homogeneous nucleation is the process through which, in the absence of any surfaces, the first

clusters of a new phase appear in the body of the mother vapor phase. Nucleation on preferential sites, such as pre-existing particles, walls etc. is called heterogeneous nucleation. Depending on the number of species involved in the process, we define unary (one-component) nucleation, binary (two components) nucleation or multicomponent (several species) nucleation.

Several nucleation mechanisms have been suggested to occur in the atmosphere. For instance, binary nucleation of water and sulphuric acid has been presumed to be the main mechanism for the new particle formation, but it is commonly admitted that it is unable to explain the observed nucleation rates [Laaksonen and Kulmala (1991); Vehkamäki et al. (2003); Lauros et al. (2006)]. Alternatively, ternary nucleation of water, sulphuric acid and ammonia has been considered as means of obtaining high enough nucleation rates to match the observations [Korhonen et al. (1999); Napari et al. (2002); Merikanto et al. (2007)]. It has also been suggested that new particles can be formed via ion induced nucleation [Raes and Janssens (1985); Laakso et al. (2002); Yu and Turco (2000)]. Laboratory measurements show that the presence of ions increases the nucleation rate with several orders of magnitude [Kim et al. (1997)]. However, the ion production rate in the lower atmosphere is usually too low to account for the real nucleation rates observed. Very recently it has been found that the neutral nucleation dominates over the ion induced mechanism [Kulmala et al. (2007)]. The presence of neutral clusters has been theoretically predicted [Kulmala et al. (2000)]; they might have an important role in particle formation via their activation [Kulmala et al. (2006)]. According to Kulmala et al. (2007), there is a continuous pool of neutral clusters (1000 to 10000 cm³) with a median size of 1.5-1.8 nm and with a concentration about 2 orders of magnitude higher than the ion cluster concentration. Because these clusters are usually lost through coagulation processes, the presence of a continuous cluster mode suggests continuous nucleation. In certain atmospheric conditions, such as a lower coagulation sink or an increase in condensable vapor concentrations, part of these clusters activate, i.e. start growing to larger sizes and can subsequently be detected by the traditional aerosol sizing instruments (e.g. Differential Mobility Particle Sizer, DMPS). The activation theory is based on the concept of activation probability and is explained in detail in Kulmala et al. (2006).

The atmosphere contains a large amount of organic compounds covering a wide range of carbon number and functional groups, also exhibiting various chemical properties. Aerosols often include a large amount of organic matter (usually sampled from particles with sizes larger than those within the nucleation mode), about 10-70% of the total

fine particle mass [Saxena and Hildemann (1996); O'Dowd et al. (2002); Kanakidou et al. (2005)], especially over continental regions [Gray et al. (1986)]. Recent studies suggest that organic compounds may have a crucial role in the formation and growth of atmospheric aerosol particles [O'Dowd et al. (2002); Kulmala et al. (2004a); Fuzzi et al. (2006)]. The gas to particle conversion of the organic compounds is thought to be dominated by their condensation on the already formed aerosol particles. However, the role of the organics in the nucleation processes represents an important issue and it should not be neglected [PAPER I, Zhang et al. (2004)]. The inclusion of an organic compound in a theoretical investigation is at least thermodynamically challenging [PAPER I, Gao et al. (2001)]. A good knowledge of the surface tension, density, vapor pressure, chemical activities is required in order to reduce the variability of the predicted nucleation rates or nucleation probabilities. In addition, it is necessary to investigate different classes of substances, both experimentally as well as theoretically.

The classical nucleation theory (CNT) [Fletcher (1958); Reiss (1950)] represents a relatively quick way of predicting the rate at which nucleation takes place in given conditions, and of mapping out the thermodynamical properties for systems not well characterized. The nucleation process is described entirely by the macroscopic thermodynamical parameters, such as liquid density, saturation vapor pressure, solid–liquid, liquid–gas and solid–gas interfacial tensions, or contact angle, and therefore problems can arise for clusters of nanometre size. The nucleated particles are at the limit between of the microscopic and macroscopic scale: they are too large to be treated at the molecular level and too small to be treated - from the thermodynamical point of view - as a macroscopic system. Therefore, classical nucleation theory includes a series of assumptions and approximations that cause its validity and accuracy to be constantly questioned. Additionally, theoreticians are confronted with a lack of direct knowledge of the fundamental parameters within the theory, or lack of experimental nucleation data (especially in the case of heterogeneous nucleation) when trying to test the reliability of CNT. For example, the solid–liquid interfacial tension or contact angles are often unavailable parameters, though not impossible to be measured. If we are to go to the molecular level of the nucleation, more contemporary theories, such as molecular dynamics, Monte Carlo simulations and quantum chemistry provide valuable insights for the nucleation process. However, they are computationally expensive and they can not be applied to real atmospheric cases [Merikanto et al. (2006); Lauri et al. (2006); Laaksonen et al. (2000); Napari and Vehkamäki (2004); Kurtén et al. (2006)].

Despite its shortcomings, the classical nucleation theory provides a powerful conceptual

understanding of the nucleation process and therefore represents the main theoretical tool in this thesis.

The main goal of thesis is to investigate the role of organics on atmospheric nucleation. The steps pursuing this goal are:

1. To investigate whether some organic vapors could be involved in nucleation processes;
2. To gain more information concerning the thermodynamics of some organic substances and their aqueous solutions or mixtures;
3. To offer reliable measurements of thermophysical properties for several dicarboxylic acids;
4. To improve the classical theory for heterogeneous nucleation by including the concept of line tension and microscopic contact angle in its derivation.

Chapter 2

Classical nucleation theory

2.1 Prelude

The process of nucleation involves the formation of clusters of a new phase in the body of the mother phase. The clusters can be formed in both subsaturated and supersaturated conditions. When the mother phase is subsaturated, the clusters are unstable and disappear, while in the case of supersaturated conditions the clusters can become stable if they exceed a certain minimum size. A supersaturated system is able to lower its energy by forming clusters of a new phase. The energy decrease is proportional to the volume of the newly formed clusters. At the same time, the formation of a new phase implies also the formation of an interface between the mother phase and the new phase, which increases the energy proportionally to the area of the interface. Over all, the energy difference between the pure mother phase and the mother phase containing clusters - known as *formation free energy* - is given by the sum of the surface and volume contributions, and exhibits a maximum in the case of supersaturation of the vapor (Figure 2.1). The cluster corresponding to the maximum point of the formation free energy is called a *critical cluster*. The formation free energy ΔG_i of a cluster containing i monomers in a supersaturated one-component system (involving a single gaseous species) can be used to determine the equilibrium distribution of clusters N_i as:

$$N_i = N_1 \exp\left(-\frac{\Delta G_i}{k_B T}\right), \quad (2.1)$$

where k_B is the Boltzmann constant and T is the temperature. This was first derived by [Volmer and Weber \(1925\)](#). Later on, [Becker and Döring \(1935\)](#) derived an expression for the rate of formation of the critical clusters. These two formulations, together with the works of [Farkas \(1927\)](#), [Zeldovich \(1942\)](#) and [Frenkel \(1946\)](#) form what nowadays is known as the classical nucleation theory (CNT). The CNT was extended by [Reiss \(1950\)](#) for two-component (binary) system. In principle, the classical nucleation theory consists of two parts: the thermodynamic part and the kinetic part. The goal of the former is to calculate the free energy of formation of a new stable phase (particle) within a metastable mother phase. This subject will be covered in the next two sections, separately for homogeneous and heterogeneous nucleation. Section [2.4](#) presents briefly the kinetics of nucleation, which describes the rate of formation of stable clusters, followed by the Section [2.5](#), where the concept of nucleation probability is formulated. The treatment of nucleation in this chapter will be all but exhaustive. For a complete overview of the classical nucleation theory the reader is referred to the book of [Vehkamäki \(2006\)](#), and the references within.

2.2 Homogeneous nucleation

In the classical nucleation theory, the thermodynamics of nucleation is based on the capillarity approximation, where the newly formed particle is assumed to have sharp boundaries and the same thermophysical properties as the bulk phase. The classical binary homogeneous nucleation theory describes the Gibbs free energy change during the formation of a spherical nucleus of radius r containing n_1 and n_2 number of molecules of two different compounds, under constant temperature T and pressure condition as [e.g. [Laaksonen et al. \(1999\)](#)]:

$$\Delta G_{\text{hom}} = -k_B T \sum_{i=1}^2 n_i \ln \left(\frac{P_i}{P_{s,i}} \right) + 4\pi\sigma r^2, \quad (2.2)$$

where P_i is the ambient partial pressure of free molecules of species i , $P_{s,i}$ is the equilibrium vapor pressure of species i above a flat solution surface, and σ is the surface tension of a flat liquid-vapor interface with the same composition as the nucleus. The fraction $S_i = \frac{P_i}{P_{s,i}}$ is known as the saturation ratio. If we were to plot the free energy of formation as a function of the number of molecules, we would obtain a surface (not a curve as in one-component case), since n_1 and n_2 are treated separately. In the multicomponent case, the number of molecules in the cluster is the sum of the core

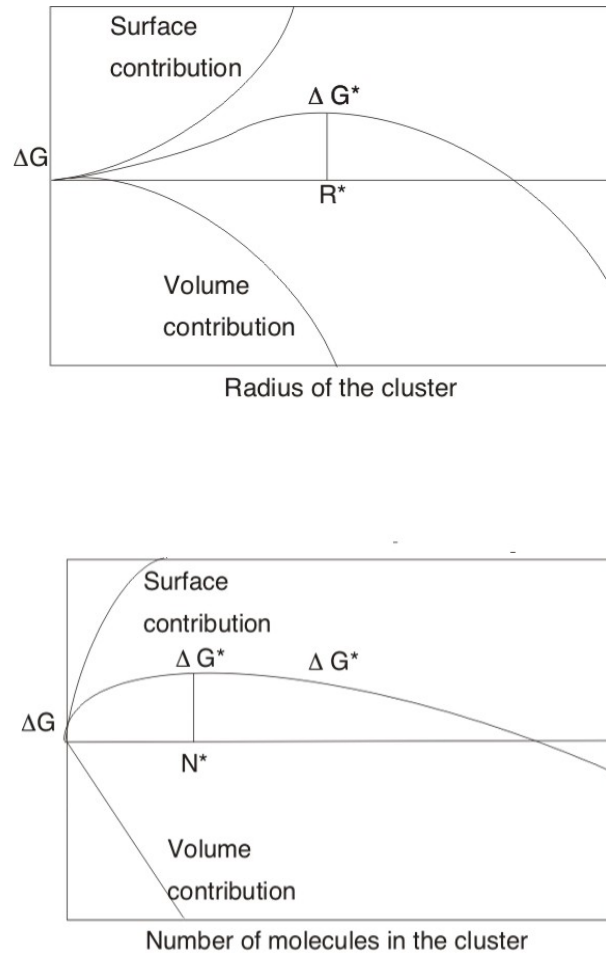


FIGURE 2.1: Nucleation free energy ΔG as a function of the radius and the number of molecules in the cluster. The classical nucleation theory describes the free energy as the sum of the surface and volume contributions.

number and the surface excess number $n_i = n_{i,l} + n_{i,s}$. The surface excess number of molecules is introduced as a correction term to the bulk number and they are both dependent on the choice of the dividing surface. The expressions for the excess surface numbers are given in **PAPER II**, Eqs. (7) and (8).

Setting $(\partial\Delta G_{\text{hom}}/\partial n_i)_{n_j} = 0$ yields the Kelvin equation, from which the composition and the radius of the critical cluster are obtained (the superscript * refers to the critical cluster):

$$r^* = \frac{2\sigma v_i}{k_B T \ln\left(\frac{P_i}{P_{s,i}}\right)}, \quad (2.3)$$

where v_i is the partial molecular volume of species i . The probability of growth is greater than the probability of shrinking for clusters with radius greater than the critical radius, while for $r = r^*$ the probabilities are equal. This implies chemical equilibrium:

$$\mu_v^* = \mu_l^*. \quad (2.4)$$

The bulk number of molecules in the critical cluster can be obtained using the volume of the cluster and the liquid density:

$$n_{2,l}^* = \frac{x^* \rho (x^*) \frac{4}{3} \pi r^{*3}}{x^* M_2 + (1 - x^*) M_1} \quad (2.5)$$

and

$$n_{1,l}^* = \frac{n_2^* (1 - x^*)}{x^*}, \quad (2.6)$$

where $x = \frac{n_{2,l}}{n_{1,l} + n_{2,l}}$ is the mole fraction and M_i is the molecular mass of species i . The height of the nucleation barrier is obtained as:

$$\Delta G_{\text{hom}}^* = \frac{4}{3} \pi r^{*2} \sigma. \quad (2.7)$$

The further away from the equilibrium the system is, in other words the higher the supersaturation is, the smaller the critical cluster and the lower the nucleation barrier will be.

2.3 Heterogeneous nucleation

Heterogeneous nucleation occurs on pre-existing surfaces. These surfaces replace some of the energetic features of the original, homogeneous configuration. Thus, their existence effectively boosts the nucleation process.

Heterogeneous nucleation can be understood better through the geometry of the system. Figure 2.2 (a) shows the case of nucleation on a wall - a flat, infinite surface - and in (b) on a spherical particle of radius R . We will consider only the latter case, with the assumptions that the seed particle is spherical, has a homogeneous uniform surface, and that the liquid cluster is cap-shaped.

The following results are obtained:

1. The radius of the critical cluster r^* is the same as in the homogeneous case (Eq. (2.3));

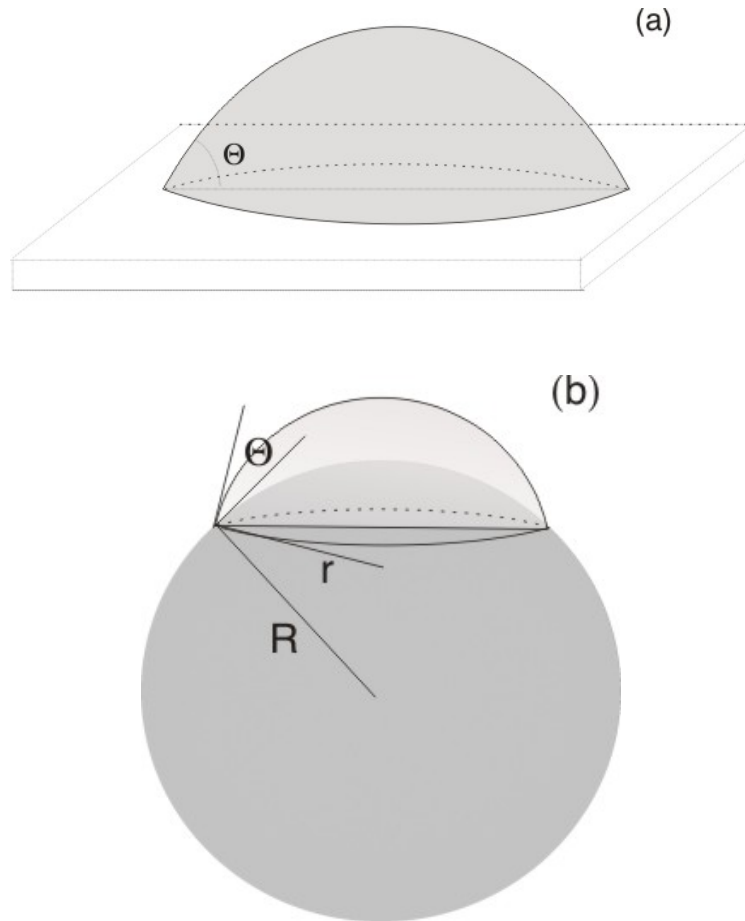


FIGURE 2.2: Heterogeneous nucleation on (a) a plane substrate and (b) on a spherical particle. θ represent the contact angle, r is the radius of the cluster and R is the radius of the seed particle.

2. The critical energy barrier is reduced from the homogeneous case by the geometric factor f_g [Lazaridis et al. (1992)]:

$$\Delta G_{\text{het}}^* = \frac{1}{2} \Delta G_{\text{hom}}^* f_g. \quad (2.8)$$

The geometric factor f_g is given, for example, in **PAPER IV**, eq.(5). A qualitative illustration of the difference between the homogeneous and heterogeneous formation free energy is presented in Figure 2.3.

3. The number of molecules in the heterogeneous cluster is connected to the number of molecules in the homogeneous cluster by another geometric factor f_n as

$$n_{\text{het}}^* = f_n n_{\text{hom}}^*, \quad (2.9)$$

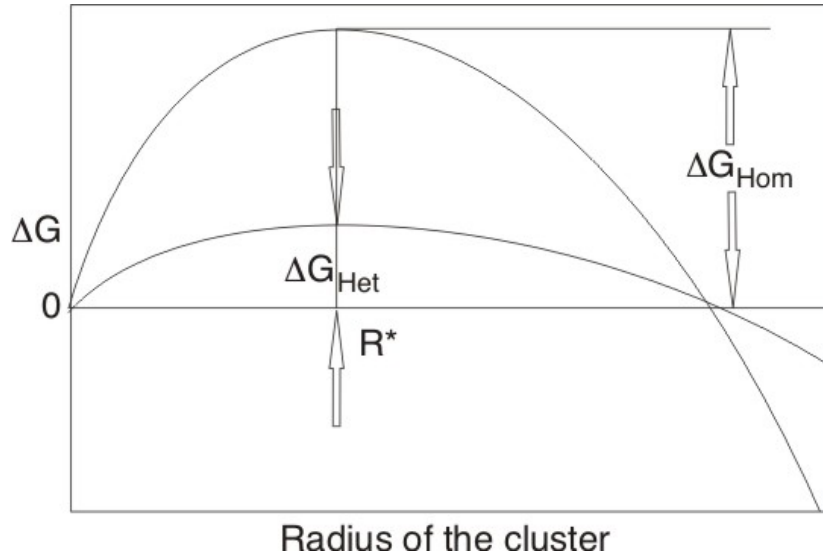


FIGURE 2.3: Illustration of the reduction of the heterogeneous free energy ΔG_{het} in comparison with the homogeneous free energy ΔG_{het} . R^* is the radius of the critical cluster.

where f_n is given by

$$f_n = \frac{1}{4} \left[2 + 3 \left(\frac{1 - Xm}{g} \right) - \left(\frac{1 - Xm}{g} \right)^3 - X^3 \left(2 - 3 \left(\frac{X - m}{g} \right) - \left(\frac{X - m}{g} \right)^3 \right) \right], \quad (2.10)$$

with $g = \sqrt{1 + X^2 - 2Xm}$ and $X = \frac{R}{r^*}$ is a size parameter giving the ratio between the radius of the seed particle R and the radius of the critical cluster r^* . m is the cosine of the contact angle θ that the liquid embryo makes with the underlying seed particle. The contact angle is specific for any given system, and describes the interactions between the three interfaces. The contact angle will be discussed in detail in Chapter 3.

2.4 Nucleation kinetics

In the previous sections, the discussion focused on the energy balance equations for the formation of a single cluster. Considering the system as a whole, we are interested in expressing the number of clusters formed per unit time and volume. According to [Stauffer \(1976\)](#), the final expression for the steady-state homogeneous nucleation rate may be written in a form similar to the one used in unary nucleation as follows:

$$I_{\text{hom}} = R_{AV} F Z \exp \left(\frac{-\Delta G_{\text{hom}}^*}{k_B T} \right), \quad (2.11)$$

where $(R_{AV}FZ)$ is the kinetic prefactor consisting of: R_{AV} - the average growth rate, F - the equilibrium concentration of monomers and Z - the Zeldovich non-equilibrium factor. **PAPERS I, II** and **VI** present more extensively the evaluation of the kinetic part. **PAPER II** includes also the accurately calculated kinetic prefactor.

The rate of heterogeneous nucleation, I_{het} , is described by a very similar equation as previously described for homogeneous nucleation, I_{hom} . The critical difference is that the heterogeneous nucleation kinetics will be influenced by both the reduction in ΔG^* (which favors heterogeneous nucleation over homogeneous nucleation) and by the number of sites available for heterogeneous nucleation. The kinetic prefactor in heterogeneous nucleation depends on the growth model used: the direct vapor deposition model or the surface diffusion model.

The direct vapor deposition approach takes into account only the vapor monomers colliding directly with the critical cluster. The surface diffusion model assumes that the monomers collide and adhere to the surface of the seed particle and then diffuse to the liquid cluster. The total number of molecules adsorbed per unit area of a solid seed particle \mathcal{N}^{ads} can be calculated as:

$$\mathcal{N}^{\text{ads}} = \sum_{i=1}^2 (\beta_i \mathcal{T}_i), \quad (2.12)$$

where β_i is the impinging rate of molecules of species i on the surface of the seed particle defined as:

$$\beta_i = n_i \sqrt{\frac{k_B T}{2\pi M_i}} \quad (2.13)$$

and \mathcal{T}_i is the residence time, defined as the time a molecule spends on the surface. In principle, both vapor deposition and surface diffusion processes take place in the same time. As the surface diffusion growth rate is typically several orders of magnitude larger than the one given by the vapor deposition, this approach has been assumed to be the growth mechanism in all the heterogeneous nucleation studies included in this thesis.

Assuming that the embryo grows via adsorption mechanism and demanding that the entire seed particle is covered by critical nuclei, the minimum nucleation rate is obtained as [[Hamill et al. \(1982\)](#)]:

$$I_{\text{het}}^{\text{min}} = \pi r^{*2} R_{AV} \mathcal{N}^{\text{ads}} Z \exp\left(\frac{-\Delta G_{\text{het}}^*}{k_B T}\right), \quad (2.14)$$

where N_p is the number concentration of the seed particles. The maximum nucleation rate is calculated assuming that only one single critical cluster is needed on each seed particle:

$$I_{\text{het}}^{\text{max}} = 4\pi R^2 R_{AV} \mathcal{N}^{\text{ads}} Z \exp\left(\frac{-\Delta G_{\text{het}}^*}{k_B T}\right) \quad (2.15)$$

The Zeldovich factor appearing in the heterogeneous nucleation rate can be approximated as being equal to the one used in the unary homogeneous nucleation calculations. The extension to the binary case it is done by introducing the concept of virtual monomer, defined as the "average" of two different monomers, having the volume:

$$v_m = xv_1 + (1-x)v_2, \quad (2.16)$$

with composition x and molecular volume v_i defined previously. Hence, the Zeldovich non-equilibrium factor for binary heterogeneous nucleation reads:

$$Z \cong \sqrt{\frac{\sigma}{k_B T} \frac{v_m}{2\pi r^*2}}. \quad (2.17)$$

The kinetic part of the nucleation is based on the thermodynamic part, by making use of the surface tension of the newly formed particles. The nucleation rate for heterogeneous nucleation must be expressed per unit surface area of the substrate in contact with the mother phase, while the homogeneous nucleation is expressed per unit volume.

2.5 Nucleation probability

Although the homogeneous nucleation rate measurements have become increasingly accurate, this is not the case for heterogeneous nucleation, where the nucleation rate is difficult, if not impossible to be experimentally observed. Instead, the measurable quantity used is nucleation probability, defined as the fraction of the activated particles in the total aerosol population. An activated particle is defined as a particle with an embryo formed on its surface through heterogeneous nucleation. According to [Lazaridis et al. \(1992\)](#), the nucleation probability in a time period t is:

$$P = 1 - \exp(-4\pi R^2 I_{\text{het}} t) \quad (2.18)$$

The nucleation probability does not depend on the number of aerosol particles, but gives the fraction of condensation nuclei activated in certain conditions. In the heterogeneous nucleation papers included in this thesis, the concept of nucleation onset is used; the onset nucleation conditions are defined as the conditions where the nucleation probability is $P=0.5$.

Chapter 3

Line tension and contact angle

3.1 Prelude

In 1878, in the second part of his famous paper "**On the equilibrium of heterogeneous Substances**", Willard Gibbs wrote: *"We may remark that a nearer approximation in the theory of equilibrium and stability might be attained by taking special account, in our general equations, of the lines in which surfaces of discontinuity meet. These lines might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity. We might recognize linear densities of energy, of entropy, and of the several substances which occur about the line, also a certain linear tension"*. That was the moment when the linear thermodynamics was born. It was about 100 years later that the investigation of line tension was undertaken and it is in full play now. Despite of its relatively long history, line tension is probably one the most controversial concepts in wetting science.

Line tensions may be defined either as mechanical or as thermodynamic tensions. The former is regarded as the 1-dimension analogue of the interfacial tension (defined as a mechanical force along the surface per unit perimeter of length) in the sense that it takes only positive values, while the latter is regarded as the excess free energy of a multiphase system (three or more phases) per unit length of the contact line and can take both positive and negative values [Rowlinson and Widom (1982)]. Theoretically, its magnitude has been estimated to be on the order of 10^{-10} - 10^{-12} N and therefore it is expected to play a major role in processes of nanometer scale, such as heterogeneous nucleation [Pompe and Herminghaus (2000)].

In the following analysis, the gas/liquid/solid system will be adopted. In addition, the solid pre-existing surface will be considered ideal (smooth, chemically homogeneous, rigid), the liquid droplet cap-shaped and the three phase contact line a circle. Both flat and curved solid surfaces will be analyzed.

3.2 Young's equation and line tension

A molecule of a certain material placed at the interface with another material experiences a different environment in comparison to its siblings located in the bulk phase. Considering this, it can be stated that the line tension arises from the imbalance of the molecular interactions in vicinity or at the three-phase contact line [Amirfazli and Neumann (2004)]. A schematic picture of the force imbalance experienced by a molecule at the contact line and at one of the interfaces is depicted in Figure 3.1. Since the relative inclination of the phases in contact determines the extent of the molecular interactions, the line tension will be dependent on the contact angle [Marmur (1997)]. The starting point for the theory of line tension is the well-known Young's equation [Young (1805)], which describes the mechanical equilibrium of the forces per unit length on the three phase contact line:

$$\cos \theta_{\infty} = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \quad (3.1)$$

where θ_{∞} represents the macroscopic contact angle (that is, the angle that can actually be measured), σ is the interfacial tension carrying the subscripts g, l, s standing for

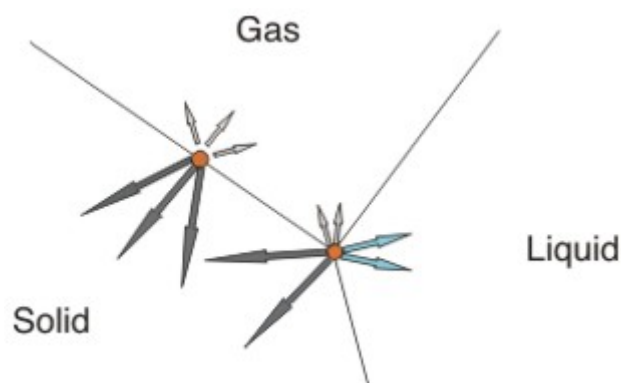


FIGURE 3.1: Cross-section of a three-phase (gas/liquid/solid) system. Molecules (circles) at the interface (symbolized by a line) and on the three phase contact line (the intersection point of the three lines). The strength of the forces is shown by the different lengths of the arrows.

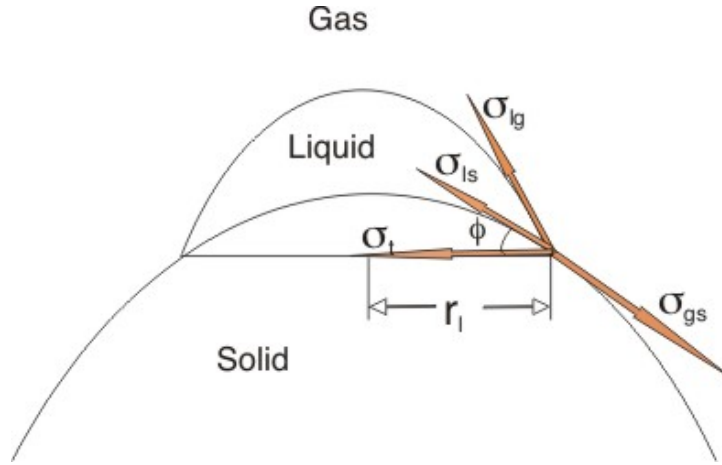


FIGURE 3.2: Representation of the balance of tensions σ along the perimeter of the three phase contact line. To account for line tension, $\sigma_t = \frac{\tau}{r_l}$ has been added to the balance of forces, where τ is the line tension and r_l is the radius of the liquid cluster. The subscripts g, l and s stand for gas, liquid and solid, respectively. The angle ϕ is the angle between the tangent to the seed particle at the intersection with the liquid cluster and the plane containing the contact line

gas, liquid and solid, respectively. Young's equation, being strictly valid only for macroscopic droplets, has to be corrected in the case of very small systems. In **PAPER IV** the generalized Young's equation – i.e. the Young's equation corrected with line tension τ – is derived using the balance of forces along the three phase contact line (shown schematically in Figure 3.2). The following equation for the microscopic – or sometimes called intrinsic – contact angle for a liquid drop on a spherical substrate with radius R has been obtained:

$$\cos \theta = \cos \theta_\infty - \frac{\tau}{\sigma_{lg} R \tan \phi}, \quad (3.2)$$

where the angle ϕ represents the angle between the tangent to the seed particle at the intersection with the liquid cluster and the plane containing the contact line, as given by the geometry in Figure 3.2.

For a flat solid surface, the angle ϕ disappears and Eq. (3.2) simply becomes:

$$\cos \theta = \cos \theta_\infty - \frac{\tau}{\sigma_{lg} r_l}, \quad (3.3)$$

where r_l is the radius of the contact line. To visualize the difference between the macroscopic and microscopic contact angles, one should regard Eq. (3.3); similar reasoning can be applied to Eq. (3.2). For a sufficiently large droplet, the influence

of the line tension can be ignored and we obtain the macroscopic contact angle, as the second term in the RHS of Eq.(3.3) is zero. For a nanometer size droplet, the

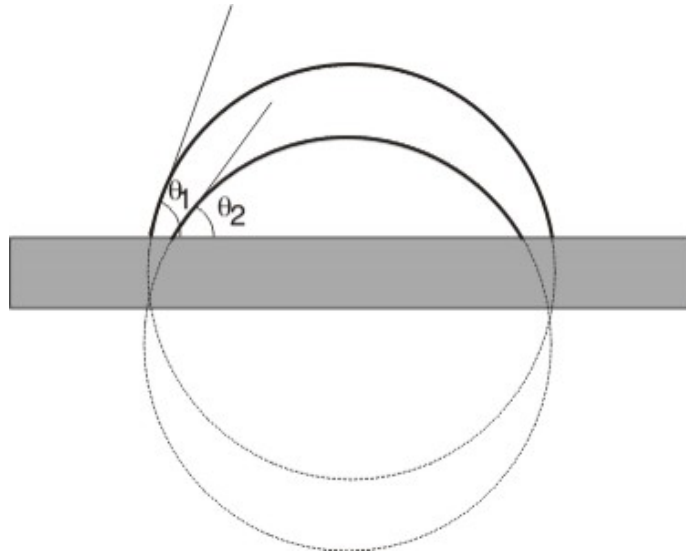


FIGURE 3.3: Two droplets with equal radii occupying different positions corresponding to two different values of the line tension. The corresponding microscopic contact angles θ_1 and θ_2 are different.

line tension cannot be disregarded and in this case the droplet intersects the surface at an angle - the microscopic contact angle - which is different than the macroscopic one. In our model, the spherical cap-shaped droplet is moved up and down to fit the microscopic contact angle with the value of the line tension. This procedure is shown in Fig. 3.3 where two droplets with equal radii occupy different positions corresponding to two different values of the line tension. This implies that the contact angles, denoted in the figure by θ_1 and θ_2 , are different. A positive line tension tends to decrease the perimeter of the contact line, creating a microscopic contact angle larger than the macroscopic one. On the other hand, a negative line tension relaxes the edges of the drop, increasing the length of the contact line. In this case the microscopic contact angle becomes smaller than the macroscopic angle.

There is little consensus in literature regarding the sign for the line tension. Both positive and negative signs are met, originating from theoretical or experimental approaches. Its value can range over several orders of magnitude, even for chemically similar systems. This reflects the complicated non-ideal factors involved. Controversy around the sign of the line tension exists.

3.3 Contact angle

Macroscopic contact angle provides important information about the wettability of the surfaces and about the surface tension of solids. Both the above mentioned properties are of interest in heterogeneous nucleation process.

A large droplet partially wets a surface if it possesses a finite contact angle ($\theta_\infty > 0$). If $\theta_\infty = 0$ it is said that the liquid totally wets the surface, in which case the line tension disappears. In the case of heterogeneous nucleation, this means that the seed particle is covered by a layer of liquid, which changes the thermodynamics of the system. Also, great attention must be paid if the calculations are done for varying temperature, as it is possible to approach a wetting transition. For certain solid-liquid systems, a wetting temperature T_w exists for which, if temperature $T < T_w$, the contact angle has a nonzero value, whereas above the temperature T_w the contact angle is $\theta_\infty = 0$.

The calculation of a vapor-solid interfacial tension from the contact angle of a liquid drop starts with Eq. (3.1). There are four quantities in Young's equation, and only two of them are measurable, namely the liquid surface tension σ_{gl} and the macroscopic contact angle θ_∞ . Therefore we need to seek for another relationship among the variables in Eq. (3.1). Several methods are available for calculating the solid-vapor interfacial tension when the contact angle is known. The one presented in **PAPER IV** involves the work of adhesion W_{ls} per unit area of a solid-liquid pair which can be expressed as a function of interfacial tensions through the Young-Dupré equation:

$$W_{ls} = \sigma_{gl} + \sigma_{gs} - \sigma_{ls} \quad (3.4)$$

or as the geometric mean of the free energy of cohesion of solid–solid W_{ss} and the work of cohesion for liquid–liquid W_{ll} as

$$W_{ls} = \sqrt{W_{ll}W_{ss}}. \quad (3.5)$$

where $W_{ll}=2\sigma_{gl}$ and $W_{ss}=2\sigma_{gs}$. The solid–liquid work of adhesion becomes

$$W_{ls} = 2\sqrt{\sigma_{gl}\sigma_{gs}}. \quad (3.6)$$

Coupling Eq.(3.6) with Eq. (3.4), we obtain an expression for the solid–liquid interfacial tension:

$$\sigma_{ls} = \sigma_{gl} + \sigma_{gs} - 2\sqrt{\sigma_{gl}\sigma_{gs}} \quad (3.7)$$

known as the Rayleigh-Good equation. Recalling now the Young's equation, the contact angle becomes:

$$\cos \theta_{\infty} = -1 + 2\sqrt{\frac{\sigma_{gs}}{\sigma_{gl}}}. \quad (3.8)$$

In the study of mixtures it is a common practice to account for the deviation from the geometrical mean by introducing a factor Φ in the geometric mean combining rule. [Li and Neumann \(1992\)](#) proposed an empirical expression for the interaction parameter Φ

$$\Phi = e^{-\beta(\sigma_{gl}-\sigma_{gs})}, \quad (3.9)$$

where $\beta=0.0001247\text{m}^4\text{mJ}^{-2}$ is an universal constant obtained from a fitting a large set of experimental data. In this case, Eq. (3.8) becomes

$$\cos \theta_{\infty} = -1 + 2\Phi\sqrt{\frac{\sigma_{gs}}{\sigma_{gl}}}. \quad (3.10)$$

Eq. (3.10) with Φ expressed as in Eq. (3.9) is known as the Neumann equation of state for interfacial tension. Thus, the vapor-solid interfacial tension can be determined when the macroscopic contact angle and the liquid-vapor interfacial tension are known.

Chapter 4

Classical heterogeneous nucleation theory corrected with line tension

4.1 Prelude

As mentioned in the previous chapter, the estimates for line tension τ indicate that this property has a small value and it is insignificant for macroscopic systems. However, it becomes important and can induce measurable changes when the system is of nanometer size. For instance, line tension has considerable relevance in wetting phenomena, stability of spherical particles at liquid/fluid interface, soap films, formation of liquid particles on solid surfaces and many other cases [[Faraudo and Bresme \(2003\)](#)].

As heterogeneous nucleation occurs at a surface in contact with a vapor, the process will be controlled by surface effects. As the scale of the system is of nanometer size, the property characterizing the substrate and the nature of the interaction between the solid, liquid and vapor is the microscopic contact angle and in connection with it, the line tension. [Gretz \(1966\)](#) was the first to call attention to the importance of line tension in heterogeneous nucleation. However, his analysis was not complete. Several other attempts to include the line tension in the treatment of CNT have been made, usually by means of fitting the theory to the experimental data [[Scheludko et al. \(1981\)](#); [Navascues and Mederos \(1982\)](#); [Lazaridis \(1993, 1994\)](#)].

4.2 Basic results of the theory

In the classical nucleation theory, the critical cluster formation rate is given by [Fletcher (1958)]:

$$I_{\text{het}} = K \exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (4.1)$$

where K is a kinetic factor, as discussed previously in Chapter 2. This equation remains valid when the line tension effect is taken into account, but the critical nucleation barrier will have an extra term. In the heterogeneous case, the free energy of formation can be written as [Fletcher (1958)]:

$$\Delta G = \Delta G_{gl}V + \sigma_{gl}S_{gl} + (\sigma_{ls} - \sigma_{gs})S_{ls}, \quad (4.2)$$

where ΔG_{gl} represents the free energy difference per unit volume of the liquid phase between matter in liquid phase and the matter in gas phase, V is the volume of the liquid cluster, and S_{ij} is the surface area of the interface. When including the line tension effect, Eq. (4.2) receives an extra term and becomes [Lazaridis (1993)]:

$$\Delta G = \Delta G_{gl}V + \sigma_{gl}S_{gl} + (\sigma_{ls} - \sigma_{gs})S_{ls} + 2\pi R\tau \sin \phi, \quad (4.3)$$

where $2\pi R \sin \phi$ is the length of the contact line. According to Lazaridis (1993) the resulting height of the nucleation barrier becomes:

$$\Delta G^* = \frac{2\pi r^{*2} \sigma_{gl}}{3} f_g - \frac{\tau}{R \tan \phi} S_{ls} + 2\pi R\tau \sin \phi. \quad (4.4)$$

It can be shown that $2\pi R\tau \sin \phi > \frac{\tau}{R \tan \phi} S_{ls}$, where $S_{ls} = 2\pi R^2(1 - \cos \phi)$, as angle ϕ takes values from 0 to π . Thus, a negative line tension decreases the height of the nucleation barrier, increasing the nucleation rate values.

Eq. (4.4) can be further simplified by replacing the line tension τ with $\sigma_{lg}R \tan \phi(\cos \theta_\infty - \cos \theta)$ from Eq. (3.2). The final form for the height of the nucleation barrier is

$$\Delta G^* = \frac{2\pi r^{*2} \sigma_{gl}}{3} f_g + \frac{\sigma_{gl}(\cos \theta_\infty - \cos \theta)}{\cos \phi} S_{ls}. \quad (4.5)$$

In this case the increase or decrease of the nucleation barrier will be given by the sign of the second term on the right hand side of the equation. For instance, if the nucleation barrier decreases (process connected to a negative line tension), then $\frac{(\cos \theta_\infty - \cos \theta)}{\cos \phi}$ should be negative, as σ_{gl} and S_{ls} are always positive. Noting that both θ and ϕ take values between 0 and π , we have two cases:

1. $0 < \phi < \pi/2$ (equivalent with $\cos \phi > 0$) and $\cos \theta_\infty < \cos \theta$ ($\theta_\infty > \theta$). In this case the liquid cluster covers less than a half of the seed particle;
2. $\pi/2 < \phi < \pi$ (equivalent with $\cos \phi < 0$) and $\cos \theta_\infty > \cos \theta$ ($\theta_\infty < \theta$), in which case the liquid cluster covers more than a half of the seed particle.

Both cases confirm the fact that a negative line tension tends to relax the contact line, moving it towards the equator of the seed particle, as explained in the text and depicted in Figure 14 in **PAPER IV**.

Although the limitations of the capillarity approximation remain, the CNT corrected with line tension can explain certain experimental data (**PAPER IV**, **PAPER V** [Gretz \(1966\)](#); [Lazaridis \(1993\)](#); [Auer and Frenkel \(2003\)](#)), allowing us to hope for the recovery of the status of the classical theory.

Chapter 5

On the thermodynamics of organics and their mixtures

5.1 Prelude

Classical nucleation theory requires the knowledge of the thermodynamic properties of the species involved, such as surface tension, liquid density, saturation vapor pressure of pure liquids, activity coefficients for the mixture and contact angle. Sometimes, no experimental data of some of the properties listed above for substances of atmospheric interest are available, in which case a theoretical prediction is required. For instance, some of the organics that are making the subject of this thesis are solid in their pure bulk states and in the temperature range considered. As they behave in the environment according to their liquid state (meaning that in the small nucleating clusters they are in liquid form), their subcooled liquid state properties have to be calculated and used.

When experimental data points are available, an appropriate fitting procedure is necessary. The fitting should not be done with any simple mathematical function that might lead to serious errors, but to use a thermodynamic consistent equation. In the following sections the properties of pure components and binary solutions will be covered. A binary liquid solution is prepared using n_1 moles of element 1 and n_2 moles of element 2 at temperature T and pressure p . At least one of the elements should be in the liquid phase, while the other should be soluble in the given liquid. The term "solution" usually means that a homogeneous single liquid phase is formed with no

chemical reaction occurring. In a mixture, each ingredient substance retains its own chemical properties. However, the properties of a mixture may differ from those of its components.

5.2 Densities of liquid mixtures and pure compounds

A reasonable estimate of the density of a mixture can be obtained by assuming that the molar volume of the liquid is an ideal mixture of the molar volumes of the elements:

$$V = x_1v_1 + x_2v_2, \quad (5.1)$$

where x_i ($i=1,2$) is the mole fraction of species i and the molar volumes v_i of the elements are calculated from the densities of pure elements $v_i = \frac{M_i}{\rho_{i,\text{pure}}}$. The effect of the temperature on the density of the solution is given through the temperature dependence of the pure densities.

For a better description of the variation of the density of a binary solution with the composition, an equation of the form [Prausnitz et al. (1999)]:

$$\frac{1}{\rho} = \frac{GM_1x}{\rho_1[M_1x + M_2(1-x)]} + \frac{HM_2(1-x)}{\rho_2[M_1x + M_2(1-x)]} \quad (5.2)$$

can be fitted to experimental data, as it is explained in **PAPER III**. Here G and H are fitting parameters.

It is possible that the densities of pure components are not available or, as mentioned above, the subcooled liquid state has to be considered. In such a case, several methods to predict liquid densities of pure elements are available. One of the most successful correlations for the prediction of liquid density of pure fluids is by Yen and Woods (1966), which is based on three parameter (reduced temperature $T_r = \frac{T}{T_c}$, critical density ρ_c , compressibility factor Z_c) corresponding state theory. The Yen and Woods' scheme reads:

$$\frac{\rho}{\rho_c} = 1 + \sum_{j=1-4} K_j(1 - T_r)^{j/3}, \quad (5.3)$$

where the coefficients K_j are functions of the compressibility factor Z_c as follows:

$$K_1 = 17.4425 - 214.578Z_c + 989.625Z_c^2 - 1522.06Z_c^3$$

$$K_2 = -3.28257 - 13.6377Z_c + 107.4844Z_c^2 - 384.211Z_c^3 (Z_c < 0.26)$$

$$K_2 = 60.2091 - 402.063Z_c + 501.0Z_c^2 + 641.0Z_c^3 (Z_c > 0.26)$$

$$K_3 = 0$$

$$K_4 = 0.93 - K_2$$

5.3 Surface tension

The interface between the gas and liquid phases can be regarded as a third phase with properties intermediate between those of liquid and gas, where unequal forces are acting upon molecules. For pure (subcooled) liquids, the Macleod-Sugden method based on parachor is judged to be fairly accurate when the experimental data are compared with the estimated values [Reid et al. (1987)]. The equation relates the surface tension of the pure liquid with the liquid and vapor densities:

$$\sigma = [Pch](\rho_l + \rho_v) \quad (5.4)$$

The parachor Pch – a temperature-independent parameter – can be easily estimated from the structure of the molecule. If the liquid is well below the boiling point, the vapor density can be neglected.

The surface tension of a mixture is not a trivial function of the surface tensions of the pure components. Both aqueous and non-aqueous mixtures can show pronounced nonlinear characteristics. The nonlinear behavior is typical for organics, which, even in small concentrations, affect the surface tension of the mixture significantly. In this thesis, the surface tension were measured for all the mixtures and then fitted to a thermodynamically consistent equation, such as Szyskowski-Langmuir equation [Reid et al. (1987)] for aqueous solutions of succinic acid and glutaric acid (**PAPER I**), generalized Langmuir equation [Pineiro et al. (2001)] for n -nonane- n -propanol mixture (**PAPERS II and IV**), and Chunxi equation [Chunxi et al. (2000)] for aqueous solutions of malonic, succinic and adipic acid aqueous solutions (**PAPERS III and VI**). Although none of the correlations mentioned are able to reproduce exactly the measured data, the overall fit to the experimental points can be considered satisfactory.

5.4 Saturation vapor pressure

The saturation vapor pressure is defined as the pressure of a vapor phase in equilibrium with its liquid phase and depends solely on the temperature. As the temperature rises, the saturation vapor pressure rises nonlinearly. When experimental data on saturation vapor pressure of a pure liquid exist, a temperature-dependent expression of the form:

$$\ln P_{\text{sat}} = A - \frac{B}{T} - C \ln T \quad (5.5)$$

can be used for fitting, assuming a linear temperature dependence of the vaporization enthalpy $\Delta H_{\text{vap}} = R(B - CT)$. Eq. (5.5) applies for the saturation vapor pressure above a liquid. In the case of solids, the latent heat of sublimation is used instead of the vaporization enthalpy. However, over small temperature intervals, the latent heat of vaporization can be considered constant and Eq.(5.5) becomes:

$$\ln P_{\text{sat}} = A - \frac{B}{T} \quad (5.6)$$

As in this thesis we deal only with the liquid vapor pressure, we need to convert the solid state vapor pressure to the subcooled liquid vapor pressure. This can be done by using enthalpy of fusion ΔH_{fus} and melting points T_m as described in [Prausnitz et al. \(1999\)](#) and in **PAPER I**.

5.5 Activity coefficients

The liquid phase activity of component i in a binary solution at a certain temperature, pressure and composition is defined as the ratio between the pressure above the solution at these conditions and the saturation vapor pressure above the pure liquid:

$$a_i = \frac{P_{i,\text{sol}}}{P_{\text{sat}}} \quad (5.7)$$

The activity coefficient is given by the ratio of the activity a_i to a convenient measure of concentration, usually mole fraction x :

$$\gamma_i = \frac{a_i}{x_i} = \frac{P_{i,\text{sol}}}{x_i P_{\text{sat}}} \quad (5.8)$$

5.5.1 Van Laar

The Van Laar theory is one of the earliest and most significant theoretical works for vapor-liquid equilibrium prediction using activity coefficients. The aim of the theory is to express the dependence of the molar excess Gibbs energy g^E on temperature and composition.

In order to correlate and extend limited experimental data for activities in liquid phase, one can start with the Gibbs-Duhem equation, which states that, for a binary mixture, the activity coefficients of the components are related to each other. Practically this can be done through the concept of the excess Gibbs energy (the Gibbs energy beyond what it would be for an ideal solution). The molar excess Gibbs energy for a binary mixture is defined as

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (5.9)$$

The Van Laar method provides an expression for the molar Gibbs energy as a function of two constants A and B :

$$g^E = \frac{Ax_1x_2}{x_1(A/B) + x_2}, \quad (5.10)$$

Differentiation of g^E with respect to composition yields the activity coefficients. The expressions for the activity coefficients are presented in **PAPER I**. If only few experimental data are available, the van Laar method represents a simple, thermodynamically consistent way for interpolating and extrapolating the data with respect to composition.

5.5.2 UNIFAC

UNIFAC is a well-known model for reliable prediction of phase equilibria. UNIFAC regards the molecules as an aggregate of functional groups and considers that the physical properties of the fluid can be seen as a sum of the contributions of the functional groups. Experimentally obtained activity coefficients are used to calculate the parameters characterizing the interactions between pairs of groups. These parameters can then predict the activity coefficients for other solutions containing the same functional groups, but for which no experimental data are available.

For comparison purposes, both the original UNIFAC [[Fredenslund et al. \(1975\)](#)] and the modified version Dortmund UNIFAC [[Larsen et al. \(1987\)](#); [Gmehling et al. \(1998\)](#)];

Lohmann et al. (1998)] have been used in this thesis. When first developed, the aim of the original UNIFAC was to predict the vapor liquid equilibrium (VLE) for a certain temperature range (from 290 to 400 K) by using van der Waals volumes and surface areas, as well as the fitted binary group interaction parameters. The UNIFAC model showed weakness outside the range of the temperatures mentioned above, as well as in characterizing the phase behavior in the dilute region. The modified Dortmund UNIFAC tends to solve these problems by introducing temperature-dependent parameters to describe the temperature dependence of the activity coefficient correctly and by using measured activity coefficients at infinite dilution. UNIFAC starts also from the excess Gibbs energy, calculated as a sum of combinatorial and residual contributions:

$$g^E = g_c^E + g_r^E. \quad (5.11)$$

The combinatorial term accounts for the size of the molecules, while the residual term is related to the energetic group interaction parameter among different functional groups. The activity coefficient is calculated as a sum of combinatorial and residual terms

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r. \quad (5.12)$$

Chapter 6

Calculations

6.1 Homogeneous nucleation

Homogeneous nucleation calculations based on the classical nucleation theory are presented in **PAPERS I, II** and, to a lesser extent, in **PAPER VI**. Water - succinic acid and water glutaric acid systems are the subject of the investigations in **PAPER I** and, together with malonic acid and adipic acid aqueous systems in **PAPER VI**. **PAPER II** presents calculations for the *n*-nonane - *n*-propanol binary homogeneous nucleation. No theoretical work on succinic acid - water and *n*-nonane - *n*-propanol binary nucleation has been published before, and only one study on binary nucleation of glutaric acid - water system has been reported previously [[Gao et al. \(2001\)](#)].

Beside the homogeneous nucleation calculations for succinic acid – water and glutaric acid – water mixtures, the focus in **PAPER I** was centered on two other issues: the thermophysical properties of these systems that have not been extensively studied before, and the variation of the nucleation rate with respect to independent fluctuations in the system parameters. The input parameters for the homogeneous nucleation calculations were the temperature and the vapor phase activities. The relative humidity and temperature were fixed, while the organic acid activities in the gas phase were allowed to vary. The size of the critical cluster was calculated using Kelvin equation (Eq.(2.3)).

The thermophysical properties of the organic acids and their aqueous solutions, namely activity coefficients, density, vapor pressure and surface tension are discussed extensively in **PAPER I**. The activity coefficients were calculated with both original UNI-

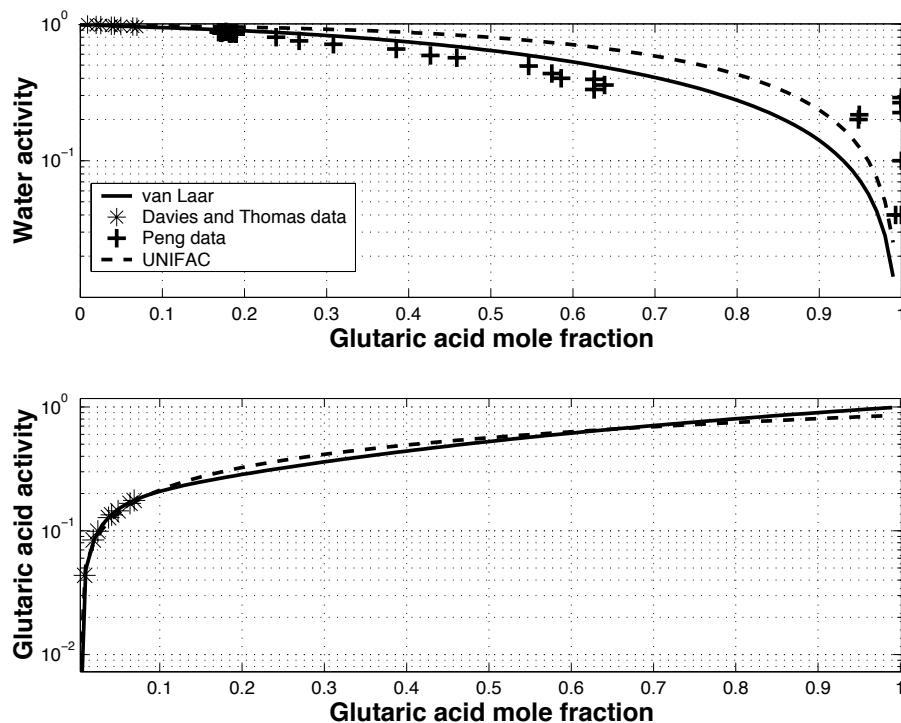


FIGURE 6.1: Activities of water and glutaric acid calculated with van Laar equations (solid line) based on experimental data (stars and pluses) and UNIFAC group contribution method (dashed line).

FAC and van Laar equations, the latter one being based on some old and rather strange experimental data. However, both methods give very similar results, as it is shown in Figure 6.1 for water-glutaric acid solution.

The subcooled liquid state vapor pressures for succinic and glutaric acid were estimated by converting the solid state vapor pressures found in the literature using the molar enthalpy of fusion (ΔH_{fus}) and melting points (T_m) as described in Prausnitz et al. (1999). The fugacity of the subcooled liquid (f^L) at temperature T in terms of the solid state fugacity (f^S) and measurable thermodynamic properties ΔH_{fus} and T_m is

$$\ln \frac{f^L}{f^S} = \frac{\Delta H_{\text{fus}}}{RT_m} \left(\frac{T_m}{T} - 1 \right), \quad (6.1)$$

where R is the molar gas constant. Fugacity is a measure of chemical potential in the form of 'adjusted pressure'. The fugacity, which has units of pressure, represents the tendency of a fluid to escape or expand. For gases at low pressures where the ideal gas law holds, fugacity equals the pressure.

The values for the melting temperatures and the enthalpy of fusion, are given in Table

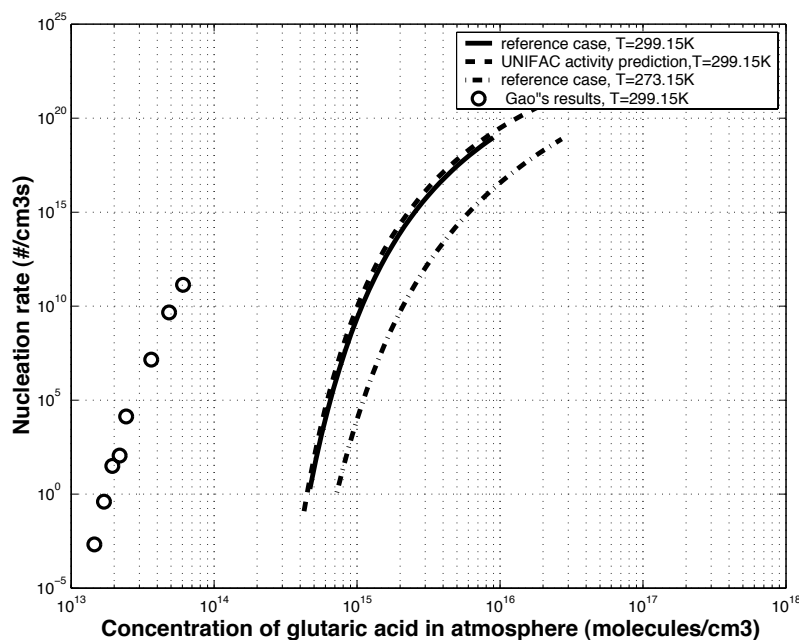


FIGURE 6.2: Binary nucleation rate of water and glutaric acid vs. concentration of glutaric acid in gas phase: solid line - reference case at 298K; dash-dotted line: reference case at 273K; dashed line: UNIFAC activity prediction; circles: Gao's results [Gao et al. (2001)]. RH=65.7%.

1 in **PAPER I**. As it will be seen later in **PAPER VI**, the estimated vapor pressures using the above formula are significantly different than the measured ones, leading to nucleation rates higher by several orders of magnitude.

The nucleation rate was calculated according to eq. (6) in **PAPER I** and in accordance to the theory presented in Chapter 2. Given the delicate nature of the nucleation process, it is important to assess the effects of the uncertainties in the parameters governing the nucleation. A sensitivity analysis was undertaken to explore what effects the temperature, density, surface tension and activity coefficient variations have on the homogeneous nucleation rate. This has been done by either directly varying the parameters – as in the case of temperature, by changing the functional form (for density) or by using different methods for calculating the thermophysical data (the activity coefficients and surface tension). As an example, Figure 6.2 shows the difference in the nucleation rate for glutaric acid-water given by UNIFAC or Van Laar equations for calculating the activity coefficients or by using different temperatures.

The results presented in **PAPER I** represent the first steps towards a better understanding of the involvement of the organics in the nucleation processes. According to the calculations, the binary homogeneous nucleation of water-glutaric acid and

water-succinic acid can not take place in atmospheric conditions, as the measured atmospheric concentrations for these organics are about 7 orders of magnitude smaller than the ones provided by the model. The theoretically predicted thermophysical properties (for instance vapor pressure for the subcooled liquids) introduce some level of uncertainty in the nucleation rate calculations. As it will be shown later in **PAPER VI**, the use of properly derived values for the saturation vapor pressure will decrease the difference between the concentration in gas phase and the concentrations required for nucleation in the model from 7 orders of magnitude to 3 orders of magnitude only.

Unlike **PAPER I**, where homogeneous nucleation experimental data and a significant part of the thermophysical properties were missing, **PAPER II** is based on nucleation measurements of *n*-nonane and *n*-propanol and is devoted to the comparison with CNT. The composition and the size of the critical cluster were calculated as explained in Chapter 2. In addition, the expressions for the excess surface number of molecules are considered (eq. (7) and (8) in **PAPER II**). The surface numbers of molecules can be regarded as sensitive indicators of the failure of CNT. They should be just a minor correction to the bulk number rather than a dominant contribution for the theory to be valid. The effect of the expressions for the kinetic prefactor were analyzed, as extensively describe in the paper. The input parameters were the same as provided by the experiments: the temperature and the activity fraction, defined as $f = \frac{a_1}{a_1+a_2}$, with a_i being the vapor phase activities of the two components. The nucleation rates were calculated using two kinetic models and compared to the experimental data (Figure 6.3). Both theoretical estimations are accurate for higher activity fractions (towards the *n*-propanol end), while the approximate kinetics presents large deviations from the experimental data towards the *n*-nonane end. The onset activities for *n*-nonane and *n*-propanol corresponding to a constant nucleation rate, represents a sensitive way

of comparing the experimental data with the theoretical predictions, as shown in Figure 6.4. The theoretical curves bend strongly away from the experimental data, forming an almost right angle, which suggest that these two vapors do not conucleate.

When plotting the measured cluster composition in comparison with the theoretical values for total and core numbers of molecules, one can see that CNT predicts quite accurately the cluster composition (see Figure 12 in **PAPER II**). The difference between the total and core number of molecules is about 1, suggesting that CNT performs well for this system.

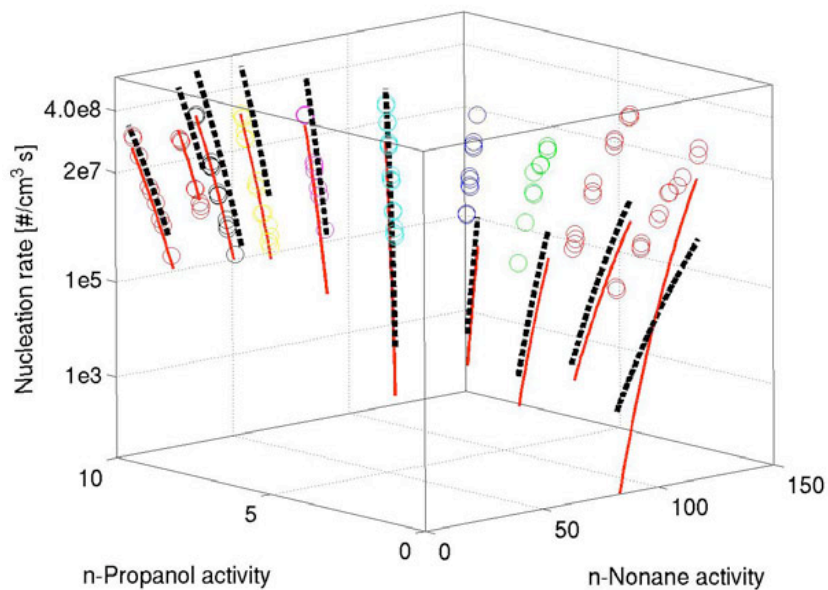


FIGURE 6.3: Binary nucleation rate of *n*-nonane and *n*-propanol: theoretical predictions (solid line for approximate kinetics and dashed line for accurate kinetics) and experimental data (circles)

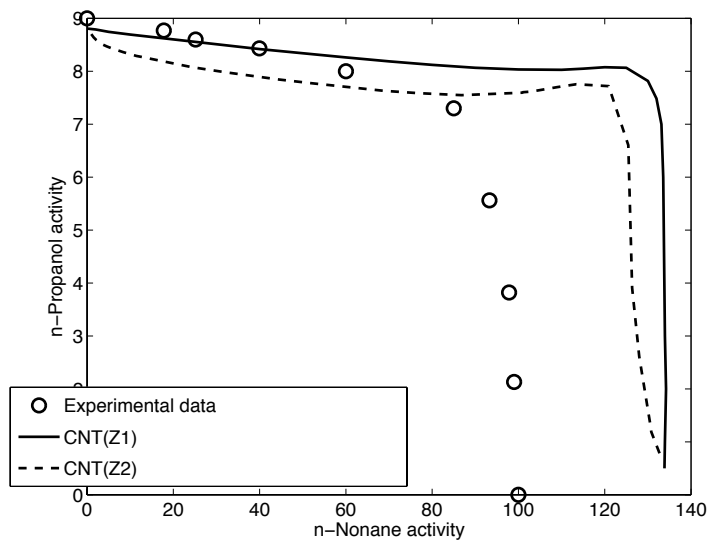


FIGURE 6.4: The vapor phase activities required for a constant nucleation rate of $10^7/\text{cm}^3 \cdot \text{s}$. The theoretical predictions (solid line for approximate kinetics and dashed line for accurate kinetics) are compared with the experimental data (circles) from Viisanen et al. (1998)

The departure of the predicted onset activities from the experimental data for intermediate to small concentrations of *n*-propanol is probably caused by an incorrect parameterization of some thermophysical property or by the fact that the CNT fails since the system is surface active. Also, the use of bulk thermophysical properties for very small clusters can be one of the reasons. However, the difference between the predicted and experimental nucleation rates at the *n*-nonane rich end is not more than 2 orders of magnitude. Also, the accurate kinetic prefactor reduces this difference and corrects the slope of the nucleation rate for pure *n*-nonane. For high *n*-propanol concentration, the CNT predicts fairly well the experimental results.

6.2 Heterogeneous nucleation

The classical theory of heterogeneous nucleation corrected with line tension (see the theory presented in Chaptres 3 and 4) is the subject of **PAPERS IV** and **V**. **PAPER IV** deals with unary and binary heterogeneous nucleation of *n*-nonane, *n*-propanol and their mixture on silver particles and **PAPER V** investigates the unary heterogeneous nucleation of *n*-nonane on different seed particles. Both **PAPERS IV** and **V** present experimental data and use the classical heterogeneous nucleation theory corrected with line tension, as explained in Chapter 4. **PAPERS VI** presents only theoretical predictions of heterogeneous nucleation for four dicarboxylic acids and water. In this calculations the line tension effect has been not considered.

First of all, the vapor-solid interfacial tension has to be calculated by means of the macroscopic contact angle (providing that such information is available), the surface tension of a liquid and with the help of Eq.(3.10). Using again the same equation for the same solid, but for a different liquid (either pure or mixture), the macroscopic contact angle formed by the liquid drop with the solid surface can be calculated. The size of the critical cluster can be calculated using the Kelvin equation (Eq. (2.3)) and the critical Gibbs free energy by Eq.(4.4). The input parameters were temperature, vapor phase activities and the nucleation probabilities provided by the experimental setup. The microscopic contact angle (connected to the line tension through Eq.(3.2)) was then varied in one-parameter-fit procedure until the theoretical nucleation probability equaled the experimental one. In this way the microscopic contact angle and line tension are obtained as a function of the radii of the seed particle and the liquid cluster. The variation of the cosine of the microscopic contact angle and the line tension with the cluster and seed particle radii is shown in Figure 6.5.

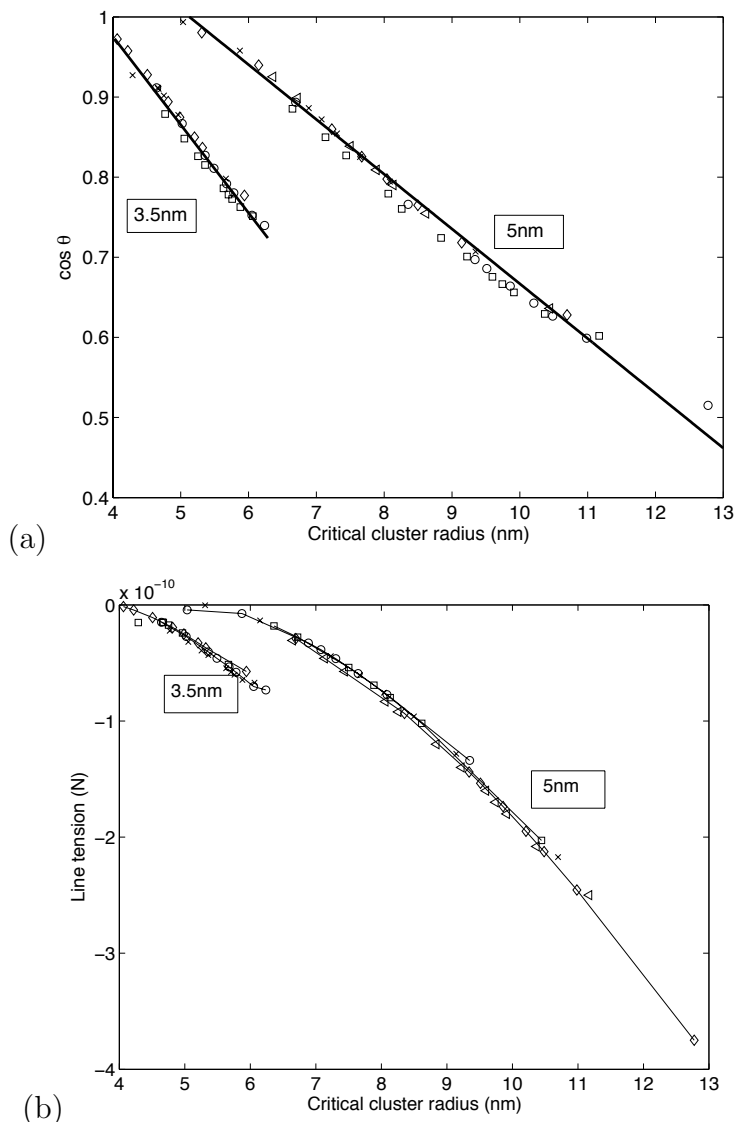


FIGURE 6.5: Microscopic contact angle [a] and line tension [b] for *n*-nonane and *n*-propanol on silver particles vs. the radius of the critical cluster. The values have been obtained by fitting the theoretical predictions to the experimental nucleation probability.

To visualize better the difference between the CNT and the line tension corrected CNT version, the onset saturation ratio can be plotted against the inverse of the seed particle diameter. In addition, Kelvin equation is included for comparison. Thermodynamically, the initial growth of the particles should start at the Kelvin diameter, corresponding to the size at which the vapor and aerosol particles are at equilibrium. In principle, if the particle size is bigger than the Kelvin diameter, the aerosol particles will grow; if smaller, they will evaporate. The experimental results, however, show that that growth starts well below Kelvin diameter, as presented in Figure 6.6 where

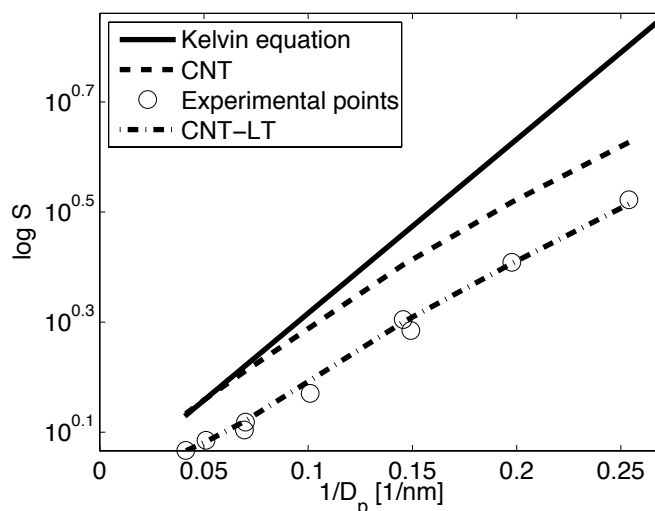


FIGURE 6.6: Onset saturation ration vs. the inverse of the seed particle diameter in comparison with Kelvin equation(solid line), CNT (dashed line), line tension corrected CNT (dash-dotted line) and experimental data (circles) for *n*-nonane on ammonium sulfate, silver and WO_x seed particles.

the calculations have been conducted for *n*-nonane on ammonium sulfate, silver and WO_x seed particles (the subject of **PAPER V**). The experimental points are all on a single line and the only satisfactory agreement is given by the CNT corrected with line tension.

The results of **PAPERS IV** and **V** underline the relevance of the microscopic substrate-liquid cluster interaction in heterogeneous nucleation, which has to be taken into account through the concepts of line tension and microscopic contact angle for a better characterization of the process. Unfortunately, this can not be achieved unless well defined experimental data for heterogeneous nucleation and knowledge of the substrate characteristics are available. Well defined experiments can be accomplished in laboratory, but in atmospheric conditions the theoretical studies of heterogeneous nucleation are difficult to relate to observations. The main part of the problem arises from the fact that the composition of the solid pre-existing particles is simply not known. This is the case in **PAPER VI**, where the binary homogeneous and heterogeneous nucleation of four dicarboxylic acids (succinic, glutaric, malonic and adipic acids) and water has been investigated. The model calculations follow the theory presented in Chapter 2. The aim of the study was to investigate whether the heterogeneous nucleation of the four organic acids and water is relevant in atmospheric conditions, as well as to compare the likelihood of the heterogeneous and homogeneous nucleation. The input

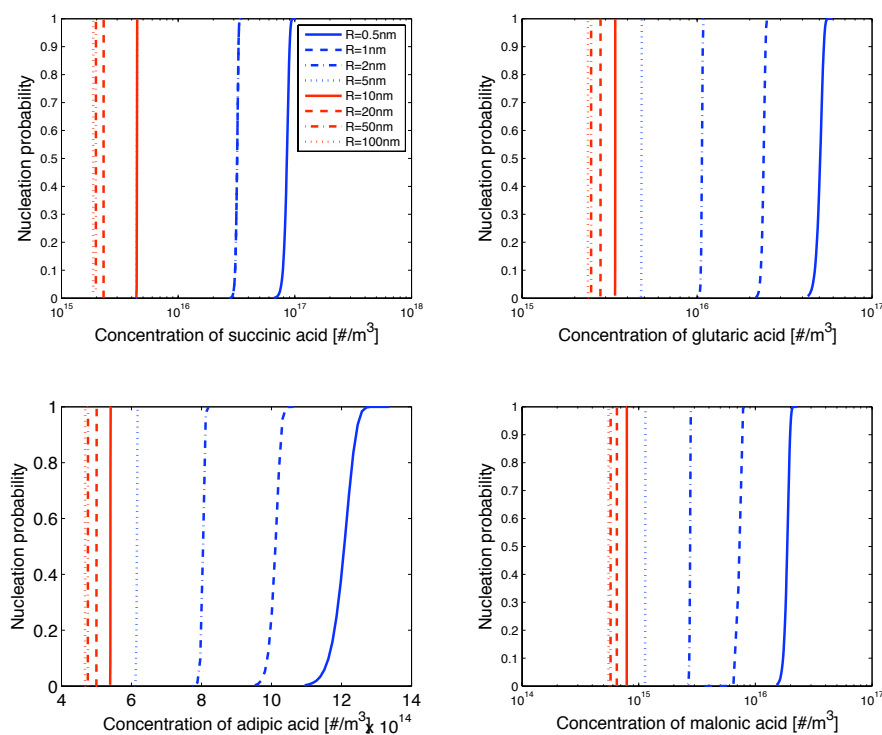


FIGURE 6.7: Nucleation probability for dicarboxylic acid-water systems vs. dicarboxylic acid concentration in gas phase. The radius of the seed particle is varied while temperature, relative humidity and macroscopic contact angle are fixed at $T=273\text{K}$, $RH=70\%$, $\theta=0$

parameters, namely the temperature, the relative humidity, the macroscopic contact angle and the diameter of the seed particle were varied one at the time, while the others were kept constant. The default values, considered relevant for the atmosphere, were set as: $T=273\text{ K}$, $RH=70\%$, contact angle ($\theta=0$ corresponding to total wetting) and seed particle radius $R=1\text{ nm}$.

As the nature of the substrate is not known, we analyzed its influence on the nucleation probability by considering different wetting properties, that is, by changing the values of the macroscopic contact angle. The nucleation probability depends on the contact angle, but not significantly, the required onset concentrations of the organic acids remaining within the same order of magnitude. Because the aerosol size distribution in atmosphere is very wide, the seed particle size influence was considered by including in the model calculations radii ranging from 0.5 nm to 100 nm. The smallest particles are less effective than the larger particles in reducing the nucleation barrier, but they are still able to promote nucleation. However, for large particles, with $R > 5\text{ nm}$,

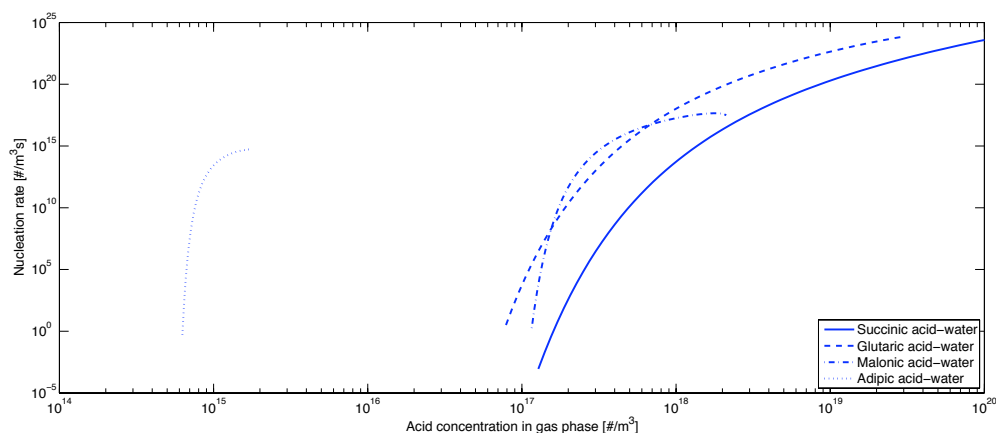


FIGURE 6.8: Modeled homogeneous nucleation rate for dicarboxylic acid-water system vs. dicarboxylic acid concentration in gas phase at $T=273$ K, $RH=70\%$ and $\theta=0$.

the calculated nucleation probabilities show an insignificant dependence on the seed particle radius (Figure 6.7).

The water vapor content, as well as the temperature in the atmosphere are expected to affect the rate of nucleation. The influence of the relative humidity is relatively weak, while the temperature seems to be the most important parameter in governing the binary nucleation rate of the systems.

The heterogeneous nucleation calculations were compared with the homogeneous nucleation rates for the same conditions. Figure 6.8 presents the homogeneous nucleation rates for the aqueous solutions of all four dicarboxylic acids. Succinic, glutaric and malonic systems require gas phase concentrations of about one order of magnitude higher for homogeneous nucleation, while for adipic acid, both types of nucleation take place at nearly the same concentration.

Information about the gas to particle partitioning of dicarboxylic acids is very sparse, and therefore it is difficult to compare the derived results with the literature data. Dicarboxylic acid concentrations vary with location and have a seasonal dependence [Legrand et al. (2007); Ho et al. (2007)]. According to the data presented by Limbeck et al. (2005), the dicarboxylic acid concentrations in the particulate phase ranged from 20 to 80 ng/m³, while the gaseous dicarboxylic acids were found to be 2-5 times smaller, equivalent with about 10¹³ molecules/m³. This implies that the binary heterogeneous nucleation of three out of four organic acids and water can not happen in atmospheric

conditions. Only adipic acid might be involved in the nucleation process in conditions occurring in the upper boundary layer.

6.3 Thermophysical properties

Knowledge of the thermophysical properties of the atmospheric relevant organics is crucial for modeling their contribution in the nucleation process. **PAPER III** provides temperature and composition-dependent surface tension and density measurements for aqueous solutions of several dicarboxylic acids. In ambient conditions, these acids have limited solubility in water and the measurements can be conducted only for concentrations under this limit. At the other end, the pure subcooled liquid properties of these organics can be estimated. Very often, the surface tension and density data for nucleation calculations are needed outside the bulk solubility limit. To cover the gap between the measured and the theoretically estimated properties, the data should be interpolated using thermodynamically consistent fitting equations.

In this work, the surface tension has been measured using the Wilhelmy plate method [Wilhelmy \(1863\)](#) and the density was determined as the weight/volume measurement of the bulk liquid. The density of the pure subcooled liquid compounds was determined by the Yen-Woods method, while their surface tension was determined using Macleod-Sugden method, as described in Chapter 5.

Several methods are available for modeling the surface tension and density of multi-component systems. For surface tension, the Chunxi method [[Chunxi et al. \(2000\)](#)] based on the thermodynamic definition of surface tension and on the expression for the Gibbs free energy was chosen for fitting the experimental data. The solution surface tension is a function of the pure liquid surface tensions, temperature and the composition, and includes four fitting parameters (Eq. (3) in **PAPER III**). The parameters were estimated by fitting the equation to the surface tension data measured at a constant temperature. Temperature - dependent surface tension measurements were then conducted and compared to the surface tensions estimated by the Chunxi equation. In a similar way the data for the binary solution density were used to fit Eq.(5.2). Overall, both equations are able to reproduce the measured surface tensions and densities, as well as to compensate for the missing values between the measured data and pure liquid surface tensions in a thermodynamically consistent way.

Chapter 7

Review of the papers

Six articles published in peer-reviewed journals are gathered in this thesis.

- **PAPER I** was one of the first studies to deal with binary homogeneous nucleation of water-succinic acid and water-glutaric acid systems using the classical nucleation theory. The thermodynamics involved is considered in detail. Both acids are in solid state at room temperature, but in small clusters they behave according to their liquid state properties. Therefore their subcooled liquid state thermodynamic has to be used. The model calculations show that these binary systems will not nucleate in atmospheric conditions.
- Homogeneous nucleation of binary *n*-nonane - *n*-propanol mixture is the subject of **PAPER II**. CNT predictions of the nucleation rates using both rigorous and approximate kinetics are compared to the previously reported experimental data. At the *n*-propanol rich end, the predicted rates resemble the experimental results, while on the *n*-nonane rich side the theoretical predictions are 2 orders of magnitude lower than the experiments when accurate kinetics is used and 3 orders lower for the approximate kinetics. The numbers of molecules in the critical cluster are approximated by CNT reasonably well.
- In **PAPER III** the densities of aqueous solutions of six dicarboxylic acids (oxalic, malonic, succinic, maleic, malic and *cis*-pinonic acids) were measured as a function of composition at a constant temperature, while the surface tensions – determined using Wilhelmy plate method – were measured also as a function of

temperature. The experimental data were fitted with thermodynamically consistent equations for mole fractions from 0 to 1. Assuming that the pure acids were in subcooled liquid state, their properties were theoretically estimated.

- **PAPER IV** describes a method of estimating the line tension and the microscopic contact angle using heterogeneous nucleation experimental data. Classical nucleation theory corrected with the line tension was fitted to the experimental results on heterogeneous nucleation of unary and binary n -nonane and n -propanol systems. The generalized Young's equation for the line tension and the Li and Neumann equation for the interfacial tensions were used. It has been found that the line tension is negative and the microscopic contact angle is larger than the macroscopic one for this systems. This has been explained by the fact that the liquid cluster covers more than a half of the seed particle and the negative line tensions tend to move the three phase contact line towards the equator of the particle, thus increasing the value of the microscopic contact angle above the macroscopic one. The study shows the importance of understanding the concept of line tension in heterogeneous nucleation.
- **PAPER V** is a continuation of **PAPER IV**. In this paper the heterogeneous nucleation of n -nonane on seed particles of different sizes and compositions has been investigated. The experimental data were compared to the classical nucleation corrected with the line tension and to the Kelvin equation. Apparently, the heterogeneous nucleation of n -nonane seems to be independent of the nature of the substrate and starts well below the Kelvin curve. This shows that the vapor considered would rather nucleate on pre-existing particles than to form new ones via homogeneous nucleation. The calculated microscopic contact angles are significantly different than the macroscopic ones and depend on the radii of the cluster and the seed particle. The line tension was found to be negative, result that comes in agreement with the previously calculated values presented in **PAPER IV**.
- **PAPER VI** comes as an extension of **PAPER I**. Both homogeneous and heterogeneous nucleation of succinic and glutaric acids with water were investigated. In addition, two other dicarboxylic acids, namely adipic and malonic, were examined using the classical nucleation theory. As the exact nature of the pre-existing particles is not known, the line tension concept was not included in the study. However, the substrate - liquid interaction was taken into account by varying the macroscopic contact angle. It has been shown that only adipic acid might

take part in the nucleation process in conditions occurring in the upper boundary layer. New thermodynamical properties were included for succinic acid and glutaric acid; while the new surface tension and density parameterizations for the aqueous solutions of these two acids do not bring any significant difference in the computed nucleation rates, the newly derived vapor pressures decrease the required acid concentrations with about 3 orders of magnitude in comparison with the results from **PAPER I**. Although heterogeneous nucleation needs a lower acid vapor pressure, it still can not take place in atmospheric conditions.

Author's contribution

I am alone responsible for the summary of this thesis.

In **PAPER I** and **PAPER II** I was responsible for the numerical calculations, as well as for the derivations of the thermophysical properties. I wrote nearly completely all the sections of the paper. For **PAPER III** I was responsible for calculating the subcooled liquid phase properties and I did most of the fittings. I also wrote parts of the text. In **PAPER IV** I modified the computational model for heterogeneous nucleation by including the line tension and the microscopic contact angle, I did the numerical calculations, and the comparison with the experimental data. I wrote almost the entire text of the article, except the experimental part. In **PAPER V** I was responsible for the model calculations, I wrote the nucleation part of the theory and part of the results. In **PAPER VI** I carried out the numerical calculations and wrote almost the entire text.

Chapter 8

Conclusions

This thesis is a collection of six studies. Five of them have as subject the nucleation - homogeneous or heterogeneous - of different organic compounds, while the sixth comes as a tool, a support for the others, providing measurements of thermophysical properties of aqueous solutions of six dicarboxylic acids and their thermodynamically consistent parameterizations.

Two issues have been questioned here: first, whether some atmospherically relevant organic compounds could be part of the new particle formation process in atmospheric conditions, and second, whether the classical nucleation theory can be "safely" used or modified for describing the nucleation process of organics.

To take the first steps towards answering the first question, theoretical investigations on the homogeneous and heterogeneous nucleation of four dicarboxylic acids (succinic, glutaric, adipic and malonic) and water have been conducted within the framework of classical nucleation theory. According to the model calculations, it appears that the binary nucleation of the succinic, glutaric and malonic acids and water can not happen in atmospheric conditions, the required concentration of organics theoretically estimated being 2-4 orders of magnitude higher than the measured concentration in ambient air. Adipic acid on the other hand might be involved in the process of particle formation in the upper boundary layer. However, atmospheric aerosol nucleation takes place in a multicomponent system containing a variety of gaseous species (sulfuric acid, ammonia, water, organic compounds, etc.), ions, molecular clusters, and particulate matter with different properties. Therefore one can not rule out the possible implication of the above mentioned organics in multicomponent nucleation. Many uncertainties in understanding the importance of atmospheric organic species for the

formation of the aerosol nucleation mode remain, and further – and probably more sophisticated – studies have to be considered.

The next question arises as a consequence of the investigations above: could CNT perform accurately enough to predict satisfactory nucleation rates for the organic compounds? This can be achieved by comparing the theory with well defined nucleation experimental results. Although the classical nucleation theory needs improvements to accurately predict the nucleation process, reasonable results can be obtained even for non-ideal systems, as is the case of homogeneous nucleation of *n*-nonane and *n*-propanol. On the other hand, the heterogeneous nucleation theory can be easily ameliorated by including the concepts of line tension and microscopic contact angle. In such a case the experimental results can be excellently explained by the CNT.

From the point of view of atmospheric aerosols and their climate interaction, the results of this work underpin the essential processes involved in organic new particle formation and provide a mechanism for more accurate representation of organic aerosol formation processes in global climate prediction models.

Here are the main results of this thesis:

- This thesis brings theoretical knowledge on the homogeneous and heterogeneous nucleation of atmospherically relevant dicarboxylic acid - water systems;
- Binary homogeneous and heterogeneous nucleation of dicarboxylic acid-water systems can not take place in atmospheric conditions, except for the adipic acid water system;
- The classical heterogeneous nucleation theory has been improved by including properly defined microscopic contact angles and line tension;
- The magnitude and sign of the line tension have been estimated for *n*-nonane, *n*-propanol and their mixtures on spherical silver particles;
- Thermophysical properties of some organic compounds have been measured and parameterized;
- The thermodynamics of dicarboxylic acid aqueous solutions has been extensively discussed and methods for calculating/predicting their properties have been offered.

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