

# The Dynamics of the Becker-Döring Model of Nucleation

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## Abstract

The early stage of phase transition is termed as *nucleation*. In this thesis we study one of the widely used nucleation models, which was developed by Becker and Döring in 1935. The model consists of large linear or nonlinear systems of ordinary differential equations. Our main emphasis is on the thermodynamically consistent Becker-Döring model which was introduced by Dreyer and Duderstadt [*J. Stat. Phys.*, 123, No. 1 (2006)]. Motivated by an industrial application concerning nucleation of liquid droplets in crystalline semi-insulating Gallium Arsenide, they developed a model which is consistent with the second law of thermodynamics. With condensation rates from the kinetic theory of gases, their model contains a singularity in the number of free molecules.

The mathematical theory of the Dreyer-Duderstadt version of the Becker-Döring model was studied by Herrmann et al. [*Physica D*, 222:116 - 130 (2006)]. They avoided the singularity by making a choice of condensation rates which transformed the model to a different time scale. In this work we discuss conditions under which the solutions of the transformed problem can be used to solve the original singular problem. We also show that the singular problem can be solved directly if appropriate initial conditions are chosen. In particular, due to the structure of the model solutions avoid the singularity.

With an aim of determining steady-state nucleation rates, we study in details the existence and uniqueness of steady-state solutions to the thermodynamically consistent model. We consider finite systems obtained by two different truncations. One is given by a zero flux to clusters larger than a specified maximum size, say  $n$ . The second one is obtained by setting the number of clusters larger than  $n$  to zero. We investigate the existence of steady-state solutions to the model in the limit  $n \rightarrow \infty$ .

Some applications such as fog formation as well as nucleation experiments include inert substances. For instance, experiments on homogeneous nucleation of water vapor, Argon and crystallization in solutions. For this reason, we extend the thermodynamically consistent model of Dreyer and Duderstadt by incorporating an inert substance. The extended model is non singular for all classes of condensation rates. The existence and uniqueness results for the extended model are analogous to those by Herrmann et al. [*Physica D*, 222:116 - 130 (2006)]. We derive a new correction for the classical nucleation rates from the extended model and compare the results with those from experiments.

This thesis also contains the proof for the existence of a metastable class of solutions to the thermodynamically consistent model. We make use of the theory of metastability by Penrose [*Commun. Math. Phys.*, 124:515 - 541 (1989)]. Interestingly, the results of this work show that there is no metastability in the Gallium Arsenide system studied by Dreyer and Duderstadt.

To our knowledge there are no analytical solutions for the Becker-Döring models. Here we describe an efficient numerical algorithm for solving the thermodynamically consistent model. Finally, we give numerical results for a particular example.



## Zusammenfassung

Mit Nukleation bezeichnen wir das Anfangsstadium des Phasenüberganges. In der vorliegenden Arbeit untersuchen wir ein weitverbreitetes Nukleations- bzw. Tröpfchenmodell, welches im Jahre 1935 von Becker und Döring entwickelt wurde. Es basiert auf einem großen System linearer oder nichtlinearer gewöhnlicher Differentialgleichungen. Unser Hauptaugenmerk liegt auf dem thermodynamisch konsistenten Becker-Döring-Modell, welches von Dreyer und Duderstadt eingeführt wurde [J. Stat. Phys., 123, No. 1 (2006)]. Motiviert durch eine neue industrielle Anwendung, die Nukleation von flüssigen Tropfen in kristallinem halbleitendem Gallium-Arsenid betreffend, entwickelten sie ein Modell, welches zum zweiten Hauptsatz der Thermodynamik konsistent ist. Ausgehend von Kondensationsraten aus der kinetischen Gastheorie, enthält ihr Modell eine Singularität in der Anzahl freier Moleküle.

Die mathematische Theorie der Dreyer-Duderstadt-Version des Becker-Döring-Modells wurde von Herrmann et al. [Physica D, 222:116 - 130 (2006)] untersucht. Hierbei wurde die Singularität durch eine neue Wahl von Kondensationsraten vermieden, welche das Modell auf eine andere Zeitskala transformiert. In der vorliegenden Arbeit diskutieren wir Bedingungen, unter denen die Lösungen des transformierten Modells zur Lösung des originalen singulären Problems benutzt werden können. Ferner zeigen wir, dass das singuläre Problem sogar direkt gelöst werden kann, wenn geeignete Anfangsbedingungen gewählt werden, da die Struktur des Modells die Singularität vermeidet.

Im Detail untersuchen wir Existenz und Eindeutigkeit stationärer Lösungen des thermodynamisch konsistenten Modells. Wir betrachten zwei unterschiedliche reduzierte endliche Systeme. Eins erhält man, indem man Flüsse zu Clustern ab einer speziellen maximalen Größe  $n$  ausschließt. Das andere Modell gewinnt man durch Setzen der Anzahl der Cluster größer  $n$  auf 0. Wir untersuchen jeweils die Existenz stationärer Lösungen für  $n \rightarrow \infty$ .

Zahlreiche Anwendungen wie Nebelbildung oder Nukleationsexperimente enthalten inerte Substanzen, z.B. Experimente zur homogenen Nukleation von Wasserdampf, Argon und Kristallisation in Lösungen. Aus diesem Grund erweitern wir das Dreyer-Duderstadt-Modell durch Berücksichtigung einer weiteren inerten Phase. Das erweiterte Modell ist nichtsingulär für alle Klassen von Kondensationsraten. Die Existenz- und Eindeutigkeitsresultate für das erweiterte Modell sind analog zu den Resultaten von Herrmann et al. [Physica D, 222:116 - 130 (2006)]. Wir leiten eine neue Korrektur für die klassischen Nukleationsraten vom erweiterten Modell her und vergleichen die Resultate mit experimentellen Daten.

Die vorliegende Arbeit enthält weiterhin einen Existenzbeweis für eine Klasse metastabiler Lösungen des thermodynamisch konsistenten Modells. Dafür wird die Theorie metastabiler Lösungen von Penrose [Commun. Math. Phys., 124:515 - 541 (1989)] benutzt. Interessanterweise zeigen die Resultate dieser Arbeit, dass es keine Metastabilität im Gallium-Arsenid-System von Dreyer, Duderstadt gibt.

Nach Kenntnis des Verfassers gibt es keine analytische Lösung für das Becker-Döring-Modell. In der vorliegenden Arbeit wird ein effizienter numerischer Algorithmus zur Lösung des ther-

modynamisch konsistenten Modells beschrieben. Abschließend werden numerische Resultate für ausgewählte Beispiele gegeben.



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# Chapter 1

## Introduction

In this chapter we give a general introduction to the Becker-Döring model, including the model description and its different versions together with the terminologies and notation used. Simultaneously, we review some of the existing literature. In the end we outline the structure of the thesis and briefly mention the new results of our work.

### 1.1 The standard Becker-Döring model

Burton [7] as well as Seinfeld and Pandis [52, Chapter 11] pointed out that it is widely believed that cooling humid air to its dew point results into condensation. Similarly it is generally thought that at a pressure of 1 atm, water boils at  $100^{\circ}\text{C}$ . These views are incorrect if taken as generalizations applicable under all conditions. Clean water, free of foreign materials or wall surfaces, can be superheated before boiling. Pure water vapor can as well be under-cooled before condensation. These curious phenomena are manifestations of *metastability*, which is the ability of a non-equilibrium physical state to persist for a long time.

A transformation of a phase  $\alpha$  into  $\beta$  doesn't occur the instant the free energy of  $\beta$  is lower than that  $\alpha$ . Rather tiny nuclei of  $\beta$  must form initially in  $\alpha$ . This is schematically represented in Figure 1.1. Initially, tiny clusters of  $\beta$  form in the  $\alpha$  phase (a). These then grow (b) until the

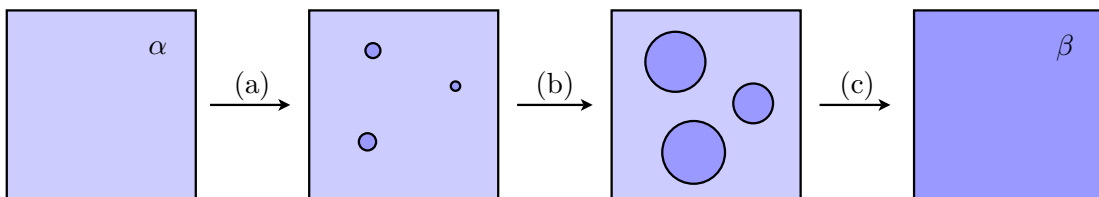


Figure 1.1: Schematic representation of a transformation from an unstable phase  $\alpha$  to a stable phase  $\beta$ .

transformation is complete (c). The first step in the transformation, the nucleation step, can be extremely slow. Nucleation theory attempts to answer the question, "What is the nucleation rate at a given supersaturation?". Attempts to answer this question led to what is commonly known as the classical nucleation theory. The theory includes both purely thermodynamic

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arguments, for instance by McDonald [37], and kinetic arguments, see Becker and Döring [5]. Kashchiev [27] gave a review of both approaches while Seinfeld and Pandis [52] have a chapter on nucleation. Schmelzer [51] also gave a detailed account of nucleation theory together with some applications, which include atmospheric aerosols, crystallization, polymerization and many other phase transition processes.

The classical nucleation theory originated with the work of Volmer and Weber [65] in 1926. It was mainly developed to describe nucleation of liquid droplets in vapor. By using the kinetic theory of gases and equilibrium thermodynamics, they derived an expression for the nucleation rates. However most experiments show that the theoretically calculated nucleation rates have a stronger temperature dependence than the observed ones, see for instance Wölk and Strey [71], Brus et al. [6], and Sinha et al. [57].

In 1935 Becker and Döring [5] established the steady-state version of the so called Becker-Döring model. In this model, the smallest particle is referred to as a *molecule* and a *cluster* is a composition of two or more molecules. The size of a cluster is determined by the number  $i$  of molecules it constitutes. We call a cluster with  $i$  molecules an  $i$ -mer. Becker and Döring assumed that during nucleation, an  $i$ -mer grows by an addition of a molecule at a rate  $C_i$  referred to as the *condensation rate* or shrinks by losing a molecule at a rate  $E_i$  known as the *evaporation rate*. The rates  $C_i$  and  $E_i$  may or may not depend on time. Moreover, it is even possible to have size independent condensation and evaporation rates. The model considers finite or infinite systems of free molecules and their clusters. In the standard Becker-Döring model, we denote the *concentration* of free molecules and  $i$ -mers at time  $t$  by  $z_1(t)$  and  $z_i(t)$  respectively. The concentration has units of number per unit volume. Let  $m$  be the *molecular mass*. Denote the density of a system containing free molecules and  $i$ -mers of different sizes by  $\rho$ . Then we have

$$\rho(\mathbf{z}(t)) := m \sum_{i=1}^{\infty} i z_i(t). \quad (1.1)$$

Unless otherwise specified, we assume that a molecule has a unit mass, that is, we set  $m = 1$ .

The Becker-Döring model is given by the following set of ordinary differential equations for  $\mathbf{z}(t) := (z_i(t))_{i \in \mathbb{N}}$

$$\dot{z}_i(t) = J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)) \quad \text{for } 2 \leq i, \quad (1.2)$$

where  $\dot{z}$  denotes differentiation of  $z$  with respect to  $t$ . The *flux function*  $J_i$  for  $i \in \mathbb{N}$  is given in the form

$$J_i(\mathbf{z}(t)) = C_i z_i(t) - E_{i+1} z_{i+1}(t). \quad (1.3)$$

It is the net rate of conversion of an  $i$ -mer into an  $(i+1)$ -mer. We have not yet specified the behavior of  $z_1(t)$ . There are two common ways to do this. One is a result of the experimental technique by Becker and Döring. They added free molecules to the system in order to keep the outer pressure constant. In a steady state the concentration of free molecules is constant. However, this steady state consequence was mis-interpreted by a number of authors and they assumed that it holds even for time dependent solutions, see Kashchiev [27, Chapter 15] and

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McDonald [37]. This led to the so-called *constant free molecule model* where the concentration of free molecules is given by

$$z_1(t) = z_1(0) = \mu \quad (\mu \text{ a constant}). \quad (1.4)$$

Schmelzer [50, p. 1920] suggested that this condition implies that the supersaturation does not change in time. We point out that this case does not conserve the density (1.1).

The second prescription of  $z_1(t)$  leads to the *density-conserving model* or equivalently the *mass-conserving model* for which we have to take

$$\dot{z}_1(t) = -2J_1(\mathbf{z}(t)) - \sum_{i=2}^{\infty} J_i(\mathbf{z}(t)), \quad (1.5)$$

so that  $\rho$  becomes time independent. We note that the equation for  $\dot{z}_1(t)$  is given differently from those for bigger clusters. It is because free molecules are involved in all reactions. The formation of a di-mer makes use of two free molecules. On the other hand, when a di-mer breaks up, there are two free molecules that are formed. This explains the presence of the factor 2 in equation (1.5). The density conserving version of the model was presented by Burton [7]. There Burton also calculated the steady-state nucleation rates from the dynamic model.

The Becker-Döring model is complete when the rates  $C_i$  and  $E_{i+1}$  are specified and it is solved for initial conditions

$$z_i(0) \geq 0 \quad \text{for } i \in \mathbb{N}. \quad (1.6)$$

In the standard Becker-Döring models, see for instance Burton [7], Penrose [46], as well as Penrose and Lebowitz [48], the following constitutive assumptions are used

$$C_i(t) = a_i z_1(t), \quad E_i(t) = b_i, \quad (1.7)$$

where  $a_i$  and  $b_i$  are referred to as *kinetic coefficients* and they depend neither on the solution  $\mathbf{z}$  nor on the time  $t$ . Typical are the following examples, see Herrmann et al. [24, p. 117]

$$a_i = i^\alpha, \quad b_i = a_i \left( \mu_s + \frac{p}{i^\gamma} \right),$$

with  $\alpha \in [0, 1]$ ,  $\mu_s > 0$ ,  $\gamma < 1$ ,  $p > 0$ , and

$$\begin{aligned} \alpha = 1/3, \quad \gamma = 1/3 & \text{ for diffusion controlled kinetics in 3D,} \\ \alpha = 0, \quad \gamma = 1/2 & \text{ for diffusion controlled kinetics in 2D,} \\ \alpha = 2/3, \quad \gamma = 1/3 & \text{ for interface reaction limited kinetics in 3D,} \\ \alpha = 1/2, \quad \gamma = 1/2 & \text{ for interface reaction limited kinetics in 2D.} \end{aligned}$$

It is important to emphasize here that the *standard Becker-Döring model* consists of equation (1.2), (2.91) together with either (1.4) or (1.5) and (1.6) - (1.7), with  $\mathbf{z}$  having units of concentration.

Although the constant free molecule model is potentially less relevant in physical applications, it provides an instructive mathematical problem as a precursor to the analysis of the more

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demanding nonlinear density-conserving model. The mathematical properties of the standard mass-conserving model were discussed by Ball et al. [4]. There the authors studied the existence and uniqueness of time dependent and equilibrium solutions to the model, as well as the behavior of solutions in the limit  $t \rightarrow \infty$  under some restrictions on the kinetic coefficients and initial data. One notable restriction was the strong requirement  $\sum_{i=1}^{\infty} i^2 z_i(0) < \infty$  which they used in order to prove the uniqueness of solutions. Laurençot and Mischler [34] later proved uniqueness of the solution without such a restriction. Some of the important results regarding the solutions for the standard Becker-Döring model are summarized below.

Define the cluster partition functions

$$Q_i := \prod_{r=2}^i \frac{a_{r-1}}{b_r}, \quad Q_1 = 1. \quad (1.8)$$

There exist Lyapunov functions  $L_\mu(\mathbf{z})$  and  $L_\rho(\mathbf{z})$  for the constant free molecule and constant density models respectively. They are defined by, see Wattis [68]

$$L_\mu(\mathbf{z}(t)) := \sum_{i=1}^{\infty} z_i(t) \left( \ln \left( \frac{z_i(t)}{Q_i \mu^i} \right) - 1 \right) \text{ and } L_\rho(\mathbf{z}(t)) := \sum_{i=1}^{\infty} z_i(t) \left( \ln \left( \frac{z_i(t)}{Q_i} \right) - 1 \right), \quad (1.9)$$

where  $\mu$  is given in (1.4). The simplest solutions for the model are those for which the fluxes in (2.91) vanish. They are termed as *equilibrium solutions* and can be shown to be

$$\bar{z}_i = Q_i (\bar{z}_1)^i. \quad (1.10)$$

This structure is the motivation to consider  $\mu = \bar{z}_1$  as a free parameter. It is an arbitrary positive number which can be interpreted as the *activity* or *fugacity* of the equilibrium state. For the mass conserving model, the parameter  $\mu$  is calculated from

$$\rho = \sum_{i=1}^{\infty} i Q_i \mu^i, \quad (1.11)$$

which makes sense only if the series on the right-hand side is convergent. It is therefore natural to determine the radius  $\mu_s$  of convergence of the series, which may be infinite, finite or zero depending on the partition functions. The density  $\rho_s$  of saturated vapor is defined by

$$\rho_s := \sum_{i=1}^{\infty} i Q_i \mu_s^i \quad (1.12)$$

and may be finite or infinite.

Ball et al. [4] showed for the mass-conserving model that in the limit  $t \rightarrow \infty$  all the mass can be contained in an equilibrium solution only if the initial density in a given system is less or equal to the saturation density, that is, if  $\rho \leq \rho_s$ . In this case the solutions converge strongly to the equilibrium (1.10), where  $\mu = \bar{z}_1$  is the unique solution of (1.11). On the other hand, they proved that for  $\rho > \rho_s$ , the solutions converge in some weak sense to an equilibrium of the form (1.10) with  $\bar{z}_1 = \mu_s$  and density  $\rho_s$ . The density difference  $\rho - \rho_s$  goes to large and larger clusters. In this

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regime the cluster evolution can be determined by the Lifshitz-Slyozov-Wagner (LSW) model of coarsening, which describes the late stages of growth in a phase transition, see Laurençot and Mischler [34], Penrose [47], Collet et al. [10], Velázquez [64] as well as Niethammer [43]. Other results on the asymptotic behavior of solution for the Becker-Döring equations can be found in Slemrod [58], Wattis and King [70], Jabin and Niethammer [26], Laurençot and Wrzosek [35] as well as Niethammer [44]. For general information regarding the analysis of ordinary differential equations, one can consult the books by Hartman [23], Walter [67], Arnol'd [1] and Mattheij [36].

Other simple solutions of the standard Becker-Döring model are the non-equilibrium steady-state solutions which were constructed by Becker and Döring [5] for the constant free molecule model. Here the fluxes  $J_i$  are independent of both the size  $i$  and the time  $t$ , but are not equal to zero. The common value of the fluxes, denoted by  $J(\mu)$  is called the *nucleation rate*. It is defined as the rate per unit volume at which clusters acquire new particles in the steady state. It is given by

$$J(\mu) = \left[ \sum_{i=1}^{\infty} \frac{1}{a_i Q_i \mu^{i+1}} \right]^{-1}, \quad (1.13)$$

while the steady-state distribution, denoted by  $\mathbf{f}(\mu) = (f_i(\mu))_{i \in \mathbb{N}}$  is such that

$$f_1(\mu) = \mu \quad \text{and} \quad f_i(\mu) = J(\mu) Q_i \mu^i \sum_{r=i}^{\infty} \frac{1}{a_r Q_r \mu^{r+1}}. \quad (1.14)$$

Becker and Döring showed that for moderately small values of the difference  $\mu - \mu_s$ , the nucleation rate  $J(\mu)$  can be extremely small, so small as to be completely undetectable experimentally. This made it possible to think of the steady state as representing a metastable state in which large clusters are being formed extremely slowly. Penrose [46] went beyond the Becker-Döring steady-state consideration. He proved that, subject to some further plausible conditions on the kinetic coefficients  $a_i$  and  $b_i$ , there exists a class of time dependent metastable solutions for the model with  $\mu - \mu_s$  positive and small. The solutions take an exponentially long time to decay to their asymptotic steady states and have a lifetime which is proportional to  $\exp\{C(\mu - \mu_s)^\omega\}$  for some constants  $C, \omega > 0$ . His results were based on the theory of metastability which he developed together with Lebowitz [48]. Kreer [30] extended Penrose's results by allowing for a bigger class of the initial data and using a different method to construct metastable solutions for the constant free molecule model. Duncan and Dunwell [18] later showed that metastability for the truncated constant free molecule model can be explained in terms of the eigensystem of the resulting linear ordinary differential system.

Carr et al. [9] described an efficient numerical algorithm for solving the truncated standard mass-conserving model. They observed that for small values of the difference  $\mu - \mu_s$ , one requires numerical solutions of very large systems in order to distinguish between the metastable and equilibrium states. Duncan and Soheili [19] described numerical techniques for solving large systems of the truncated standard mass-conserving model on a reduced number of grid points.

## 1.2 The modified Becker-Döring model

Motivated by an industrial application concerning nucleation of liquid droplets in crystalline semi-insulating Gallium Arsenide (GaAs), Dreyer and Duderstadt [16] proposed a modification to the standard mass-conserving formulation. They made three notable changes to the model. Firstly they changed the interpretation of  $z_i(t)$  from concentration to *number of  $i$ -mers* at time  $t$ . Secondly, they reviewed the derivation of the condensation rate formula from the kinetic theory of gases. They obtained condensation rates of the form

$$C_i = a_i, \quad (1.15)$$

which do not explicitly contain  $z_1(t)$ , in contrast to the ones in (1.7). For the third change, they used the second law of thermodynamics to obtain a dynamic relationship between the condensation and evaporation rates. The idea was to determine the total available free energy of closed systems. Suppose the available free energy of a closed system containing an  $i$ -mer is denoted by  $\mathcal{A}_i$  and let  $k$  and  $T$  represent the Boltzmann constant and temperature respectively. Dreyer and Duderstadt [16] determined expressions of  $\mathcal{A}_i$  for two examples. These are summarized below.

**Example 1.2.1.** *This corresponds to a simple liquid-vapor system in which a liquid droplet of size  $i$  is surrounded by its vapor. At a temperature  $T$  and outer pressure  $p_0$  the availability  $\mathcal{A}_i$  is given by, see Müller and Müller [39, p. 310]*

$$\mathcal{A}_1 = 0, \quad \mathcal{A}_i = -kTi \ln \left( \frac{p_0}{\bar{p}(T)} \right) + \gamma i^{2/3}, \quad i \geq 2, \quad \gamma > 0, \quad (1.16)$$

where  $\bar{p}(T)$  is the vapor-liquid equilibrium pressure at the temperature  $T$ .

**Example 1.2.2.** *Here the system consists of a single liquid droplet of size  $i$  contained in a crystalline solid. Both are a binary mixture of gallium and arsenic. The solid is surrounded by an inert gas with prescribed pressure. For large  $i$ , the availability grows linearly with  $i$ , see Herrmann et al. [24]. This leads to the ansatz*

$$\mathcal{A}_i = \beta i, \quad \text{for } i \gg 1, \quad \beta > 0. \quad (1.17)$$

The availability  $\mathcal{A}_i$  gives the energy change when a cluster of size  $i$  is formed. Therefore the convention  $\mathcal{A}_1 = 0$  was used by Dreyer and Duderstadt [16]. They defined the total available free energy of a many cluster system as

$$\mathcal{A}(\mathbf{z}(t)) = \sum_{i=1}^{\infty} z_i(t) \mathcal{A}_i + kT \sum_{i=1}^{\infty} z_i(t) \ln \left( \frac{z_i(t)}{N_D(\mathbf{z}(t))} \right), \quad (1.18)$$

where the total number  $N_D$  of clusters and free molecules is defined as

$$N_D(\mathbf{z}(t)) := \sum_{i=1}^{\infty} z_i(t). \quad (1.19)$$

The first term in (1.18) is the sum of all the free energies of single cluster systems whereas the second term takes care of the entropy of mixing. Equivalently, the total energy can be written as

$$\mathcal{A}(\mathbf{z}(t)) = kT \sum_{i=1}^{\infty} z_i(t) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right), \quad \text{with } q_i = \exp(-\mathcal{A}_i/kT). \quad (1.20)$$



## 1.2. THE MODIFIED BECKER-DÖRING MODEL

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Differentiating  $\mathcal{A}$  with respect to  $t$  and using the mass-conserving model (1.2), (2.91), and (1.5) we obtain

$$\dot{\mathcal{A}}(\mathbf{z}(t)) = kT \sum_{i=2}^{\infty} (C_i z_i(t) - E_{i+1} z_{i+1}) \ln \left( \frac{z_{i+1} q_i}{z_i q_{i+1} N_D(\mathbf{z}(t))} \right). \quad (1.21)$$

Dreyer and Duderstadt [16] used the second law of thermodynamics,  $d\mathcal{A}(t)/dt \leq 0$ , to obtain the following relation between the condensation and evaporation rates

$$E_{i+1}(t) = \frac{q_i N_D(\mathbf{z}(t))}{q_{i+1} z_1(t)} C_i, \quad i \geq 1. \quad (1.22)$$

It is a sufficient condition to guarantee that the law holds for all  $t > 0$ . Thus they were able to describe a dynamic model which is consistent with the second law of thermodynamics. Hence we refer to it as the *modified Becker-Döring model* or the *thermodynamically consistent model*. By using (1.22) to substitute for the evaporation rates in (2.91), the flux for the modified model becomes

$$J_i(\mathbf{z}(t)) = C_i \left( z_i(t) - \frac{q_i N_D(\mathbf{z}(t))}{q_{i+1} z_1(t)} z_{i+1} \right) \quad \text{for } i \geq 1, \quad (1.23)$$

which is now singular in  $z_1(t)$ .

Some of the mathematical properties of the modified model were studied by Herrmann et al. [24]. Instead of the condensation rates in (1.15), they used the ones in (1.7), thereby avoiding the singularity of the new model. However, their choice of the condensation rates transformed the problem to a different time scale. Under some conditions on the kinetic parameter  $a_i$  and  $q_i$ , they proved the existence and uniqueness of mass-conserving solutions to the transformed problem. Unfortunately they left the important question open, whether these results can be transformed back to the original problem. This point will be addressed in this thesis.

Similarly to the standard mass-conserving model, Herrmann et al. [24] solved for the equilibrium solutions to the modified model and discussed the conditions under which such solutions exist. In the end they discussed the behavior of solutions in the limit  $t \rightarrow \infty$ . In summary, they obtained the results below. Define the following

$$R := \lim_{i \rightarrow \infty} \frac{q_i}{q_{i+1}}, \quad \tilde{q}_i := R^i q_i \quad \tilde{f}(\mu) := \sum_{i=1}^{\infty} \tilde{q}_i \mu^i \quad \text{and} \quad \tilde{g}(\mu) := \sum_{i=1}^{\infty} i \tilde{q}_i \mu^i, \quad (1.24)$$

where  $q_i$  is given in (1.20). For any given mass  $\bar{\rho} > 0$ , there exists an equilibrium state  $\bar{\mathbf{z}}$  with  $\rho(\bar{\mathbf{z}}) = \bar{\rho}$  if and only if

$$\tilde{f}(1) > 1, \quad \text{or} \quad \tilde{f}(1) = 1 \quad \text{and} \quad \tilde{g}(1) < \infty. \quad (1.25)$$

Moreover, if (1.25) is satisfied, then

- (a) there exists a unique value  $\bar{\mu} \in ]0, 1]$  such that  $\tilde{f}(\bar{\mu}) = 1$ .

(b) the equilibrium solution is given by

$$\bar{z}_i = N_D(\bar{\mathbf{z}})\tilde{q}_i\bar{\mu}^i, \quad i \geq 1, \quad N_D(\bar{\mathbf{z}}) = \frac{\bar{\rho}}{\tilde{g}(\bar{\mu})}, \quad (1.26)$$

where  $\bar{\mu}$  is the unique solution of  $f(\bar{\mu}) = 1$ .

They proved that if (1.25) is satisfied, the solutions to the modified mass-conserving model converge strongly to the above equilibrium distribution in the limit  $t \rightarrow \infty$ . In fact the equilibrium solution is the unique minimizer of the total available free energy function (1.20). On the other hand, if (1.25) is not satisfied, the distribution  $\mathbf{z}$  converges in some weak sense to zero and all the mass is contained in larger and larger clusters. In this case the infimum of  $\mathcal{A}(\mathbf{z}(t))$  is zero but there is no minimizer. To conclude this section, we write the flux (1.23) in terms of the kinetic coefficients  $a_i$  and  $b_i$  introduced already in (1.7). Our aim is to work with a notation which is closer to the one used in the standard model. We use (1.15) and  $\tilde{q}_i$  in (1.24) to define

$$b_{i+1} := C_i \frac{\tilde{q}_i}{\tilde{q}_{i+1}} = a_i \frac{\tilde{q}_i}{\tilde{q}_{i+1}}. \quad (1.27)$$

The flux (1.23) can then be written as

$$J_i(\mathbf{z}(t)) = a_i z_i(t) - b_{i+1} R \frac{N_D(\mathbf{z}(t))}{z_1(t)} z_{i+1} \quad \text{for } i \geq 1. \quad (1.28)$$

This clearly differs from the flux  $J_i(\mathbf{z}(t)) = a_i z_1(t) z_i(t) - b_{i+1} z_{i+1}$  for the standard mass-conserving model. Moreover equations (1.8), the definition of  $\tilde{q}_i$  in (1.24), and (1.27) imply that

$$\frac{b_{i+1}}{a_i} = \frac{Q_i}{Q_{i+1}}, \quad \tilde{q}_i = R Q_i, \quad \text{and} \quad q_i = Q_i (1/R)^{i-1} \quad \text{for } i \geq 1. \quad (1.29)$$

### 1.3 Thesis structure and new results

The thesis is divided into three parts. The first part consists of Chapter 2 and it is devoted to the modeling. Here we review some of the relevant formulas used in nucleation theory. These include condensation, evaporation and nucleation rate expressions. We extend the results of Dreyer and Duderstadt [16] by allowing for the possibility of having an inert substance in a given system. This was motivated by the fact that some applications like fog formation as well as nucleation experiments contain inert substances. For instance the results of Brus et al. [6] as well as Wölk and Strey [71] on homogeneous nucleation of water vapor. Even the experiments on Argon nucleation by Sinha et al. [57] contained Helium as a carrier gas. Similarly during crystallization from solutions, the solvent can be regarded as an inert substance. Our results show that the presence of an inert substance is reflected in the entropy of mixing. Like in the standard mass-conserving model, we pose a constant-free molecule model for the modified model of Dreyer and Duderstadt. This was also done recently by Wattis [69]. He used his constant free molecule version as a stepping stone to construct approximations to the cluster size distribution of the more demanding mass-conserving version by matched asymptotic expansions.

### 1.3. THESIS STRUCTURE AND NEW RESULTS

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In his formulation, Wattis used condensation rates of the form in (1.7) and evaporation rates in (1.22), while setting  $z_1(t)$  to a constant. He showed that the model constructed in this way does not possess a Lyapunov function. Here we construct a constant free-molecule model which is consistent with the second law of thermodynamics. During our discussion with Wolfgang Dreyer, he pointed out that the constant free molecule model can be realized in practice only for open systems. We therefore consider open systems to derive the model. In our version of the constant free molecule model, we maintain the condensation rates (1.15) derived by Dreyer and Duderstadt, while the expressions for the evaporation rates are now different from those for the mass-conserving model given in (1.22).

The second part of the thesis consists of Chapters 3 - 6. It contains the mathematical theory of the modified Becker-Döring models. In Chapter 3 we study the simple steady-state problem for the two versions of the modified model, in which all time derivatives are equal to zero. The method involves the analysis of the null space of the right-hand sides of the models. This technique was used by Conradi et al. [11] to determine steady-state solutions for chemical and biochemical networks. We introduce the method to the simpler constant-free molecule model and later apply the same procedure to the more demanding mass-conserving version. For each version of the model we construct finite systems of differential equations by applying two known truncations. In the first truncation, we choose the maximum cluster size, say  $n$ , which is bigger than the critical cluster and set the flux  $J_n$  to zero. We refer to this as the *zero flux truncation*. The second one is obtained by setting the number of clusters larger than  $n$  to zero. We call it the *zero particle number truncation*. The zero flux truncation was used by Dreyer and Duderstadt [16] while the zero particle number truncation was described by Burton [7]. It is important to note that the zero particle number truncation is equivalent to removing clusters of size  $n + 1$  from the system as soon as they appear and thus leads to loss of mass. We remedy this for the mass-conserving model by re-inserting a mass of free molecules which is equal to that of the removed cluster. For the zero flux truncation, we prove the existence and uniqueness of equilibrium solutions where  $J_i = 0$  for all  $1 \leq i \leq n$ . In the zero particle number truncation we obtain unique steady-state solutions in which all the fluxes have a common non-zero value known as the *steady-state nucleation rate*. We compare the steady-state solutions for the two models and also study the case where  $n \rightarrow \infty$ . We close the chapter by comparing the steady-state nucleation rates for the more relevant mass-conserving model with the ones from the classical nucleation theory. Interestingly, in the presence of an inert substance we derive a new correction for the classical nucleation rate expression. We compare the new result with the rates observed in experiments.

Chapter 4 contains the results for the existence and uniqueness of solutions to the modified model. We study a general modified model which accounts for the presence of an inert substance in a given system. The number of molecules of the inert substance is denoted by  $z_0$ , which takes on values greater or equal to zero depending on whether there is an inert substance present or not. As mentioned in the introductory section, the existence and uniqueness of solutions for the case  $z_0 = 0$  was already studied by Herrmann et al. [24]. They made a choice of condensation rates,  $C_i = a_i z_1(t)$  which removed the singularity from the model, thereby transforming the problem to a different time scale. In this chapter we discuss the conditions under which the solutions of the transformed problem can be used to solve the original singular problem. We also show that the singular problem can be solved directly if appropriate initial conditions are

## CHAPTER 1. INTRODUCTION

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chosen. In particular, due to the structure of the model solutions avoid the singularity. However, for the singular problem, we are able to prove uniqueness of solutions for all  $t \geq 0$  only for size independent condensation rates. For  $z_0 > 0$  the resulting condensation rates lead to a model without singularity. The existence and uniqueness results for this case are analogous to the results by Herrmann et al. [24]. In the presence of an inert substance, the conditions for existence of equilibrium solutions are more general than those for which there is no inert substance. In all cases, there is an upper bound  $\rho_s$  on the mass contained in an equilibrium solution. This is similar to the case for the standard mass-conserving model which was studied by Ball et al. [4]. Moreover for  $z_0 > 0$  and large initial super-saturation, it is possible to have an asymptotic solution consisting of two different phases. This is in contrast to the liquid-vapor system without inert substance, which was considered by Dreyer and Duderstadt [16]. Although not included in this thesis, we believe that for  $z_0 > 0$  and  $\rho > \rho_s$  the solutions to the model converge in some weak sense to an equilibrium with mass  $\rho_s$ , the difference  $\rho - \rho_s$  being transferred to larger and larger clusters.

In Chapter 5 we study the existence of metastable solutions to the modified mass-conserving model. With careful choices of the various parameters in the model, we show that the results by Penrose [46] also extend to this model. We consider the case where (1.25) is violated. Unlike the standard mass-conserving model where metastability is related to the concentration  $z_1(t)$  of free molecules, here the results are related to the parameter  $\tilde{\mu}(0)$  defined by  $\tilde{\mu}(0) := z_1(0)/RN_D(\mathbf{z}(0))$ , where  $R$  is given in (1.24). We show that metastable solutions exist if  $\tilde{\mu}(0) > 1$ . Since the result  $z_1(t)/N_D(\mathbf{z}(t)) \leq 1$  holds, this condition requires that  $R < 1$ . This means that there is no metastability in the Gallium Arsenide example which was studied by Herrmann et al. [24]. Importantly, the kinetic coefficients  $a_i = 1$  and  $b_{i+1} = \exp(\tilde{a}\{i^{2/3} - (i-1)^{2/3}\})$  with  $\tilde{a} = 1$ , which were used for the standard model by Carr et al. [9], do not qualify for metastability in the modified model. In particular this parameter must satisfy  $\tilde{a} > 1.2$  in order to guarantee the negation  $\tilde{f}(1) < 1$  of (1.25).

Chapter 6 is devoted to constructing numerical solutions to the modified mass-conserving model. Here we study only finite systems for the model, making use of the two truncations introduced in Chapter 3. We modify the numerical algorithm for solving the standard mass-conserving model, which was described by Carr et al. [9]. They reformulated the standard model into a system of Differential Algebraic Equations (DAE) and used the simple Euler backward difference formula to discretize the DAE. They applied the Newton method to solve the resulting non-linear system. One advantage was that the Jacobian matrix has a sparse tridiagonal arrow head structure and hence they used only two tridiagonal solves to compute the approximate cluster size distribution at each time step. As noted in Section 1.2, there is a term  $N_D$  in all the fluxes. Using the Newton method directly would then lead to a dense Jacobian matrix. Of course the resulting non-linear system can be solved by using an LU factorization, but for very large systems one may run into memory problems. Instead of computing the distribution  $\mathbf{z}$ , we introduce a new distribution  $\mathbf{F}$  defined by  $F_i(t) := \sum_{j=i}^n z_j(t)$ . Such a transformation is due to Laurençot and Mischler [34] and is also used in Chapter 4 to prove uniqueness of solutions. Now, discretizing the resulting system and applying the Newton's method lead to a sparse Jacobian matrix. In the end we solve for  $\mathbf{z}$  by  $z_i(t) = F_i(t) - F_{i+1}(t)$  for  $1 \leq i \leq n-1$  and  $z_n(t) = F_n(t)$ . This is done at the end of the algorithm in one step. We test the numerical algorithm for the pure free molecule initial data and specific kinetic parameters. Our numerical results show that the steady states

### 1.3. THESIS STRUCTURE AND NEW RESULTS

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of the zero particle number truncation are actually the metastable states of the zero flux number truncation. This is expected since the zero particle number truncation prevents the accumulation of super-critical clusters in a given system thereby restricting the system into the metastable region, see Penrose and Lebowitz [48]. There the authors described some techniques used to restrict a given system into its metastable state, one of them being the prevention of the number of super-critical clusters in a given locality from exceeding a certain prescribed bound.

The third and final part of the thesis consists of the conclusion and appendix. Chapter 7 contains the conclusions of our research work. These include the results of all the previous chapters. The Appendix contains some basic definitions and the proofs for some of the theorems used in the thesis together with a few calculation details.

We prepared two manuscripts for publication out of Chapters 2 and 3. One, with the title “Uniqueness of steady-state solutions for thermodynamically consistent Becker-Döring models” was published in the Journal of Mathematical Physics, see [60]. The second one, entitled “A new correction for the classical nucleation rates using a thermodynamically consistent Becker-Döring model”, is to be submitted. The results of Chapters 4 - 6 are to be submitted soon.

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## Chapter 2

# Modeling issues

This chapter contains the necessary information required for the full specification of the Becker-Döring models. In Section 2.1 we review some of the relevant formulae used in the classical nucleation theory. These include condensation, evaporation and nucleation rate expressions. Section 2.2 gives an extension to the liquid-vapor system which was considered by Dreyer and Duderstadt [16]. We incorporate an inert gas and give the relevant formula for condensation rates. Like Dreyer and Duderstadt, we derive the evaporation rates from the second law of thermodynamics. In Section 2.3 we determine the total available free energy for the crystallization process. We state the freezing and melting rate expressions for this process. To close the chapter we pose a thermodynamically consistent constant free molecule version of the modified Becker-Döring model. This is done in Section 2.4.2.

### 2.1 Classical nucleation theory

The classical nucleation theory originated with the work of Volmer and Weber [65]. It was mainly developed to describe nucleation of liquid droplets in vapor. In 1935 Becker and Döring [5] established a kinetic model which they used to calculate nucleation rates in a steady-state process. Although the classical nucleation theory assumes spherical clusters, we modify the relevant formulae by introducing a constant which takes care of the shape of an arbitrary cluster.

#### 2.1.1 Condensation and evaporation rates

Consider a system containing vapor at a temperature  $T$  and outer pressure  $p_0$ . Let  $m$  denote the *molecular mass* of the vapor and  $V_v(t)$  the volume of vapor at time  $t$ . The condensation rate for a cluster or  $i$ -mer of radius  $r_i$  is given by the following well-known expression from the kinetic theory of gases, see Landau and Lifshitz [33, §39],

$$C_i = \alpha_i 4\pi r_i^2 \frac{z_1(t)}{V_v(t)} \sqrt{\left(\frac{kT}{2\pi m}\right)}, \quad (2.1)$$

where  $k$  is the Boltzmann constant and  $\alpha_i$  a *sticking coefficient*. Suppose a molecule has a volume  $V_1$ . Then by assuming a uniform density  $\rho_L$  of free molecules and clusters, the volume  $V_i$  of an  $i$ -mer is given by

$$V_i = \frac{4}{3}\pi r_i^3 = V_1 i, \quad (2.2)$$

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## 2.1. CLASSICAL NUCLEATION THEORY

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from which we obtain

$$r_i = \left( \frac{3V_1 i}{4\pi} \right)^{1/3}. \quad (2.3)$$

Combining (2.1) and (2.3) we obtain the following expression for the condensation rates in terms of the number  $i$  of molecules in a cluster

$$C_i = \alpha_i 4\pi \frac{z_1(t)}{V_v(t)} \left( \frac{3V_1 i}{4\pi} \right)^{2/3} \sqrt{\left( \frac{kT}{2\pi m} \right)}. \quad (2.4)$$

This formula works only for spherical clusters. For clusters of arbitrary shape we introduce a constant  $\vartheta$  known as the *shape factor*. In this case the condensation rates become, see kashchiev [27, Equation 10.3]

$$C_i = \alpha_i \vartheta \frac{z_1(t)}{V_v(t)} V_1^{2/3} i^{2/3} \sqrt{\left( \frac{kT}{2\pi m} \right)}, \quad (2.5)$$

where  $\vartheta = (36\pi)^{1/3}$  for spheres and  $\vartheta = 6$  for cubes. The number of free molecules is related to the volume of vapor via the thermal equation of state for an ideal gas as

$$\frac{p_0}{kT} = \frac{z_1(t)}{V_v(t)}. \quad (2.6)$$

Substituting this relation into (2.5) the condensation rates are equivalent to

$$C_i = \alpha_i \vartheta \frac{p_0}{kT} V_1^{2/3} i^{2/3} \sqrt{\left( \frac{kT}{2\pi m} \right)}. \quad (2.7)$$

With  $\vartheta = (36\pi)^{1/3}$  and  $\alpha_i = 1$  this equation was also used by Dreyer and Duderstadt [16]. Seinfeld and Pandis [52] gave a slightly different formula for condensation rates as

$$C_i = \alpha_i (36\pi)^{1/3} \frac{p_0}{kT} V_1^{2/3} \left(1 + \frac{1}{i}\right) (1 + i^{1/3})^2 \sqrt{\left( \frac{kT}{2\pi m} \right)}. \quad (2.8)$$

The leading order term in  $i$  is exactly of the same form as in (2.7) for each  $i \in \mathbb{N}$ . Therefore for large  $i$  any of the two formulae can be used to give similar results.

Next we review the formulae for the evaporation rates. Kashchiev [27, Section 10.2] as well as Seinfeld and Pandis [52, Chapter 11] derived the evaporation rates using constrained equilibrium conditions. That is, each cluster is assumed to be in equilibrium with the surrounding vapor. In terms of fluxes, this is equivalent to  $J_i = 0$  for all  $i \geq 1$ , leading to

$$C_i \bar{b}_i = E_{i+1} \bar{b}_{i+1}, \quad (2.9)$$

where  $\bar{\mathbf{b}} := \{\bar{b}_i\}_{i \in \mathbb{N}}$  is the equilibrium Boltzmann distribution. It was defined by Burton [7] as

$$\bar{b}_i = \bar{b}_1 \exp(-\mathcal{A}_i/kT) \quad \text{for } i \in \mathbb{N}, \quad (2.10)$$

## CHAPTER 2. MODELING ISSUES

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where  $\mathcal{A}_i$  is the energy of formation of an  $i$ -mer. Let  $\sigma$  and  $\bar{p}(T)$  denote liquid-vapor surface energy and vapor equilibrium pressure at a temperature  $T$  respectively. Define the *supersaturation ratio*  $S$  and a constant  $\gamma$  by

$$S := \frac{p_0}{\bar{p}(T)} \quad \text{and} \quad \gamma := \vartheta V_1^{2/3} \sigma. \quad (2.11)$$

Then the energy  $\mathcal{A}_i$  is given by

$$\mathcal{A}_i = -kTi \ln S + \gamma i^{2/3} \quad \text{for } i \geq 2 \quad \text{and} \quad \mathcal{A}_1 = 0. \quad (2.12)$$

We give the derivation of this equation in Section 2.2. The equilibrium concentration  $\bar{b}_1$  of free molecules is given by the ideal gas equation of state as

$$\bar{b}_1 = \frac{p_0}{kT}. \quad (2.13)$$

Substituting (2.10) into (2.9) we get

$$E_{i+1} = C_i \frac{q_i}{q_{i+1}}, \quad \text{where } q_i = \exp(-\mathcal{A}_i/kT) \quad \text{for } i \geq 1. \quad (2.14)$$

Slezov and Schmelzer [59] criticized the assumption of constrained equilibrium used in the derivation of (2.14). They derived the same equation using a different reasoning, see their paper for details.

To derive another formula for evaporation rates we introduce the *critical cluster* which is defined as the cluster in equilibrium with vapor at the given temperature  $T$  and outside pressure  $p_0$ . In 1871 Thomson [63], who later became Lord Kelvin, derived the following formula for the critical cluster radius  $r_{crit}$ , see also Becker and Döring [5, §1],

$$r_{crit} = \frac{2m\sigma}{kT\rho_L \ln S}, \quad (2.15)$$

where  $S$  is defined in (2.11). With  $V_1 = m/\rho_L$ , this formula can be written in terms of the number  $i_{crit}$  of molecules in the critical cluster by using (2.3) and the constant  $\gamma$  in (2.11) for  $\vartheta = (36\pi)^{1/3}$ . This gives

$$i_{crit} = \left( \frac{2\gamma}{3kT \ln S} \right)^3. \quad (2.16)$$

This is the classical Thomson formula for the number of molecules in the critical size cluster and it is well defined only if  $S > 1$ . It serves as the basic law for the classical nucleation theory, because it may be interpreted as follows: If an  $i$ -mer appears by fluctuation, it will grow further for  $i > i_{crit}$ , whereas it will disappear if  $i < i_{crit}$ . The formula will serve as a basis for choosing the largest cluster when studying truncated Becker-Döring models in Chapter 3.

Still by constrained equilibrium, one may write another evaporation rate  $E_i^*$  as

$$E_i^* = C_i^*, \quad (2.17)$$



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where  $C_i^*$  is that particular value given by (2.7) when we therein change  $p_0$  to that particular value, say  $p_i$ , for which the  $i$ -mer would represent the critical cluster. Then we use the Thomson formula (2.16) for each  $i$  with  $S = p_i/\bar{p}(T)$  to obtain

$$p_i = \bar{p}(T) \exp\left(\frac{2\gamma}{3kTi^{1/3}}\right). \quad (2.18)$$

Substituting this value for  $p_0$  in (2.7), equation (2.17) becomes

$$E_i^* = C_i^* = \alpha_i \vartheta \frac{\bar{p}}{kT} V_1^{2/3} i^{2/3} \exp\left(\frac{2\gamma}{3kTi^{1/3}}\right) \sqrt{\left(\frac{kT}{2\pi m}\right)}. \quad (2.19)$$

We then eliminate the exponential function by using (2.16) to obtain

$$E_i^* = \alpha_i \vartheta \frac{\bar{p}}{kT} V_1^{2/3} i^{2/3} S^{(i_{crit}/i)^{1/3}} \sqrt{\left(\frac{kT}{2\pi m}\right)}. \quad (2.20)$$

Finally we use (2.20), which is based on equilibrium, and (2.7) with  $p_0 = S\bar{p}$  to form the non equilibrium ratio of  $E_i^*$  to  $C_i$  as

$$\frac{E_i^*}{C_i} = S^{\{(i_{crit}/i)^{1/3}-1\}}. \quad (2.21)$$

This equation implies that sub-critical clusters tend to evaporate while super-critical clusters grow. The critical cluster is in equilibrium with the surrounding vapor since  $E_{i_{crit}} = C_{i_{crit}}$ . Formula (2.21) can be found in McDonald [37, p. 32] as well as Seinfeld and Pandis [52, p. 505]. In Figure 2.1 we show the rates  $E_i$  and  $E_i^*$  together with  $C_i$  for water vapor at  $T = 290K$ ,

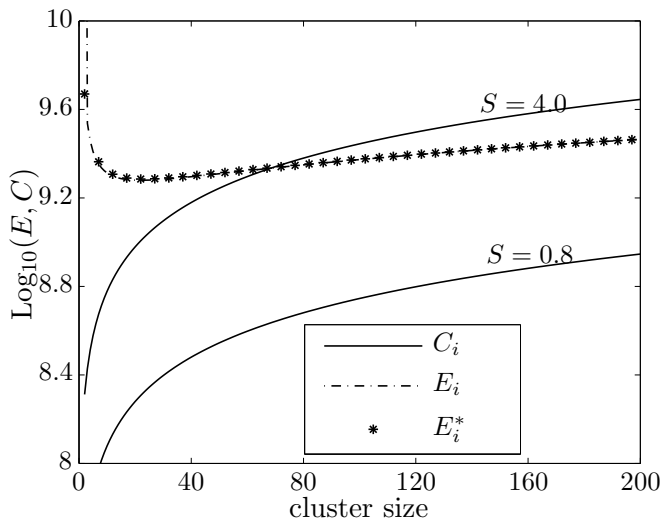


Figure 2.1: Evaporation and Condensation rates for water vapor at  $T = 290K$ .

$S = 4.0$  and  $S = 0.8$ . We observe that the two evaporation formulas give similar results for  $S > 1$  which are independent of the values of  $S$ . For  $S \leq 1$  the evaporation rate  $E_i^*$  is not defined. For  $S > 1$  the evaporation rates intersect with the condensation rates at the critical

cluster given by the Thomson formula (2.15). The figure shows that the evaporation rates are higher than the condensation rates for sub-critical clusters. The reverse is true for super-critical clusters. These confirm the fact that sub-critical cluster tend to evaporate while super-critical clusters grow. For  $S \leq 1$  there is no finite intersection point for the rates. In this case the evaporation rates are higher than condensation rates for the entire cluster size range. This means that any cluster in a system at such a state will dissolve.

### 2.1.2 Steady states and nucleation rates

Steady-state solutions to the Becker-Döring model are those for which the time derivatives in (1.2) and (1.5) are equal to zero. They were already studied by Kashchiev [27], Seinfeld and Pandis [52] as well as Burton [7]. There are two scenarios which may lead to steady-state solutions. One is the case where all fluxes vanish and leads to the equilibrium distribution, given by the recursion

$$C_i z_i = E_{i+1} z_{i+1}, \quad i \geq 1. \quad (2.22)$$

The second one occurs when all the fluxes have a common nonzero value  $J^s$ , that is,  $J_1 = J_2 = \dots = J_i = \dots = J^s$ . This was first studied by Becker and Döring [5] in 1935. In their experimental set up, they removed clusters of a specified size, say  $n$ , bigger than the critical cluster and added free molecules to the system so as to keep the outer pressure constant. In a steady state the number of free molecules in the system is constant. The steady-state distribution is written as

$$z_i^s = \frac{J^s}{C_i} \left[ 1 + \sum_{j=i+1}^n \prod_{k=i+1}^j \frac{E_k}{C_k} \right], \quad i \geq 1. \quad (2.23)$$

The common constant flux  $J^s$  is known as the nucleation rate. It depends on the values for  $C_i$  and  $E_i$  via

$$J^s = C_1 z_1^s \left[ 1 + \sum_{i=2}^n \prod_{k=2}^i \frac{E_k}{C_k} \right]^{-1}. \quad (2.24)$$

Next we substitute for the evaporation rates by using (2.14) with  $q_1 = 1$  and simplify the result to get

$$J = z_1^s \left[ \frac{1}{C_1} + \sum_{i=2}^n \frac{1}{C_i q_i} \right]^{-1}, \quad \text{where } q_i := \exp(-\mathcal{A}_i/kT). \quad (2.25)$$

We point out that one could use formula (2.21) for the evaporation rates instead of (2.14). This would not change the value of  $J^s$  quantitatively since the two formulae give the same results, see Figure 2.1.

Due to the definition of  $\mathcal{A}_i$  in (2.12), the contribution of large clusters to the nucleation rate formula (2.25) is negligible. Therefore with little loss of accuracy the value of  $n$  can be extended to  $\infty$ . This gives

$$J \approx z_1^s \left[ \frac{1}{C_1} + \sum_{i=2}^{\infty} \frac{1}{C_i q_i} \right]^{-1}, \quad \text{where } q_i := \exp(-\mathcal{A}_i/kT). \quad (2.26)$$

## 2.1. CLASSICAL NUCLEATION THEORY

By substituting for  $\mathcal{A}_i$  using (2.12), this formula is equivalent to

$$J \approx z_1^s \left[ \frac{1}{C_1} + \sum_{i=2}^{\infty} \frac{1}{C_i S^i \exp(-\tilde{a} i^{2/3})} \right]^{-1}, \quad \tilde{a} := \frac{\gamma}{kT}. \quad (2.27)$$

Next we follow Seinfeld and Pandis [52, Section 11.1.3] to simplify the above expression with the assumption that  $S > 1$ . We use some mathematical simplifications by examining the denominator of the infinite sum. We observe from (2.5) that  $C_i$ , increases as  $i^{2/3}$  for large  $i$ . The term  $S^i$  grows exponentially with  $i$  since  $S > 1$  by assumption. The expression  $\exp(-\frac{\gamma}{kT} i^{2/3})$  decreases exponentially as  $i$  increases, as  $i^{2/3}$ . The product  $S^i \exp(-\frac{\gamma}{kT} i^{2/3})$  initially decreases rapidly as  $i$  increases, reaches a minimum and then begins to increase as  $S^i$  begins to dominate. The terms in the summation are largest near the minimum in the denominator. The minimum point of the denominator is obtained by solving

$$\frac{d}{di} (C_i S^i \exp(-\frac{\gamma}{kT} i^{2/3})) = 0. \quad (2.28)$$

In practice, because  $C_i$  varies slowly with  $i$  relative to the other two terms, with little loss of accuracy it is removed from the summation and replaced with its value  $C_{i_{crit}}$  at the minimum. If we let

$$g(i) := \frac{\gamma}{kT} i^{2/3} - i \ln S \quad (2.29)$$

then (2.27) becomes

$$J \approx z_1^s C_{i_{crit}} \left[ 1 + \sum_{i=2}^{\infty} \frac{1}{\exp(-g(i))} \right]^{-1}, \quad (2.30)$$

and (2.28) can be replaced by

$$\frac{d}{di} \exp(-g(i)) = 0. \quad (2.31)$$

Solving this differential equation gives the classical Thomson formula (2.16) for the critical cluster, repeated here for convenience as

$$i_{crit} = \left( \frac{2\gamma}{3kT \ln S} \right)^3.$$

If  $i_{crit}$  is sufficiently large, then the summation in (2.30) can be replaced with an integral where the lower limit can be changed to zero to give

$$J \approx z_1^s C_{i_{crit}} \left[ \int_0^{\infty} \exp(g(i)) di \right]^{-1}. \quad (2.32)$$

It is clear that the main contribution to the integral is made by a small neighborhood of the size of the critical cluster. We therefore write  $g(i)$  as a Taylor series expansion around  $i_{crit}$  so that the integral (2.32) becomes

$$J \approx z_1^s C_{i_{crit}} \left[ \int_0^{\infty} \exp(g(i_{crit})) \exp\left( \frac{1}{2} \frac{d^2 g}{di^2} \Big|_{i_{crit}} (i - i_{crit})^2 \right) di \right]^{-1}. \quad (2.33)$$

From (2.29)

$$\left. \frac{d^2 g}{di^2} \right|_{i_{crit}} = -\frac{2\gamma}{9kT} i_{crit}^{-4/3} := -\theta. \quad (2.34)$$

Finally we define a new integration variable,  $y = i - i_{crit}$ . In doing so the lower limit of integration becomes  $-i_{crit}$ . We again use the approximation that  $i_{crit}$  is large and replace the lower limit by  $-\infty$ . The integral is then transformed into a Gaussian integral giving

$$J \approx z_1^s C_{i_{crit}} \exp(-g(i_{crit})) \left( \frac{\theta}{2\pi} \right)^{1/2}. \quad (2.35)$$

We then use (2.5), (2.6), (2.29), and (2.34) to get

$$J \approx \alpha_{i_{crit}} z_1^s \left( \frac{V_1 p_0}{kT} \right) \left( \frac{2\sigma}{\pi m} \right)^{1/2} \exp \left( \frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln S)^2} \right) := J_{CNT}. \quad (2.36)$$

Finally we apply the assumption  $z_1^s = b_1$  mentioned in Burton [7] and then use equation (2.13) for  $b_1$  to obtain

$$J_{CNT} = \alpha_{i_{crit}} V_1 \left( \frac{p_0}{kT} \right)^2 \left( \frac{2\sigma}{\pi m} \right)^{1/2} \exp \left( \frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln S)^2} \right). \quad (2.37)$$

With  $\vartheta = (36\pi)^{1/3}$ , this formula gives the classical nucleation rates. For more details about nucleation rates see the review article by Oxtoby [45].

Although the classical nucleation theory gave a good basis of most modern treatments of nucleation processes, it was not free of shortcomings. Cortney [12] argued that the theory overapproximates the nucleation rates by a factor of the supersaturation ratio. We denote his rates by  $J_C$  given by

$$J_C = \frac{1}{S} J_{CNT}. \quad (2.38)$$

Girshick and Chiu [21] corrected the classical nucleation rates by arguing that in the Becker-Döring treatment the free energy of formation of a molecule is nonzero. The nucleation rate version by Girshick and Chiu includes a temperature dependent correction. It is denoted by  $J_{GC}$  and it is defined as

$$J_{GC} = \frac{1}{S} \exp \left( \frac{(36\pi)^{1/3} V_1^{2/3} \sigma}{kT} \right) J_{CNT}. \quad (2.39)$$

## 2.2 The liquid-vapor-inert gas system

### 2.2.1 Available free energy of a many droplet system

Here we extend the liquid-vapor system considerations of Dreyer and Duderstadt [16], see also Müller and Müller [39, Section 11.1]. We investigate the effect of an inert gas on the availability of the composite system. Müller and Müller [39, Section 11.2] derived an expression for the available free energy of a system containing a single droplet in moist air. Our aim is to extend their result to a system containing many droplets in moist air. In other words, we derive an

## 2.2. THE LIQUID-VAPOR-INERT GAS SYSTEM

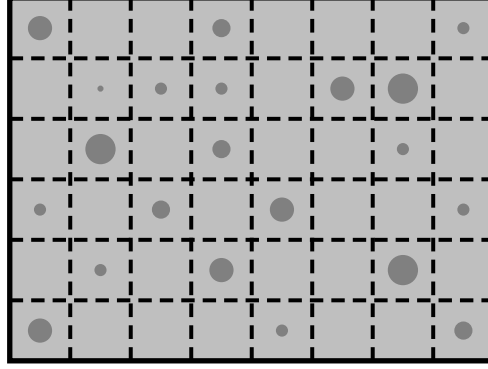


Figure 2.2: Ensemble of single droplet systems

expression for the available free energy of a system containing many droplets of a given liquid in vapor and an inert gas.

Like Dreyer and Duderstadt [16], we consider an ensemble of  $n$  subsystems as illustrated above. Each of them contains the same number of molecules  $N_0$ , has the same mean composition and is under the same external pressure  $p_0$ . At time  $t$ , for  $2 \leq i \leq n$  there are  $z_i(t)$  subsystems with a single droplet containing  $i$  molecules of liquid,  $N_i^A(t)$  inert gas molecules and  $N_0 - (N_i^A + i)$  vapor molecules. There are  $z_0(t)$  subsystems without droplets. Such subsystems contain  $N_0^A$  inert gas molecules and  $N_0 - N_0^A$  vapor molecules. We denote the total number of vapor molecules at time  $t$  by  $z_1(t)$  so that we may write

$$z_1(t) = (N_0 - N_0^A)z_0(t) + \sum_{i=2}^n (N_0 - (N_i^A + i))z_i(t). \quad (2.40)$$

The total number of inert gas molecules are given by

$$z_A = N_0^A z_0(t) + \sum_{i=2}^n N_i^A z_i(t). \quad (2.41)$$

The total number  $N$  of molecules in the system is given by

$$N = z_A + z_1(t) + \sum_{i=2}^n i z_i(t) = \text{constant}. \quad (2.42)$$

Substituting for  $z_1(t)$  and  $z_A$  by using (2.40) and (2.41) respectively, we obtain

$$\begin{aligned} N &= (N_0 - N_0^A)z_0(t) + \sum_{i=2}^n (N_0 - (N_i^A + i))z_i(t) + N_0^A z_0(t) + \sum_{i=2}^n N_i^A z_i(t) \\ &\quad + \sum_{i=2}^n i z_i(t). \end{aligned}$$

This gives

$$N = N_0 z_0(t) + \sum_{i=2}^n N_0 z_i(t). \quad (2.43)$$

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Denote the molecular masses of the inert gas and the substance considered by  $m_a$  and  $m_w$  respectively. Let  $g_i^L$ ,  $g^V$  and  $g^A$  be the specific Gibbs free energies of an  $i$ -mer liquid cluster, vapor and inert gas respectively. The Gibbs free energies  $G^L$  and  $G^V$  for the liquid and vapor phases can then respectively be written as

$$G^L = m_w \sum_{i=2}^n i z_i(t) g_i^L \quad (2.44)$$

and

$$\begin{aligned} G^V &= (N_0 - N_0^A) z_0(t) m_w g^V + \sum_{i=2}^n (N_0 - (N_i^A + i)) z_i(t) m_w g^V \\ &+ N_0^A z_0(t) m_a g^A + \sum_{i=2}^n N_i^A z_i(t) m_a g^A. \end{aligned} \quad (2.45)$$

Furthermore we denote the surface free energies by  $\Omega^I$  and write

$$\Omega^I = \sum_{i=2}^n \frac{4\pi}{3} \sigma r_i^2 z_i(t), \quad (2.46)$$

see Dreyer and Duderstadt [16]. The total available free energy of a many droplet system consisting of liquid droplets in vapor and inert gas is represented by

$$\mathcal{A}(\mathbf{z}(t)) = G^V + G^L + \Omega^I + kT \left[ z_A \ln \left( \frac{z_A}{z_A + N_D(t)} \right) + \sum_{i=1}^n z_i(t) \ln \left( \frac{z_i(t)}{z_A + N_D(t)} \right) \right]. \quad (2.47)$$

The term in square brackets accounts for the entropy of mixing. The total number  $N_D$  of liquid droplets and vapor molecules is given by

$$N_D(t) = \sum_{i=1}^n z_i(t). \quad (2.48)$$

Substituting for  $G^V$  and  $G^L$  we obtain

$$\begin{aligned} \mathcal{A}(\mathbf{z}(t)) &= N_0 \left( z_0(t) + \sum_{i=2}^n z_i(t) \right) m_w g^V + \left( N_0^A z_0(t) + \sum_{i=2}^n N_i^A z_i(t) \right) \left( m_a g^A - m_w g^V \right) + \Omega^I \\ &+ \sum_{i=2}^n m_w i z_i(t) (g_i^L - g^V) + kT \left[ z_A \ln \left( \frac{z_A}{z_A + N_D(t)} \right) + \sum_{i=1}^n z_i(t) \ln \left( \frac{z_i(t)}{z_A + N_D(t)} \right) \right]. \end{aligned}$$

Next we use (2.41) and (2.43) to obtain

$$\begin{aligned} \mathcal{A}(\mathbf{z}(t)) &= N m_w g^V + z_A \left( m_a g^A - m_w g^V \right) + \sum_{i=2}^n m_w i z_i(t) (g_i^L - g^V) + \Omega^I \\ &+ kT \left[ z_A \ln \left( \frac{z_A}{z_A + N_D(t)} \right) + \sum_{i=1}^n z_i(t) \ln \left( \frac{z_i(t)}{z_A + N_D(t)} \right) \right]. \end{aligned} \quad (2.49)$$

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For spherical clusters, the difference  $g_i^L - g^V$  is given according to Dreyer and Duderstadt [16, eq (42) and (45)] by

$$g_i^L(T, p_0 + \frac{2\sigma}{r_i}) - g^V(T, p_0) = -\frac{kT}{m_w} \ln\left(\frac{p_0}{p(T)}\right) + \frac{2\sigma}{\rho_L r_i}, \quad (2.50)$$

where  $p(T)$  is the saturation pressure at temperature  $T$  and  $\rho_L$  the liquid density. The derivation of (2.50) uses the assumption that each  $i$ -mer cluster in the system is in mechanical equilibrium with the gas phase. We use (2.46) and (2.50) into (2.49) and then apply the incompressibility relation (2.2) with  $V_1 = m_w/\rho_L$  to obtain

$$\begin{aligned} \mathcal{A}(\mathbf{z}(t)) &= Nm_w g^V + z_A \left( m_a g^A - m_w g^V \right) + \sum_{i=2}^n \left[ -kTi \ln\left(\frac{p_0}{p(T)}\right) + 4\pi r_i^2 \sigma \right] z_i(t) \\ &+ kT \left[ z_A \ln\left(\frac{z_A}{z_A + N_D(t)}\right) + \sum_{i=1}^n z_i(t) \ln\left(\frac{z_i(t)}{z_A + N_D(t)}\right) \right]. \end{aligned} \quad (2.51)$$

We can use (2.3) to write the radius  $r_i$  in terms of  $i$ . Up to a constant, the total available free energy of the many droplet system containing an inert gas is given by

$$\mathcal{A}(\mathbf{z}(t)) = \sum_{i=1}^n \mathcal{A}_i z_i(t) + kT \left[ z_A \ln\left(\frac{z_A}{z_A + N_D(t)}\right) + \sum_{i=1}^n z_i(t) \ln\left(\frac{z_i(t)}{z_A + N_D(t)}\right) \right], \quad (2.52)$$

where  $\mathcal{A}_i$  is given in (2.12) as

$$\mathcal{A}_i = -kTi \ln(S) + \gamma i^{2/3}, \quad \text{for } 2 \leq i \leq n \quad \text{and} \quad \mathcal{A}_1 = 0.$$

The constants  $S$  and  $\gamma$  are defined in (2.11). The presence of the inert gas modifies the entropy of mixing. Figure 2.3 shows the variation of the availability  $\mathcal{A}_i$  with number of molecules in a given cluster for water vapor at  $T = 290K$  and  $S = 4$ .

### 2.2.2 Condensation and evaporation rates

Here we consider condensation processes which result from collisions of vapor molecules with a given liquid cluster. They are given by (2.5) with  $m = m_w$ . We give the rates here for convenience as

$$C_i = \alpha_i \vartheta \frac{z_1(t)}{V_v(t)} V_1^{2/3} i^{2/3} \sqrt{\left(\frac{kT}{2\pi m}\right)}.$$

Suppose the partial pressure  $p_v(t)$  of vapor at time  $t$  is given by

$$p_v(t) = \omega(t)p_0, \quad 0 < \omega(t) \leq 1. \quad (2.53)$$

Then by Dalton's law the inert gas partial pressure  $p_a(t)$  is

$$p_a(t) = (1 - \omega(t))p_0. \quad (2.54)$$

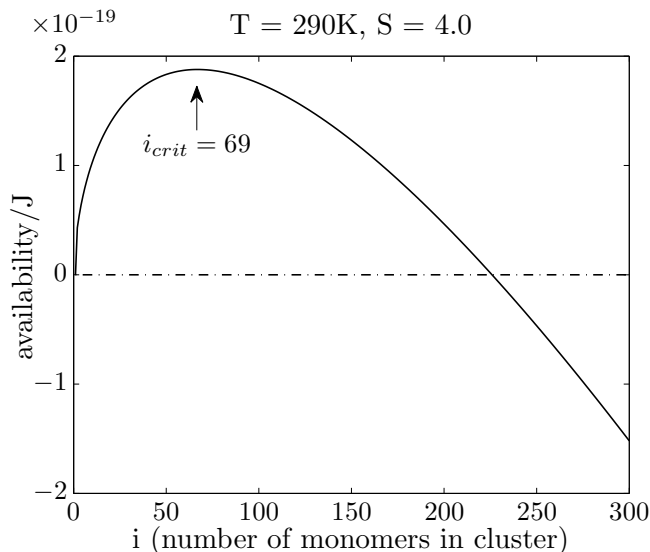


Figure 2.3: Available free energy for vapor containing a single liquid droplet.

We assume that the vapor and inert gas behave like ideal gases so that we can write, see Müller and Müller [39, Chapter 10]

$$\frac{z_A}{V_v(t)} = \frac{p_a(t)}{kT} = \frac{(1 - \omega(t))p_0}{kT}, \quad (2.55)$$

$$\frac{z_1(t)}{V_v(t)} = \frac{p_v(t)}{kT} = \frac{\omega(t)p_0}{kT}. \quad (2.56)$$

Dividing (2.55) by (2.56) we obtain

$$\frac{z_A}{z_1(t)} = \frac{1 - \omega(t)}{\omega(t)} \quad \text{or} \quad \omega(t) = \frac{z_1(t)}{z_1(t) + z_A}. \quad (2.57)$$

The case  $\omega = 1$  corresponds to situation where there is no inert gas in the liquid-vapor system. By using (2.56) the condensation rates become

$$C_i = \alpha_i \vartheta \frac{\omega(t)p_0}{kT} V_1^{2/3} i^{2/3} \sqrt{\left(\frac{kT}{2\pi m}\right)}.$$

Next we substitute for  $\omega(t)$  using (2.57) to obtain

$$C_i = a_i \frac{z_1(t)}{z_1(t) + z_A}, \quad \text{where} \quad a_i := \alpha_i \vartheta \frac{p_0}{kT} V_1^{2/3} i^{2/3} \sqrt{\left(\frac{kT}{2\pi m}\right)}. \quad (2.58)$$

By applying the second law of thermodynamics to (2.52) as was done by Dreyer and Duderstadt [16], the evaporation rates are given by

$$\frac{E_{i+1}}{C_i} = \frac{q_i}{q_{i+1}} \frac{(z_A + N_D(t))}{z_1(t)}, \quad q_i = \exp(-\mathcal{A}_i/kT). \quad (2.59)$$

Combining (2.58) and (2.59), the fluxes  $J_i$  in (2.91) become

$$J_i(\mathbf{z}(t)) = a_i \left( z_i(t) \frac{z_1(t)}{z_1(t) + z_A} - \frac{q_i}{q_{i+1}} \left( \frac{z_A + N_D(t)}{z_1(t) + z_A} \right) z_{i+1}(t) \right). \quad (2.60)$$



## 2.3 Crystal nucleation process

### 2.3.1 Available free energy of a single crystal in solution

We follow the classical nucleation theory consideration of a crystal germ. It is assumed that the germ is of a spherical shape with an averaged value  $\sigma$  of the surface energy, see Debenedetti [13, p. 189]. The liquid solution phase consists of the solvent and dissolved crystal molecules. We

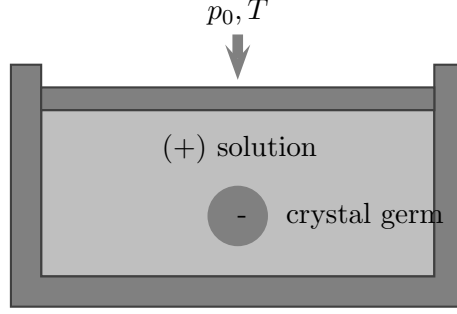


Figure 2.4: crystal in solution

denote the solvent by  $w$  and the crystal particles in solution by  $c^+$ . There is one solid crystal which is assumed to be spherical with radius  $r$ . It is denoted by  $c^-$ . The masses of the crystal in the two phases are denoted by  $M_c^+$  and  $M_c^-$  while the mass of the solvent is denoted by  $M_w$ . The available free energy for the system in Figure 2.4 is given by

$$\mathcal{A} = F^+ + F^- + 4\pi r^2 \sigma + p_0(V^+ + V^-),$$

where  $F$  denotes the free energy. With  $F^+ = F_w + F_c^+$  we have

$$\mathcal{A} = F_w(T, M_w, V^+) + F_c^+(T, M_c^+, V^+) + F_c^-(T, M_c^-, V^-) + 4\pi r^2 \sigma + p_0(V^+ + V^-).$$

There are four variables,  $M_c^-, M_c^+, V^-$  and  $V^+$  of which only  $M_c^-, V^- := 4\pi r^3/3$  and  $V^+$  are independent since

$$M_c^- + M_c^+ = M_c$$

is constant. We denote by  $G = F + pV$  the total Gibbs free energy of a given component. With the chemical potential  $\mu_\alpha := \partial G / \partial M_\alpha = \partial F / \partial M_\alpha$  and  $p = -\partial F / \partial V$ , the necessary equilibrium conditions are

$$\frac{\partial \mathcal{A}}{\partial M_c^-} = -\frac{\partial F_c^+}{\partial M_c^+} + \frac{\partial F_c^-}{\partial M_c^-} = 0 \quad \Rightarrow \quad \mu_c^+ = \mu_c^-, \quad (2.61)$$

$$\frac{\partial \mathcal{A}}{\partial V^-} = \frac{\partial F_c^-}{\partial V^-} + p_0 + \frac{2\sigma}{r} = 0 \quad \Rightarrow \quad p^- = p_0 + \frac{2\sigma}{r}, \quad (2.62)$$

$$\frac{\partial \mathcal{A}}{\partial V^+} = \frac{\partial F_c^+}{\partial V^+} + \frac{\partial F_w}{\partial V^+} + p_0 = 0 \quad \Rightarrow \quad p^+ := p_c^+ + p_v = p_0. \quad (2.63)$$

Equation (2.61) represents the condition for phase equilibrium while (2.62) and (2.63) are dynamical or mechanical equilibrium conditions. We assume that dynamical equilibrium is always

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established while phase equilibrium is slowly attained. Therefore the available free energy can be written as

$$\begin{aligned}
 \mathcal{A} &= F^+ + p^+ V^+ + F^- + p^- V^- + 4\pi r^2 \sigma + (p_0 - p^+) V^+ + (p_0 - p^-) V^-, \\
 &= G^+ + G^- + 4\pi r^2 \sigma - \frac{2\sigma}{r} V^-, \\
 &= G^+ + G^- + 4\pi r^2 \sigma - \frac{2}{3} 4\pi r^2 \sigma, \\
 &= G^+ + G^- + \frac{4}{3} \pi r^2 \sigma.
 \end{aligned} \tag{2.64}$$

The Gibbs free energies are given by

$$G^+ = M_w \mu_w + M_c^+ \mu_c^+ \quad \text{and} \quad G^- = M_c^- g_c^-, \tag{2.65}$$

where  $g_c^-$  is the specific Gibbs free energy of the crystal. If the chemical potentials are those of an ideal dilute mixture we have, see Atkins [2, p. 173] and Müller and Müller [39, p. 218]

$$\mu_c^+ = g_c^+(T, p^+) + \frac{kT}{m_c} \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right), \tag{2.66}$$

$$\mu_w = g_w(T, p^+) + \frac{kT}{m_w} \ln \left( \frac{N_w}{N_c^+ + N_w} \right), \tag{2.67}$$

where  $N$  denotes the number of molecules of a given kind. By using (2.65) - (2.67) the available free energy in (2.64) becomes

$$\begin{aligned}
 \mathcal{A} &= M_w \left[ g_w(T, p^+) + \frac{kT}{m_w} \ln \left( \frac{N_w}{N_c^+ + N_w} \right) \right] + (M_c - M_c^-) \left[ g_c^+(T, p^+) + \frac{kT}{m_c} \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right) \right] \\
 &\quad + M_c^- g_c^-(T, p^-) + \frac{4}{3} \pi r^2 \sigma.
 \end{aligned}$$

We define the energy  $\bar{\mathcal{A}}$  of formation of a crystal by  $\bar{\mathcal{A}} := \mathcal{A} - M_c g_c^+(T, p^+) - M_w g_w(T, p^+)$ . Then by using  $N_\alpha = M_\alpha / m_\alpha$  we obtain

$$\begin{aligned}
 \bar{\mathcal{A}} &= kT N_w \ln \left( \frac{N_w}{N_c^+ + N_w} \right) + kT N_c^+ \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right) + M_c^- \left[ g_c^-(T, p^-) - g_c^+(T, p^+) \right] \\
 &\quad + \frac{4}{3} \pi r^2 \sigma.
 \end{aligned} \tag{2.68}$$

By writing  $p^- = p^+ + (p^- - p^+)$  and making a Taylor series expansion of  $g_c^-(T, p^-)$  about  $p^+$  we obtain

$$g_c^-(T, p^-) = g_c^-(T, p^+) + (p^- - p^+) \frac{\partial g_c^-}{\partial p} + \frac{1}{2} (p^- - p^+)^2 \frac{\partial^2 g_c^-}{\partial p^2} + \dots$$

We then use  $\partial g / \partial p = 1/\rho$ . The incompressibility condition for the solid crystal means that  $\rho$  is constant. This implies that  $\partial g / \partial p$  is constant and all higher order derivatives in the above expansion are equal to zero. We obtain

$$g_c^-(T, p^-) = g_c^-(T, p^+) + \frac{1}{\rho_c} (p^- - p^+),$$

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where  $\rho_c^-$  is the density of the solid crystal. Then the difference of the Gibbs free energies in (2.68) becomes

$$g_c^-(T, p^-) - g_c^+(T, p^+) = g_c^-(T, p^+) - g_c^+(T, p^+) + \frac{1}{\rho_c^-}(p^- - p^+).$$

Next we use the dynamical equilibrium conditions (2.62) and (2.63) to substitute for  $p^-$  and  $p^+$ . This gives

$$g_c^-(T, p^-) - g_c^+(T, p^+) = g_c^-(T, p_0) - g_c^+(T, p_0) + \frac{M_c^-}{\rho_c^-} \frac{2\sigma}{r}. \quad (2.69)$$

Suppose that  $T_e$  is the saturation temperature corresponding to the pressure  $p_0$ . Following Debenedetti [13, p. 188] we expand the Gibbs free energies  $g_c^\pm(T, p_0)$  about  $T_e$  to obtain

$$\begin{aligned} g_c^-(T, p_0) - g_c^+(T, p_0) &= g_c^-(T_e, p_0) - g_c^+(T_e, p_0) + (T - T_e) \left( \frac{\partial g_c^-}{\partial T} - \frac{\partial g_c^+}{\partial T} \right) \\ &\quad + \frac{1}{2} (T - T_e)^2 \left( \frac{\partial^2 g_c^-}{\partial T^2} - \frac{\partial^2 g_c^+}{\partial T^2} \right) + \dots \end{aligned} \quad (2.70)$$

Let  $s^\pm$  and  $h_c^\pm$  denote the specific values of the entropies and enthalpies of the liquid and solid phases. Since  $g_c^\pm := h_c^\pm - T s^\pm$ , we have, see Atkins [2, p. 128]

$$\frac{\partial g_c^\pm}{\partial T} = -s^\pm = \frac{g_c^\pm - h_c^\pm}{T}.$$

The first two terms on the right-hand side of (2.70) are equal. Therefore, with  $\Delta T := T_e - T$ , we have

$$\begin{aligned} g_c^-(T, p_0) - g_c^+(T, p_0) &= -\Delta T \left[ \frac{g_c^-(T_e, p_0) - h_c^-(T_e, p_0)}{T_e} - \frac{g_c^+(T_e, p_0) - h_c^+(T_e, p_0)}{T_e} \right] \\ &\quad + \frac{1}{2} \left( \frac{\Delta T}{T_e} \right)^2 \left[ T_e \left( \frac{\partial h_c^+}{\partial T} - \frac{\partial h_c^-}{\partial T} \right) - (h_c^+ - h_c^-) \right] + \dots \end{aligned} \quad (2.71)$$

Since the outside pressure  $p_0$  is constant, then by definition, see Atkins [2, p. 61]

$$\frac{\partial h_c^\pm}{\partial T} = c_p^\pm,$$

where  $c_p^\pm$  are the specific heat capacities at constant pressure. Then (2.71) becomes

$$g_c^-(T, p_0) - g_c^+(T, p_0) = -\Delta T \left( \frac{h_c^+ - h_c^-}{T_e} \right) + \frac{1}{2} \left( \frac{\Delta T}{T_e} \right)^2 \left[ T_e (c_p^+ - c_p^-) - (h_c^+ - h_c^-) \right] + \dots$$

The difference  $\Delta h := h_c^+(T_e, p_0) - h_c^-(T_e, p_0)$  is the heat of fusion, see Atkins [3, p. 50]. Usually, it is assumed that the heat capacity change upon solidification is negligible so that to a good approximation, we have

$$g_c^-(T, p_0) - g_c^+(T, p_0) = -\frac{\Delta T \Delta h}{T_e}. \quad (2.72)$$

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This equation was used by a number of authors, see for instance Miyazawa and Pound [38]. Combining (2.69) with (2.72), equation (2.68) becomes

$$\begin{aligned} \bar{\mathcal{A}} = & kTN_w \ln \left( \frac{N_w}{N_c^+ + N_w} \right) + kTN_c^+ \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right) + \frac{4}{3}\pi r^2 \sigma + \frac{M_c^-}{\rho_c^-} \frac{2\sigma}{r} \\ & - M_c^- \Delta T \frac{\Delta h}{T_e}. \end{aligned}$$

Finally we use  $M_c^-/\rho_c^- = V^- = 4\pi r^3/3$  and simplify the result into

$$\bar{\mathcal{A}} = kTN_w \ln \left( \frac{N_w}{N_c^+ + N_w} \right) + kTN_c^+ \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right) + 4\pi r^2 \sigma - \frac{4\pi r^3}{3} \rho_c^- \Delta T \frac{\Delta h}{T_e}. \quad (2.73)$$

This is an expression for the energy of formation of a spherical crystal cluster of radius  $r$  in a solution. Now suppose that the crystal cluster is made up of  $i$  molecules. Then due to incompressibility we can write

$$\frac{4\pi r^3}{3} \rho_c^- = m_c i, \quad (2.74)$$

so that (2.73) becomes

$$\bar{\mathcal{A}} = kTN_w \ln \left( \frac{N_w}{N_c^+ + N_w} \right) + kTN_c^+ \ln \left( \frac{N_c^+}{N_c^+ + N_w} \right) + \gamma i^{2/3} - m_c i \Delta T \frac{\Delta h}{T_e}, \quad (2.75)$$

where  $\gamma$  is defined in (2.11) with  $\vartheta = (36\pi)^{1/3}$  and  $V_1 = m_c/\rho_c^-$ . Differentiating  $\bar{\mathcal{A}}$  with respect to  $i$  the maximum availability occurs at the critical size cluster given by

$$i_{crit} = \left( \frac{2\gamma T_e}{3m_c \Delta T \Delta h} \right)^3. \quad (2.76)$$

By using (2.74) we can write the critical cluster in terms of the radius as

$$r_{crit} = \frac{2\sigma T_e}{\rho_c^- \Delta T \Delta h}. \quad (2.77)$$

Equation (2.77) was also given in Debenedetti [13, p. 188]. The author uses the molecular volume  $v_c^- := 1/\rho_c^-$ . Let  $c(T)$  denote the solute concentration at temperature  $T$ . The classical Thomson [63] formula for the critical cluster can also be written as

$$r_{crit} = \frac{2\sigma m_c}{\rho_c^- kT \ln(c(T)/c_e(T))}, \quad (2.78)$$

where the subscript  $e$  is used to denote equilibrium values. Comparing (2.77) with (2.78) implies that

$$\ln \left( \frac{c(T)}{c_e(T)} \right) = \frac{m_c \Delta h}{k} \left( \frac{1}{T} - \frac{1}{T_e} \right), \quad \text{or} \quad \ln \left( \frac{c_e(T_e)}{c_e(T)} \right) = \frac{m_c \Delta h}{k} \left( \frac{1}{T} - \frac{1}{T_e} \right) \quad (2.79)$$

where  $k$  is Boltzmann constant. This relation is known in literature as the van't Hoff equation for ideal solutions, see Mullin [40, p. 98] or Myerson [41, p. 12]. In case of real solutions, a factor  $\beta$  known as the activity coefficient is introduced to give

$$\ln \left( \frac{\beta c_e(T_e)}{c_e(T)} \right) = \frac{m_c \Delta h}{k} \left( \frac{1}{T} - \frac{1}{T_e} \right). \quad (2.80)$$

### 2.3.2 Available free energy of a many crystal system

Here we consider a system consisting of many crystal germs of arbitrary shape in a solution. By following the same procedure as was done for the liquid-vapor system, the total available free energy is given by (2.52) with  $\mathcal{A}_i$  taken from (2.75) as

$$\mathcal{A}_i := -m_c i \Delta T \frac{\Delta h}{T_e} + \gamma i^{2/3}, \quad \text{for } 2 \leq i \leq n \quad \text{and} \quad \mathcal{A}_1 = 0, \quad (2.81)$$

where  $\gamma = \vartheta \sigma (m_c / \rho_c^-)^{2/3}$ . The constant  $\vartheta$  represents the shape factor.

### 2.3.3 Freezing and melting rates

We consider freezing as a result of transfer of liquid molecules across the crystal-liquid phase boundary. The liquid molecule to be attached is in immediate contact with the crystal cluster. It can join the cluster by making a random jump over a distance comparable with its diameter  $d_1$ . Let  $D$  and  $\alpha_i$  denote the diffusion and sticking coefficient respectively. The freezing rates are given in Kashchiev [27, p. 155] as

$$C_i = \alpha_i \vartheta \frac{V_1^{2/3}}{d_1} D z_1(t) i^{2/3}. \quad (2.82)$$

In the above formula,  $z_1(t)$  denotes the concentration of free molecules but not their number. The diffusion coefficient is related to the radius  $r_1$  of a molecule and the viscosity  $\eta$  of the solution by the Einstein's equation, see Kashchiev [27, p. 143]

$$D = \frac{kT}{6\pi\eta r_1}. \quad (2.83)$$

The melting rates are given by (2.59) with  $z_A$  replaced by  $z_w$ . In this case the fluxes are defined by

$$J_i(\mathbf{z}(t)) = a_i \left( z_i(t) z_1(t) - \frac{q_i}{q_{i+1}} (z_w + N_D(t)) z_{i+1}(t) \right), \quad a_i = \alpha_i \vartheta \frac{V_1^{2/3}}{d_1} D i^{2/3}. \quad (2.84)$$

In this equation, the terms  $z_1(t)$  and  $(z_w + N_D(t))$  have units of concentration while  $\bar{a}_i$  has units of  $s^{-1}$ . Hence the fluxes  $J_i$  give the number of  $i$ -mers per unit volume per second.

To conclude this section we give a general Becker-Döring model which allows for an inert substance in a given system. Suppose that  $z_0(t)$  represents the number of the inert molecules in the system at time  $t$ . Then the thermodynamically consistent mass-conserving Becker-Döring model is given by

$$\begin{aligned} \dot{z}_0(t) &= 0, \quad \text{or} \quad z_0(t) = z_0, \text{ a constant,} \\ \dot{z}_1(t) &= -J_1(\mathbf{z}(t)) - \sum_{i=1}^{\infty} J_i(\mathbf{z}(t)), \\ \dot{z}_i(t) &= J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)) \quad \text{for } 2 \leq i \leq \infty, \end{aligned} \quad (2.85)$$

where, depending on the process, the fluxes are either given by

$$J_i(\mathbf{z}(t)) = a_i z_i(t) \frac{z_1(t)}{z_1(t) + z_0} - b_{i+1} R \frac{N_D(t)}{z_1(t) + z_0} z_{i+1}(t) \quad (2.86)$$

or

$$J_i(\mathbf{z}(t)) = a_i z_i(t) z_1(t) - b_{i+1} R N_D(\mathbf{z}(t)) z_{i+1}(t). \quad (2.87)$$

The coefficients  $b_{i+1}$  and  $R$  were introduced already in (1.28). The total mass  $\rho$  and number  $N_D$  of clusters together with free molecules are now generally given by

$$\rho = z_0 + \sum_{i=1}^{\infty} i z_i(t) \quad \text{and} \quad N_D(\mathbf{z}(t)) = \sum_{i=0}^{\infty} z_i(t). \quad (2.88)$$

## 2.4 Open systems

Here we consider two open systems containing free molecules and their clusters of different sizes at a constant outer pressure  $p_0$  and temperature  $T$ . Large clusters of size  $n+1$  are removed from the system as soon as they appear. In one of the systems, we add free molecules so as to keep their number  $z_1(t)$  constant. In the second system we add a number of free molecules equivalent to those which are removed through the large clusters. This procedure maintains a constant number of molecules or mass in the system. Both processes are schematically represented in Figure 2.5.

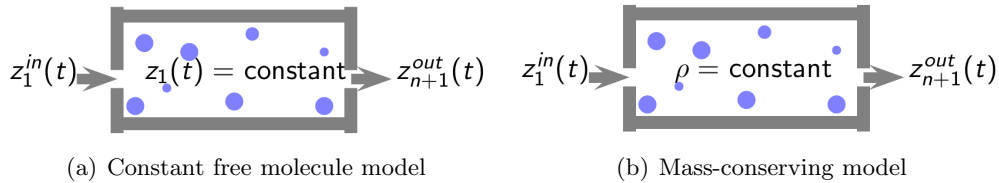


Figure 2.5: Open liquid-vapor systems

The formation of  $i$ -mers is modeled according to the Becker-Döring model as

$$\dot{z}_i(t) = J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)), \quad 2 \leq i \leq n, \quad (2.89)$$

while the number of free molecules changes according to

$$\dot{z}_1(t) = \dot{z}_1^{in} - 2J_1(\mathbf{z}(t)) - \sum_{i=1}^n J_i(\mathbf{z}(t)). \quad (2.90)$$

In this equation,  $\dot{z}_1^{in}$  represents the rate at which free molecules are added to the system. It will be determined from the nature of the system. The fluxes are defined by

$$J_i(\mathbf{z}(t)) := C_i z_i(t) - E_{i+1} z_{i+1}(t). \quad (2.91)$$

### 2.4.1 Energy balances

Let  $E$ ,  $\dot{Q}$ ,  $h^{in}$ ,  $s^{in}$  denote the total energy, heat power, molecular enthalpy and entropy respectively. Denote the enthalpy and entropy per  $(n + 1)$ -mer by  $h^{out}$  and  $s^{out}$  respectively. Then the first law of thermodynamics requires that

$$\dot{E}(t) = \dot{Q}(t) - p_0\dot{V}(t) + h^{in}\dot{z}_1^{in}(t) - h^{out}\dot{z}_{n+1}^{out}(t). \quad (2.92)$$

At a constant temperature, the entropy  $S$  evolves according to

$$\dot{S}(t) \geq \frac{\dot{Q}(t)}{T} + s^{in}\dot{z}_1^{in}(t) - s^{out}\dot{z}_{n+1}^{out}(t), \quad (2.93)$$

where the equality holds at equilibrium. These ideas were also used by Dreyer et al. [17] during the modeling of hysteresis and phase transition in many-particle storage systems. Define the following quantities

$$\mathcal{A}(t) := E(t) - TS(t) + p_0V(t), \quad G^{in} := h^{in} - Ts^{in} \quad \text{and} \quad G^{out} := h^{out} - Ts^{out}. \quad (2.94)$$

We now eliminate  $\dot{Q}$  from (2.92) and (2.93) to obtain

$$E(t) - TS(t) + p_0V(t) + (h^{out} - Ts^{out})\dot{z}_{n+1}^{out}(t) - (h^{in} - Ts^{in})\dot{z}_1^{in}(t) \leq 0.$$

Next we use (2.94) to get

$$\dot{\mathcal{A}}(t) + G^{out}\dot{z}_{n+1}^{out}(t) - G^{in}\dot{z}_1^{in}(t) \leq 0. \quad (2.95)$$

This inequality expresses the second law of thermodynamics for the considered open system. For a many cluster system, the total available free energy is expressed as

$$\mathcal{A}(\mathbf{z}(t)) = kT \sum_{i=1}^n z_i(t) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right), \quad \text{with} \quad q_i = \exp(-\mathcal{A}_i/kT).$$

Differentiating this equation with respect to  $t$  gives

$$\dot{\mathcal{A}}(\mathbf{z}(t)) = kT \sum_{i=1}^n \dot{z}_i(t) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right). \quad (2.96)$$

We point out that in all cases, large clusters are removed at a rate given by

$$\dot{z}_{n+1}^{out}(t) = J_n(\mathbf{z}(t)). \quad (2.97)$$

### 2.4.2 The modified constant free molecule model

Wattis [69] posed a constant free molecule version of the modified model of Dreyer and Duderstadt [16]. In his formulation, Wattis used condensation rates of the form in (1.7) and evaporation rates in (1.22), while setting  $z_1(t)$  to a constant. He showed that the model constructed in this way does not possess a Lyapunov function. Here we construct a constant free-molecule model which is consistent with the second law of thermodynamics. We must choose the rate  $\dot{z}_1^{in}(t)$

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so as to have  $\dot{z}_1(t) = 0$ . This maintains a constant number  $z_1(t) = \alpha$  of free molecules in the system. The input rate of free molecules is therefore obtained from (2.90) as

$$\dot{z}_1^{in}(t) = 2J_1(\mathbf{z}(t)) + \sum_{i=2}^n J_i(\mathbf{z}(t)). \quad (2.98)$$

Now we use (2.96) and (2.97) as well as (2.98) into (2.95) to get

$$\begin{aligned} \dot{\mathcal{A}}(\mathbf{z}(t)) + G^{out} \dot{z}_{n+1}^{out}(t) - G^{in} \dot{z}_1^{in}(t) = & kT \sum_{i=1}^n \dot{z}_i(t) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right) + G^{out} J_n(\mathbf{z}(t)) \\ & - G^{in} \left( 2J_1(\mathbf{z}(t)) + \sum_{i=2}^n J_i(\mathbf{z}(t)) \right). \end{aligned}$$

Define the following quantities

$$q^{in} := \exp(-G^{in}/kT) \quad \text{and} \quad q^{out} := \exp(-G^{out}/kT). \quad (2.99)$$

Then substitute for the time derivatives by using (2.89) and  $\dot{z}_1 = 0$  to get

$$\begin{aligned} \dot{\mathcal{A}}(\mathbf{z}(t)) + G^{out} \dot{z}_{n+1}^{out}(t) - G^{in} \dot{z}_1^{in}(t) = & kT \sum_{i=2}^n (J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t))) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right) \\ & - kT J_n(\mathbf{z}(t)) \ln(q^{out}) + kT \left( 2J_1(\mathbf{z}(t)) + \sum_{i=2}^n J_i(\mathbf{z}(t)) \right) \ln(q^{in}). \end{aligned}$$

This equation can be simplified to give

$$\begin{aligned} \dot{\mathcal{A}}(\mathbf{z}(t)) + G^{out} \dot{z}_{n+1}^{out}(t) - G^{in} \dot{z}_1^{in}(t) = & kT \left[ J_1(\mathbf{z}(t)) \ln \left( \frac{z_2(q^{in})^2}{N_D(\mathbf{z})q_2} \right) + \sum_{i=2}^{n-1} J_i(\mathbf{z}(t)) \ln \left( \frac{z_{i+1}q_i q^{in}}{z_i q_{i+1}} \right) \right] \\ & - kT J_n(\mathbf{z}(t)) \left[ \ln \left( \frac{z_n(t)}{q_n N_D(\mathbf{z}(t))} \right) - \ln \left( \frac{q^{in}}{q^{out}} \right) \right]. \quad (2.100) \end{aligned}$$

As a simpler case we consider the situation where no bigger clusters are removed from the system. From (2.97), this means that

$$\dot{z}_{n+1}^{out}(t) = 0 \quad \text{or} \quad J_n(\mathbf{z}(t)) = 0.$$

We then use (2.91) for the fluxes to get

$$\dot{\mathcal{A}}(\mathbf{z}(t)) - G^{in} \dot{z}_1^{in}(t) = kT \left[ (C_1 z_1 - E_2 z_2) \ln \left( \frac{z_2(q^{in})^2}{N_D(\mathbf{z})q_2} \right) + \sum_{i=2}^{n-1} (C_i z_i - E_{i+1} z_{i+1}) \ln \left( \frac{z_{i+1}q_i q^{in}}{z_i q_{i+1}} \right) \right].$$

To guarantee the second law (2.95) of thermodynamics, we first consider the summation on the right-hand side and compare each term with the function  $f(x) = (x - y) \ln(y/x)$ , which satisfies  $f(x) \leq 0$ . This then gives  $x = C_i z_i(t)$  and  $y = E_{i+1} z_{i+1}(t)$  so that the quotient leads to

$$E_{i+1} = \frac{q_i q^{in}}{q_{i+1}} C_i, \quad q_i = \exp(-\mathcal{A}_i/kT), \quad i \geq 2. \quad (2.101)$$



Using the same trick for the first term on the right-hand side we obtain

$$E_2 = \frac{z_1(q^{in})^2}{q_2 N_D(\mathbf{z}(t))} C_1. \quad (2.102)$$

We point out that these choices of evaporation rates may also apply to the case where  $J_n(\mathbf{z}(t)) \neq 0$ . This can be guaranteed by specifying the Gibbs free energy of in-coming free molecules and then calculating the Gibbs free energy of the removed clusters such that the term involving  $J_n$  in (2.100) vanishes. In this case we must have

$$\frac{q^{in}}{q^{out}} = \frac{z_n(t)}{q_n N_D(\mathbf{z}(t))}. \quad (2.103)$$

By using (2.101) and (2.102) the fluxes for the constant free molecule model are given by

$$J_1(\mathbf{z}(t)) = C_1 \left( z_1(t) - \frac{z_1(t)(q^{in})^2}{q_2 N_D(\mathbf{z}(t))} z_2(t) \right), \quad J_i(\mathbf{z}(t)) = C_i \left( z_i(t) - \frac{q_i q^{in}}{q_{i+1}} z_{i+1}(t) \right), \quad i \geq 2.$$

Like equation (1.28), we use  $C_i = a_i$  and  $b_{i+1} = C_i \tilde{q}_i / \tilde{q}_{i+1}$ , where  $\tilde{q}_i$  is defined in (1.24). The fluxes can then be written as

$$J_1(\mathbf{z}(t)) = a_1 z_1(t) - b_2 R \frac{z_1(t)(q^{in})^2}{N_D(\mathbf{z}(t))} z_2(t), \quad J_i(\mathbf{z}(t)) = a_i z_i(t) - b_{i+1} R q^{in} z_{i+1}(t), \quad (2.104)$$

for  $i \geq 2$ . These fluxes constitute the modified constant free molecule model together with equations (1.2) and (1.4). The model is nonlinear for  $i = 2$  and linear for all the other sizes  $i \geq 3$ .

### 2.4.3 The mass-conserving model for open systems

Here we add free molecules in order to maintain a constant number  $\rho = \sum_{i=1}^n i z_i(t)$  of molecules in the system. This means that the rate  $\dot{z}_1^{in}(t)$  of free molecule in-put is equivalent to the rate at which molecules are removed through the large clusters of size  $n + 1$ . According to (2.97), this must be given by

$$\dot{z}_1^{in}(t) = (n + 1) \dot{z}_{n+1}^{out} = (n + 1) J_n(\mathbf{z}(t)). \quad (2.105)$$

Now we use (2.96) and (2.97) as well as (2.105) into (2.95). This leads to

$$\dot{A}(\mathbf{z}(t)) + G^{out} \dot{z}_{n+1}^{out}(t) - G^{in} \dot{z}_1^{in}(t) = kT \sum_{i=1}^n \dot{z}_i(t) \ln \left( \frac{z_i(t)}{q_i N_D(\mathbf{z}(t))} \right) + [G^{out} - (n + 1)G^{in}] J_n(\mathbf{z}(t)).$$

Next we substitute for the derivatives  $\dot{z}_i(t)$  by using the model (2.89) and (2.90) as well as (2.105). To minimize space we represent the left-hand side of the above equation by LHS. This gives

$$\begin{aligned} \text{LHS} = & kT \left[ n J_n(\mathbf{z}(t)) \ln \left( \frac{z_1(t)}{q_1 N_D(\mathbf{z}(t))} \right) + \sum_{i=1}^{n-1} J_i(\mathbf{z}(t)) \ln \left( \frac{z_{i+1}(t) q_i N_D(\mathbf{z}(t))}{z_i(t) q_{i+1} z_1(t)} \right) \right] \\ & - kT J_n(\mathbf{z}(t)) \ln \left( \frac{z_n(t)}{q_n N_D(\mathbf{z}(t))} \right) + [G^{out} - (n + 1)G^{in}] J_n(\mathbf{z}(t)). \end{aligned}$$

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We then use  $q_1 = 1$  as well as (2.99) and simplify the result to obtain

$$\begin{aligned} \text{LHS} = & -kT J_n(\mathbf{z}(t)) \left[ \ln \left\{ \left( \frac{z_n(t)}{q_n N_D(\mathbf{z}(t))} \right) \left( \frac{N_D(\mathbf{z}(t))}{z_1(t)} \right)^n \right\} - \ln \left( \frac{(q^{in})^{n+1}}{q^{out}} \right) \right] \\ & + kT \sum_{i=1}^{n-1} J_i(\mathbf{z}(t)) \ln \left( \frac{z_{i+1}(t) q_i N_D(\mathbf{z}(t))}{z_i(t) q_{i+1} z_1(t)} \right). \end{aligned}$$

A sufficient condition to guarantee the second law (2.95) is such that

$$\frac{E_{i+1}}{C_i} = \frac{q_i N_D(\mathbf{z}(t))}{q_{i+1} z_1(t)} \quad \text{for } i \geq 1, \quad (2.106)$$

and

$$\frac{q^{in}}{q^{out}} = \left( \frac{z_n(t)}{q_n N_D} \right) \left( \frac{N_D(\mathbf{z}(t))}{q^{in} z_1(t)} \right)^n. \quad (2.107)$$

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## Chapter 3

# Steady-state solutions

In this chapter we study the simple steady-state problem for the modified Becker-Döring models. This occurs when all the time derivatives involved are equal to zero. The aim is to determine steady-state nucleation rates from these models. The method involves the analysis of the null space of the right-hand sides of the models. This technique was used by Conradi et al. [11] to determine steady-state solutions for chemical and biochemical networks. In Section 3.1 we demonstrate the method to the simpler constant free molecule model and later adapt the results to the more demanding mass-conserving version in Section 3.2. For each version we construct finite systems of differential equations by applying two known truncations. In the first truncation, we choose the maximum cluster size, say  $n$ , which is bigger than the critical cluster  $i_{crit}$  defined by the Thomson formula (2.16) and set the flux  $J_n$  to zero. We refer to this as the *zero flux truncation*. The second one is obtained by setting the number of clusters larger than  $n$  to zero and we call it the *zero particle number truncation*. For each model and truncation we study the existence of steady-state solutions in the limiting case  $n \rightarrow \infty$ . Section 3.3 contains a comparison of the steady-state solutions for the constant free molecule model with those for the mass-conserving one. In Section 3.4 we make some assumptions to derive the nucleation rates for the liquid-vapor-inert gas and crystal nucleation systems from the mass-conserving model. The chapter is closed by Section 3.5 where we compare the rates derived in Section 3.4 with those from experiments. For liquid-vapor-inert gas systems, we consider the experimental data for water vapor by Brus et al. [6], Wölk and Strey [71] as well as that for Argon by Sinha et al. [57]. For crystal nucleation, we use the data by Miyazawa and Pound [38] for crystallization of Gallium from its melt.

### 3.1 Finite versions of the constant free molecule model

Here we truncate the infinite system (1.2) and (1.4) at  $i = n$ , where  $n > i_{crit}$ , and either set  $J_n = 0$  or  $z_i = 0$  for  $i \geq n + 1$ . The flux  $J_n = 0$  means that there is no interaction of clusters of size  $n$  with larger clusters. This truncation was used by Ball et al. [4, Section 2] when approximating the infinite Becker-Döring system in order to study existence of solutions. The condition is equivalent to taking  $C_n = 0$  and  $z_{n+1} = 0$  at the same time as in Dreyer and Duderstadt [16]. It means that by some miracle or demon these are the largest possible clusters in the system and they lose their power to bind free molecules. The other possibility  $z_i = 0$  for all  $i \geq n + 1$  means that size  $n + 1$  clusters are immediately removed from the system by a

## CHAPTER 3. STEADY-STATE SOLUTIONS

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demon. This is part of the mechanism that Becker and Döring [5] already suggested in order to achieve a steady state. Thermodynamics for the constant free molecule model was discussed in Section 2.4.2.

### 3.1.1 The zero flux truncation for the constant free molecule model

Here we set  $J_n = 0$  in (1.2) and obtain for a given  $\mu \geq 0$  the finite system below

$$\begin{aligned} z_1 &= \mu, \\ \dot{z}_i(t) &= J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)), \quad 2 \leq i \leq n-1, \\ \dot{z}_n(t) &= J_{n-1}(\mathbf{z}(t)), \end{aligned} \quad (3.1)$$

where the fluxes are given by (2.104), repeated here for the finite system as

$$J_1(\mathbf{z}(t)) = a_1 z_1(t) - b_2 R \frac{z_1(t) (q^{in})^2}{N_D(\mathbf{z}(t))} z_2(t), \quad J_i(\mathbf{z}(t)) = a_i z_i(t) - b_{i+1} R q^{in} z_{i+1}(t), \quad (3.2)$$

for  $2 \leq i \leq n-1$ . We introduce an  $n \times (n-1)$  matrix

$$\mathbf{A} = \begin{pmatrix} 0 & 0 & \dots & & 0 \\ 1 & -1 & 0 & & \\ 0 & 1 & -1 & 0 & \\ \vdots & & & \ddots & \vdots \\ & & & 0 & 1 & -1 & 0 \\ & & & & 0 & 1 & -1 \\ 0 & & \dots & & & 0 & 1 \end{pmatrix},$$

with  $\text{rank}(\mathbf{A}) = n-1$ . Then the model can be written as

$$\dot{\mathbf{z}}(t) = \mathbf{A}\mathbf{j}(\mathbf{z}(t)), \quad (3.3)$$

where  $\mathbf{z} = (z_1(t), z_2(t), \dots, z_n(t))$  and  $\mathbf{j}(\mathbf{z}(t)) = (J_1(\mathbf{z}(t)), J_2(\mathbf{z}(t)), \dots, J_{n-1}(\mathbf{z}(t)))$ . Our interest here is to determine all the possible steady states for the system (3.3). The model is said to have multiple steady states if for any given set of vectors  $(a_1, a_2, \dots, a_{n-1})^T$ ,  $(b_2, b_3, \dots, b_n)^T$  and any constants  $\mu \geq 0$  and  $R > 0$ , two distinct positive vectors  $\mathbf{g}, \mathbf{h} \in \mathbb{R}_{>0}^n$  can be found such that the following conditions hold

$$\mathbf{A}\mathbf{j}(\mathbf{g}) = \mathbf{0}, \quad \mathbf{A}\mathbf{j}(\mathbf{h}) = \mathbf{0} \quad \text{and} \quad g_1 = h_1 = \mu. \quad (3.4)$$

We now show that there is only one steady state which is an equilibrium.

**Lemma 3.1.1** (Uniqueness). *There exists at most one equilibrium solution to (3.1).*

*Proof.* The first two equations in (3.4) can be satisfied if either  $\mathbf{j} = \mathbf{0}$  or if  $\mathbf{j} \in \ker(\mathbf{A})$ . Since  $\text{rank}(\mathbf{A}) = n-1$  and  $\mathbf{j}$  is a vector of size  $n-1$ , these equations can only be satisfied if and only if

$$\mathbf{j}(\mathbf{g}) = \mathbf{j}(\mathbf{h}) = \mathbf{0}. \quad (3.5)$$

### 3.1. FINITE VERSIONS OF THE CONSTANT FREE MOLECULE MODEL

This means that the fluxes must vanish. Therefore the steady states are equilibria in this case. Using the flux definition, we have for the solution  $\mathbf{g}$

$$a_1 g_1 = b_2 R \frac{g_1 (q^{in})^2}{N_D(\mathbf{g})} g_2, \quad a_2 g_2 = b_3 R q^{in} g_3, \quad \dots, \quad a_{n-1} g_{n-1} = b_n R q^{in} g_n. \quad (3.6)$$

This system can also be written for the steady-state solution  $\mathbf{h}$  as

$$a_1 h_1 = b_2 R \frac{h_1 (q^{in})^2}{N_D(\mathbf{h})} h_2, \quad a_2 h_2 = b_3 R q^{in} h_3, \quad \dots, \quad a_{n-1} h_{n-1} = b_n R q^{in} h_n. \quad (3.7)$$

We assume that  $a_i > 0$  and  $b_{i+1} > 0$  for all  $1 \leq i \leq n-1$ . Suppose there exists a zero component of any of the equilibrium solutions  $\mathbf{g}$  and  $\mathbf{h}$ . Then equations (3.6) and (3.7) imply that such an equilibrium is trivial with  $N_D = 0$ . In this case the first equation in (3.6) is undefined. Therefore equilibrium solutions to the model have positive components. We can thus apply logarithms to each of the equations in systems (3.6) and (3.7). Subtracting the logarithmic equations for (3.7) from the corresponding ones in (3.6) and using  $\nu_i := \ln(g_i/h_i)$  we obtain

$$\nu_2 = \nu_3 = \dots = \nu_n, \quad (3.8)$$

which implies that there exists a constant  $\kappa$  such that

$$g_i = \kappa h_i, \quad 2 \leq i \leq n. \quad (3.9)$$

The first equations in (3.6) and (3.7) can be simplified to

$$a_1 N_D(\mathbf{g}) = b_2 R q^{in} g_2, \quad \text{and} \quad a_1 N_D(\mathbf{h}) = b_2 R q^{in} h_2. \quad (3.10)$$

Using the finite version of (1.19) and applying the last equation in (3.4) together with (3.9), equations (3.10) can be solved to give  $\kappa = 1$ . This leads to  $g_i = h_i$  or equivalently  $\nu_i = 0$  for all  $1 \leq i \leq n$ .  $\square$

It therefore remains to solve for the unique equilibrium solution. We can easily show by solving (3.6) and using  $\bar{\mathbf{z}}^F := \mathbf{g}$ , that

$$\bar{z}_i^F = R Q_i \bar{N}_D^F \left( \frac{1}{R q^{in}} \right)^i, \quad \text{for } i \geq 2 \quad \text{and} \quad \bar{z}_1^F = \mu, \quad (3.11)$$

where the constants  $Q_i$  are defined in (1.8). The superscript  $F$  is represents the constant free molecule model. The equilibrium number of clusters can directly be obtained by summing (3.11) from 1 to  $n$  and rearranging to obtain

$$\bar{N}_D^F = \frac{\alpha}{1 - R \sum_{i=2}^n Q_i (1/R q^{in})^i}, \quad Q_i = \prod_{r=2}^i \frac{a_{r-1}}{b_r}, \quad i \geq 2. \quad (3.12)$$

For positive values of  $\bar{N}_D^F$  we require that

$$R \sum_{i=2}^n Q_i (1/R q^{in})^i < 1. \quad (3.13)$$

The above equilibrium solutions can be written in terms of  $\tilde{q}_i$  or  $q_i$  by using (1.29). In summary we have obtained the result

**Theorem 3.1.2.** *The system (3.1) has a unique equilibrium solution given by (3.11) - (3.13).*

### 3.1.2 The zero particle number truncation for the constant free molecule model

Here we truncate the infinite Becker-Döring system (1.2) at  $n$  and set  $z_i = 0$  for all  $i \geq n + 1$ . We obtain the following system

$$\begin{aligned} z_1 &= \mu, \\ \dot{z}_i(t) &= J_{i-1} - J_i, \quad 2 \leq i \leq n-1, \\ \dot{z}_n(t) &= J_{n-1} - J_n, \end{aligned} \tag{3.14}$$

with  $J_i$  given by (3.2) for  $1 \leq i \leq n-1$  and  $J_n = a_n z_n$ . We introduce an  $n \times n$  matrix

$$\mathbf{B} = \begin{pmatrix} 0 & 0 & & \dots & & & 0 \\ 1 & -1 & 0 & & & & \\ 0 & 1 & -1 & 0 & & & \\ \vdots & & & \ddots & & & \vdots \\ & & & & 0 & 1 & -1 & 0 \\ & & & & & 0 & 1 & -1 & 0 \\ 0 & & \dots & & & & 0 & 1 & -1 \end{pmatrix},$$

with  $\text{rank}(\mathbf{B}) = n - 1$ . Then the system can be recast into the form already used in (3.3) as

$$\dot{\mathbf{z}}(t) = \mathbf{B}\mathbf{j}(\mathbf{z}(t)), \tag{3.15}$$

where  $\mathbf{z} = (z_1(t), z_2(t), \dots, z_n(t))$  and  $\mathbf{j}(\mathbf{z}(t)) = (J_1(\mathbf{z}(t)), J_2(\mathbf{z}(t)), \dots, J_n(\mathbf{z}(t)))$ .

**Lemma 3.1.3** (uniqueness). *There exists at most one steady state solution to (3.14).*

*Proof.* Steady states for (3.15) imply that either  $\mathbf{j} = \mathbf{0}$  or  $\mathbf{j} \in \ker(\mathbf{B}) \cap \mathbb{R}^n$ . Suppose that  $\mathbf{x}$  and  $\mathbf{y}$  are two distinct steady states to (3.15). For  $\mathbf{j}(\mathbf{x}) = \mathbf{0}$  or  $\mathbf{j}(\mathbf{y}) = \mathbf{0}$  the definition of  $J_n$  would imply that  $x_n = 0$  or  $y_n = 0$ . By use of back substitution this would lead to the trivial equilibria  $x_i = 0$  or  $y_i = 0$  for all  $1 \leq i \leq n$ . This is not even a solution to the model due the presence of  $N_D$  as a denominator in the definition of  $J_1$  in (3.2). Therefore we must have  $\mathbf{j} \in \ker(\mathbf{B}) \cap \mathbb{R}^n$ . The kernel,  $\ker(\mathbf{B})$ , of  $\mathbf{B}$  is generated by only one vector  $\mathbf{v} = (1, 1, \dots, 1)^T \in \mathbb{R}^n$ . Then there exist scalars  $\gamma > 0$  and  $\eta > 0$  such that

$$\mathbf{j}(\mathbf{x}) = \gamma \mathbf{v} = \gamma(1, 1, \dots, 1)^T, \quad \mathbf{j}(\mathbf{y}) = \eta \mathbf{v} = \eta(1, 1, \dots, 1)^T, \quad \text{with } x_1 = y_1 = \mu. \tag{3.16}$$

These equations imply that

$$J_1(\mathbf{x}) = J_2(\mathbf{x}) = \dots = J_n(\mathbf{x}) = \gamma > 0 \text{ and } J_1(\mathbf{y}) = J_2(\mathbf{y}) = \dots = J_n(\mathbf{y}) = \eta > 0. \tag{3.17}$$

Equations (3.16) show that the flux equations for the two steady state solutions  $\mathbf{x}$  and  $\mathbf{y}$  are related by

$$J_i(\mathbf{x}) = \xi J_i(\mathbf{y}) \quad \text{for all } 1 \leq i \leq n, \quad \text{where } \xi := \gamma/\eta. \tag{3.18}$$

Using (3.2) we consider (3.18) starting with  $i = n$  and go backwards to  $i = 2$ . It can easily be seen that

$$x_i = \xi y_i, \quad \text{for } 2 \leq i \leq n. \tag{3.19}$$

### 3.1. FINITE VERSIONS OF THE CONSTANT FREE MOLECULE MODEL

Since we are assuming  $\mathbf{x} \neq \mathbf{y}$  the relations  $x_1 = y_1$  and (3.19) both imply that  $\xi \neq 1$ . The equations for the flux  $J_1$  are handled in a different way due to the presence of the term  $N_D$  in the denominator. We use (3.2) and (3.17) to get

$$J_1(\mathbf{x}) = a_1 x_1 - b_2 R \frac{x_1 (q^{in})^2}{N_D(\mathbf{x})} x_2 = \gamma \quad \text{and} \quad J_1(\mathbf{y}) = a_1 y_1 - b_2 R \frac{y_1 (q^{in})^2}{N_D(\mathbf{y})} y_2 = \eta. \quad (3.20)$$

By using the relation  $x_1 = y_1 = \mu$  and (3.19) in the definition of  $N_D$  we obtain

$$N_D(\mathbf{x}) = x_1(1 - \xi) + \xi N_D(\mathbf{y}). \quad (3.21)$$

Now taking the difference of the two equations in (3.20), with  $\gamma = \xi\eta$ , and using (3.19) for  $i = 2$  we obtain

$$b_2 R (q^{in})^2 x_1 y_2 \left[ \frac{N_D(\mathbf{x}) - \xi N_D(\mathbf{y})}{N_D(\mathbf{x}) N_D(\mathbf{y})} \right] = \eta(\xi - 1). \quad (3.22)$$

Inserting (3.21) into (3.22) it can easily be seen that for  $\xi \neq 1$

$$\eta = -\frac{b_2 R (q^{in})^2 x_1^2 y_2}{N_D(\mathbf{x}) N_D(\mathbf{y})} < 0. \quad (3.23)$$

This contradicts the requirement that  $\eta > 0$ . Therefore we must have  $\xi = 1$  which implies that the zero particle number truncation gives only one steady-state solution to the model.  $\square$

Next we determine the unique steady state  $\mathbf{z}^{s,F}$  and the steady-state flux  $J^F := \gamma = \eta$ . We start with the flux  $J_n = a_n z_n^{s,F}$  to express  $z_n$  in terms of the common flux and then use back substitution to determine all the sizes for  $1 \leq i \leq n$ , see Appendix B.1 for details. This gives

$$z_1^{s,F} = \mu, \quad z_i^{s,F} = J^F Q_i (1/Rq^{in})^i \sum_{r=i}^n \frac{1}{a_r Q_r (1/Rq^{in})^r}, \quad 2 \leq i \leq n, \quad (3.24)$$

and the steady-state flux

$$J^F = z_1^{s,F} \left( \frac{1}{a_1} + \frac{\bar{\lambda}}{R} \sum_{r=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} \right)^{-1}, \quad \bar{\lambda} := \frac{z_1^{s,F}}{N_D(\mathbf{z}^{s,F})}. \quad (3.25)$$

The flux  $J^F$  is the kinetic expression for the nucleation rate and it gives the number of nucleating clusters per second. For fixed  $n$  and  $R$  the parameter  $\bar{\lambda}$  can be calculated by summing (3.24) from 1 to  $n$  and using (3.25) to obtain

$$\frac{\bar{\lambda}^2}{R} \sum_{r=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} + \bar{\lambda} \left[ \frac{1}{a_1} - \frac{1}{R} \sum_{r=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} \left( 1 - R \sum_{i=2}^r Q_i (1/Rq^{in})^i \right) \right] = \frac{1}{a_1}. \quad (3.26)$$

In order to convert the units of the nucleation rate  $J^F$  into number per unit volume per second we divide (3.25) by the total volume of the system which is constant in a steady state. In summary we have obtained the result

**Theorem 3.1.4.** *The system (3.14) has a unique steady state solution given by (3.24) - (3.26).*

### 3.1.3 The limiting steady-state solutions for the constant free molecule model

First we consider the existence of the equilibrium solutions (3.11) - (3.13) in the limit  $n \rightarrow \infty$ . By using the last equation in (1.29) we note that in this limit, the inequality (3.13) is equivalent to

$$\sum_{i=2}^{\infty} q_i / (q^{in})^i < 1, \quad q_i = \exp\left(-\frac{\mathcal{A}_i}{kT}\right).$$

We then use (2.12) to substitute for  $\mathcal{A}_i$ . This leads to the requirement

$$G(S) := \sum_{i=2}^{\infty} S^i \exp\left(-\tilde{a}i^{2/3} - i \ln(q^{in})\right) < 1, \quad \tilde{a} := \frac{\gamma}{kT}. \quad (3.27)$$

The radius  $R_G$  of convergence of  $G(S)$  is given by

$$\frac{1}{R_G} = \limsup_{i \rightarrow \infty} \left[ \exp\left(-\tilde{a}i^{2/3} - i \ln(q^{in})\right) \right]^{1/i},$$

giving  $R_G = q^{in}$ . Moreover, the series converges also for  $S = R_G$  because <sup>1</sup>

$$G(R_G) \leq \int_0^{\infty} \exp(-\tilde{a}i^{2/3}) di = \frac{3\sqrt{\pi}}{4\tilde{a}^{3/2}}.$$

Note that the function  $G(S)$  is monotonically increasing in  $S$  on  $[0, R_G]$ . Therefore in order to satisfy the above inequality on this interval, it is sufficient to have

$$G(S) \leq G(R_G) \leq \frac{3\sqrt{\pi}}{4\tilde{a}^{3/2}} < 1,$$

which leads to the sufficient condition

$$\tilde{a} \geq \left(\frac{9\pi}{16}\right)^{1/3} \approx 1.21. \quad (3.28)$$

Typical values of  $\tilde{a}$  for water vapor at temperatures in the range  $0^{\circ}C - 100^{\circ}C$  exceed the value 1.21 given by inequality (3.28),<sup>2</sup> see Wagner and Kretschmar [66]. Therefore within the above temperature range the infinite system can be solved for all  $S \in [0, R_G]$ .

We now turn our attention to the non-equilibrium steady-state solution (3.24) - (3.26). By using  $q_i$  from (1.29) and  $\mathcal{A}_i$  in (2.12) the limiting version of (3.26) becomes

$$\begin{aligned} \frac{1}{a_1} = \bar{\lambda} & \left[ \frac{1}{a_1} - \sum_{r=2}^{\infty} \frac{1}{a_r (S/R_G)^r \exp(-\tilde{a}r^{2/3})} \left( 1 - \sum_{i=2}^r (S/R_G)^i \exp(-\tilde{a}i^{2/3}) \right) \right] \\ & + \bar{\lambda}^2 \sum_{r=2}^{\infty} \frac{1}{a_r (S/R_G)^r \exp(-\tilde{a}r^{2/3})}. \end{aligned}$$

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<sup>1</sup>Using the substitution  $i^{1/3}\sqrt{\tilde{a}} = x$ , the expression  $\int_0^{\infty} \exp(-\tilde{a}i^{2/3}) di$  becomes  $\frac{3}{\tilde{a}^{3/2}} \int_0^{\infty} x^2 \exp(-x^2) dx$ . This can then be solved using integration by parts to give  $\frac{3}{\tilde{a}^{3/2}} \left\{ \left[-\frac{1}{2}x \exp(-x^2)\right]_0^{\infty} + \frac{1}{2} \int_0^{\infty} \exp(-x^2) dx \right\}$ . Therefore  $\int_0^{\infty} \exp(-\tilde{a}i^{2/3}) di = \frac{3\sqrt{\pi}}{4\tilde{a}^{3/2}}$ .

<sup>2</sup>For example at  $T = 275[K]$ ,  $\sigma = 75[g/s^2]$  or for  $T = 298.2[K]$ ,  $\sigma = 71.97[g/s^2]$ . In both cases  $m = 2.99 \times 10^{-23}[g]$  and  $\rho_L = 9.97 \times 10^5[g/m^3]$ . With the Boltzmann constant  $k = 1.38 \times 10^{-20}[g \cdot m^2/K \cdot s^2]$ , temperatures of  $275[K]$  and  $298.2[K]$  lead to  $\tilde{a} = 9.22$  and  $\tilde{a} = 8.16$  respectively.



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### 3.2. FINITE VERSIONS OF THE MASS-CONSERVING MODEL

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The denominator of the first series on the left of this equation is dominated by the term  $S^r$  for large  $r$  and will converge if  $S > R_G$ . On the other hand, for very large values of  $r$  the sums from 2 to  $r$  lead to the series  $G(S)$  defined in (3.27). We have seen that this series converges only for  $S \in [0, R_G]$ , which contradicts the convergence requirement  $S > R_G$  obtained above. Hence there are no non-equilibrium steady-state solutions for the constant free molecule model in the limit  $n \rightarrow \infty$ .

## 3.2 Finite versions of the mass-conserving model

In this section we consider the modified mass-conserving model which was introduced by Dreyer and Duderstadt [16]. We study the finite versions of the model by considering the two truncations introduced in the previous section. Essential to this model is the mass conservation property

$$\rho = \sum_{i=1}^n i z_i(t) = \text{constant}. \quad (3.29)$$

### 3.2.1 The zero flux truncation for the modified mass-conserving model

We truncate the system (1.2) and (1.5) at  $n > i_{crit}$  and set  $J_n(\mathbf{z}(t))$  to zero. This gives

$$\begin{aligned} \dot{z}_1(t) &= -2J_1(\mathbf{z}(t)) - \sum_{i=2}^{n-1} J_i(\mathbf{z}(t)), \\ \dot{z}_i(t) &= J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)) \quad 2 \leq i \leq n, \\ \dot{z}_n(t) &= J_{n-1}(\mathbf{z}(t)), \end{aligned} \quad (3.30)$$

where the fluxes are obtained from (1.28) as

$$J_i(\mathbf{z}(t)) = a_i z_i(t) - \frac{b_{i+1} R}{\lambda(\mathbf{z})} z_{i+1} \quad \text{for } 1 \leq i \leq n-1, \quad \lambda(\mathbf{z}) := \frac{z_1(t)}{N_D(\mathbf{z}(t))} \quad (3.31)$$

Define the  $n \times (n-1)$  matrix  $\mathbf{C}$  by

$$\mathbf{C} = \begin{pmatrix} -2 & -1 & -1 & \dots & -1 \\ 1 & -1 & 0 & & 0 \\ 0 & 1 & -1 & 0 & \\ \vdots & & & \ddots & \vdots \\ & & & & \vdots \\ & & & 0 & 1 & -1 & 0 \\ & & & & 0 & 1 & -1 \\ 0 & \dots & & & 0 & 1 \end{pmatrix}.$$

The finite model (3.30) can then be reformulated as

$$\dot{\mathbf{z}}(t) = \mathbf{C}\mathbf{j}(\mathbf{z}(t)), \quad (3.32)$$

where  $\mathbf{z} = (z_1(t), z_2(t), \dots, z_n(t))$  and  $\mathbf{j}(\mathbf{z}(t)) = (J_1(\mathbf{z}(t)), J_2(\mathbf{z}(t)), \dots, J_{n-1}(\mathbf{z}(t)))$ . We note that the second up to the last row of  $\mathbf{C}$  are linearly independent but due to mass conservation the first one is a linear combination of all the others. Thus  $\text{rank}(\mathbf{C}) = n-1$ .

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**Lemma 3.2.1** (Uniqueness). *There exists at most one equilibrium solution to (3.30).*

*Proof.* Since  $\mathbf{j}$  is a vector of length  $n - 1$ , any two steady states  $\mathbf{g}$  and  $\mathbf{h}$  for (3.30) are such that

$$\mathbf{j}(\mathbf{g}) = \mathbf{j}(\mathbf{h}) = \mathbf{0}. \quad (3.33)$$

For solution  $\mathbf{g}$  we have

$$a_1 g_1 = \frac{b_2 R}{\lambda(\mathbf{g})} g_2, \quad a_2 g_2 = \frac{b_3 R}{\lambda(\mathbf{g})} g_3, \quad \dots, \quad a_{n-1} g_{n-1} = \frac{b_n R}{\lambda(\mathbf{g})} g_n. \quad (3.34)$$

This system of equations can also be written for the steady state solution  $\mathbf{h}$  as

$$a_1 h_1 = \frac{b_2 R}{\lambda(\mathbf{h})} h_2, \quad a_2 h_2 = \frac{b_3 R}{\lambda(\mathbf{h})} h_3, \quad \dots, \quad a_{n-1} h_{n-1} = \frac{b_n R}{\lambda(\mathbf{h})} h_n. \quad (3.35)$$

By arguing in the same way as was done in the proof of Theorem 3.1.1, it can be shown that the solutions  $\mathbf{g}$  and  $\mathbf{h}$  are positive. We can therefore divide the equations in (3.35) by corresponding equations in (3.34) and use  $\kappa := \lambda(\mathbf{h})/\lambda(\mathbf{g})$  to obtain

$$\frac{h_i}{g_i} = \kappa^{i-1} \frac{h_1}{g_1}, \quad \text{for all } 1 \leq i \leq n. \quad (3.36)$$

Using this equation in the definition for  $\kappa$  and the finite version of (1.19), we require that

$$\sum_{i=1}^n \kappa^i g_i = \sum_{i=1}^n g_i.$$

This equation can only be satisfied if  $\kappa = 1$ . Next we apply the mass conservation condition (3.29) to get

$$\sum_{i=1}^n i(h_i - g_i) = 0.$$

Substituting (3.36) for  $\kappa = 1$  into this equation, we obtain

$$\sum_{i=1}^n i g_i \left( \frac{h_1}{g_1} - 1 \right) = 0.$$

Since we are interested in nontrivial solutions, this equation is satisfied if and only if  $h_1 = g_1$ . Then (3.36) implies that  $h_i = g_i$  for all  $1 \leq i \leq n$ , hence uniqueness of the equilibrium solution.  $\square$

It remains to solve for the equilibrium distribution  $\bar{\mathbf{z}}^M$ . By solving (3.34) and setting  $\mathbf{g} = \bar{\mathbf{z}}^M$  we get

$$\bar{z}_i^M = R \bar{N}_D^M Q_i \left( \frac{\lambda}{R} \right)^i, \quad 1 \leq i \leq n \quad \text{where} \quad \lambda := \frac{\bar{z}_1^M}{\bar{N}_D^M}. \quad (3.37)$$

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The constants  $Q_i$  are defined in (1.8). This equation can equivalently be written as

$$\bar{z}_i^M = \bar{z}_1^M Q_i \left( \frac{\lambda}{R} \right)^{i-1}, \quad 1 \leq i \leq n. \quad (3.38)$$

By summing both sides of (3.37) from 1 to  $n$  we obtain the condition

$$\sum_{i=1}^n R Q_i \left( \frac{\lambda}{R} \right)^i = 1, \quad (3.39)$$

from which  $\lambda$  can be calculated, see [16] for more details. Multiplying (3.38) by  $i$  and summing the result from 1 to  $n$ , the number  $\bar{z}_1^M$  of free molecules in equilibrium is obtained from the mass-conservation property as

$$\bar{z}_1^M = \rho \left[ \sum_{i=1}^n i Q_i (\lambda/R)^{i-1} \right]^{-1}. \quad (3.40)$$

In summary we have obtained the result

**Theorem 3.2.2.** *The system (3.30) has a unique equilibrium solution given by (3.37) - (3.40).*

#### 3.2.2 The zero particle number truncation for the modified mass-conserving model

Note that this truncation would not conserve mass if we applied it without further modification due to the out going flux  $J_n = a_n z_n$ . Therefore we modify the equation for the free molecules  $z_1$ . We imagine a demon that breaks up a  $n$ -mer into molecules at a rate  $k_d := a_n$  which are then fed back into the system as free molecules. The finite system then becomes

$$\begin{aligned} \dot{z}_1(t) &= nJ_n - J_1(\mathbf{z}(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}(t)), \\ \dot{z}_i(t) &= J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)) \quad 2 \leq i \leq n-1 \\ \dot{z}_n(t) &= J_{n-1}(\mathbf{z}(t)) - J_n(\mathbf{z}(t)). \end{aligned} \quad (3.41)$$

This formulation comes close to the mechanism that Becker-Döring [5] suggested in order to achieve a steady state dynamically with finite cluster sizes. It is based on the system suggested by Burton [7, System (16)] with the modification that we allow the possibility of evaporation from a cluster of size  $n$  to  $n-1$ . Via the flux  $J_n$  in the equation for  $z_n$  clusters of size  $n+1$  are formed and inserted via the flux  $(n+1)J_n$  into the equation for  $z_1$ . We are reinserting the too large clusters broken up into free molecules in a manner that conserves mass. The thermodynamics for this open system was discussed in Section 2.4.3. Actually Becker and Döring suggested that the free molecules be inserted in a manner that keeps the pressure constant while the system

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approaches the steady state. We introduce the  $n \times n$  matrix

$$\mathbf{D} = \begin{pmatrix} -2 & -1 & -1 & \dots & & -1 & n \\ 1 & -1 & 0 & & & 0 & 0 \\ 0 & 1 & -1 & 0 & & & \\ \vdots & & & \ddots & & \vdots & \vdots \\ & & & & 0 & 1 & -1 & 0 \\ & & & & & 0 & 1 & -1 & 0 \\ 0 & \dots & & & & 0 & 1 & -1 \end{pmatrix}.$$

Then the finite model (3.41) can be reformulated as

$$\dot{\mathbf{z}}(t) = \mathbf{D}\mathbf{j}(\mathbf{z}(t)), \quad (3.42)$$

where  $\mathbf{z} = (z_1(t), z_2(t), \dots, z_n(t))$  and  $\mathbf{j}(\mathbf{z}(t)) = (J_1(\mathbf{z}(t)), J_2(\mathbf{z}(t)), \dots, J_n(\mathbf{z}(t)))$ .

**Lemma 3.2.3** (Uniqueness). *There exists at most one steady state solution to (3.41).*

*Proof.* Steady states of (3.42) imply that either  $\mathbf{j} = 0$  or  $\mathbf{j} \in \ker(\mathbf{D})$ . Analogously to the results in Theorem 3.1.3 there are no solutions for the case  $\mathbf{j} = 0$ . The mass conservation condition (3.29) implies that the first row is linearly dependent on all the other rows. Thus  $\text{rank}(\mathbf{D}) = n - 1$ . The null space of  $\mathbf{D}$  is generated by the vector  $\mathbf{v} = (1, 1, \dots, 1)^T$ . Now suppose  $\mathbf{x}$  and  $\mathbf{y}$  are two distinct steady-state solutions of (3.42). Then there exist scalars  $\gamma > 0$  and  $\eta > 0$  such that

$$\mathbf{j}(\mathbf{x}) = \gamma\mathbf{v} = \gamma(1, 1, \dots, 1)^T, \quad \mathbf{j}(\mathbf{y}) = \eta\mathbf{v} = \eta(1, 1, \dots, 1)^T \quad \text{with} \quad \sum_{i=1}^n ix_i = \sum_{i=1}^n iy_i. \quad (3.43)$$

The first two equations in (3.43) imply that

$$J_i(\mathbf{x}) = \xi J_i(\mathbf{y}) \quad \text{for all} \quad 1 \leq i \leq n, \quad \text{where} \quad \xi := \gamma/\eta. \quad (3.44)$$

We substitute for the fluxes starting from  $i = n$  with  $J_n(\mathbf{z}) = a_n z_n$  giving

$$x_n = \xi y_n. \quad (3.45)$$

Now we go backwards using (3.31), i.e.  $J_i(\mathbf{z}) := a_i z_i - b_{i+1} R z_{i+1} / \lambda(\mathbf{z})$  where  $\lambda(\mathbf{z}) = z_1 / N_D(\mathbf{z})$ . For  $i = n - 1$  equation (3.44) states that

$$a_{n-1} x_{n-1} - \frac{b_n R}{\lambda(\mathbf{x})} x_n = a_{n-1} \xi y_{n-1} - \frac{b_n R}{\lambda(\mathbf{y})} \xi y_n.$$

Define  $\kappa := \lambda(\mathbf{x})/\lambda(\mathbf{y})$  so that this equation becomes

$$a_{n-1} x_{n-1} - \frac{b_n R}{\lambda(\mathbf{x})} x_n = a_{n-1} \xi y_{n-1} - \kappa \frac{b_n R}{\lambda(\mathbf{x})} \xi y_n.$$

Next we substitute for  $\xi y_n$  by using (3.45) and rearrange the result while eliminating the quotient  $b_n/a_{n-1}$  with the first relation in (1.29) to give

$$\xi y_{n-1} = x_{n-1} + \frac{(\kappa - 1)}{\kappa} \left( \frac{\kappa}{\lambda(\mathbf{x})} \right) \frac{b_n R}{a_{n-1}} x_n = x_{n-1} + \frac{(\kappa - 1)}{\kappa} \left( \frac{\kappa R}{\lambda(\mathbf{x})} \right) \frac{Q_{n-1}}{Q_n} x_n. \quad (3.46)$$

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For  $i = n - 2$  equation (3.44) leads to

$$a_{n-2}x_{n-2} - \frac{b_{n-1}R}{\lambda(\mathbf{x})}x_{n-1} = a_{n-2}\xi y_{n-2} - \frac{b_{n-1}R}{\lambda(\mathbf{y})}\xi y_{n-1}.$$

We again write  $\lambda(\mathbf{y})$  in terms of  $\kappa$  and use the first equation in (1.29) to obtain

$$\xi y_{n-2} = x_{n-2} + \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right) \frac{Q_{n-2}}{Q_{n-1}} \xi y_{n-1} - \frac{1}{\kappa} \frac{Q_{n-2}}{Q_{n-1}} \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right) x_{n-1}.$$

Using (3.46) to substitute for  $\xi y_{n-1}$  and simplifying the result give

$$\xi y_{n-2} = x_{n-2} + \frac{(\kappa - 1)}{\kappa} \left[ \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right) \frac{Q_{n-2}}{Q_{n-1}} x_{n-1} + \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^2 \frac{Q_{n-2}}{Q_n} x_n \right]. \quad (3.47)$$

The above procedure is repeated for  $i = n - 3, n - 4, \dots, 1$ . We obtain the general formula

$$\xi y_i = x_i + \frac{(\kappa - 1)}{\kappa} \sum_{j=i+1}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^{j-i} \frac{Q_i}{Q_j} x_j, \quad 1 \leq i \leq n - 1. \quad (3.48)$$

By summing (3.48) from 1 to  $n - 1$  and adding the result to (3.45) we obtain

$$\xi N_D(\mathbf{y}) = N_D(\mathbf{x}) + \frac{(\kappa - 1)}{\kappa} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^{j-i} \frac{Q_i}{Q_j} x_j.$$

Dividing this equation by  $N_D(\mathbf{x})$  and using the definition (3.31) of  $\lambda$  for each of the solutions  $\mathbf{x}$  and  $\mathbf{y}$  together with  $\kappa = \lambda(\mathbf{x})/\lambda(\mathbf{y})$ , we obtain

$$\kappa \xi y_1 = x_1 + \frac{(\kappa - 1)\lambda(\mathbf{x})}{\kappa} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^{j-i} \frac{Q_i}{Q_j} x_j. \quad (3.49)$$

Inserting (3.48) for  $i = 1$  into this formula and rearranging the result give

$$(\kappa - 1) \left[ x_1 + \sum_{j=2}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^{j-1} \frac{Q_1}{Q_j} x_j \right] = \frac{(\kappa - 1)\lambda(\mathbf{x})}{\kappa} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^{j-i} \frac{Q_i}{Q_j} x_j.$$

Now we change the order of summation in the right-hand side and simplify the result into

$$(\kappa - 1) \left[ x_1 + \frac{\lambda(\mathbf{x})}{\kappa R} \sum_{j=2}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^j \frac{1}{Q_j} \left( Q_1 - \sum_{i=1}^{j-1} \left(\frac{\lambda(\mathbf{x})}{\kappa R}\right)^i R Q_i \right) x_j \right] = 0. \quad (3.50)$$

This equation is satisfied if either  $\kappa = 1$  or if the term in square brackets is equal to zero. Since we are interested only in situations where  $x_1 > 0$ , then for a given  $R > 0$  the latter case requires that

$$\frac{\lambda(\mathbf{x})}{\kappa R} \sum_{j=2}^n \left(\frac{\kappa R}{\lambda(\mathbf{x})}\right)^j \frac{1}{Q_j} \left( Q_1 - \sum_{i=1}^{j-1} \left(\frac{\lambda(\mathbf{x})}{\kappa R}\right)^i R Q_i \right) x_j < 0, \quad \text{for all } n.$$

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For  $n = 2$  this gives the inequality

$$\frac{\lambda(\mathbf{x})}{\kappa} > 1,$$

or equivalently after substituting for  $\kappa$  we have

$$\lambda(\mathbf{x}) > \frac{\lambda(\mathbf{x})}{\lambda(\mathbf{y})}.$$

This leads to

$$\lambda(\mathbf{y}) = \frac{y_1}{N_D(\mathbf{y})} = \frac{y_1}{y_1 + y_2} > 1, \quad (3.51)$$

which is satisfied only if  $y_2 < 0$ . This contradicts the requirement of positive solutions. Thus (3.50) can only be solved if  $\kappa = 1$ . Equation (3.45) and (3.48) for  $\kappa = 1$  imply that

$$\xi y_i = x_i \quad \text{for all } 1 \leq i \leq n. \quad (3.52)$$

Finally we use the mass conservation condition in (3.43) to obtain  $\xi = 1$  and therefore

$$x_i = y_i \quad \text{for all } 1 \leq i \leq n.$$

This gives the uniqueness result.  $\square$

Now we want to determine the formula for the unique steady-state solution which is denoted by  $\mathbf{z}^{s,M}$ . It is given by, see Appendix B.2

$$z_i^{s,M} = J^M Q_i (\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r (\lambda/R)^r}, \quad \lambda := \frac{z_1^{s,M}}{N_D(\mathbf{z}^{s,M})}, \quad (3.53)$$

where the common flux  $J^M$  is obtained by setting  $i = 1$  in the above equation and using  $Q_1 = 1$ . This gives

$$J^M = z_1^{s,M} \left( \sum_{r=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \right)^{-1}. \quad (3.54)$$

Unlike the constant free molecule model, the value for  $z_1^{s,M}$  is not yet specified for the mass-conserving model. In the following we determine its value together with the parameter  $\lambda$ . Summing both sides of (3.53) from 1 to  $n$  and simplifying the result, we obtain

$$\sum_{i=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} = \lambda \sum_{i=1}^n Q_i (\lambda/R)^i \sum_{i=1}^n \frac{1}{a_r Q_r (\lambda/R)^r}. \quad (3.55)$$

Changing the order of summation on the right-hand side leads to

$$f_n(\lambda) := \sum_{r=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \left( 1 - \sum_{i=1}^r R Q_i (\lambda/R)^i \right) = 0. \quad (3.56)$$

Clearly there exists a solution  $\lambda \in ]0, 1]$  satisfying (3.56) since

$$f_n(\lambda) \rightarrow +\infty \quad \text{for } \lambda \rightarrow 0,$$

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and

$$f_n(1) < 0 \quad \text{due to} \quad Q_1 = 1 \quad \text{and} \quad Q_i > 0 \quad \text{for} \quad 2 \leq i \leq n.$$

For a given  $R > 0$  we fix the value of  $n$  and calculate  $\lambda$  from (3.56). Multiplying (3.53) by  $i$ , summing the result from 1 to  $n$  and using the conservation relation (3.29) we can calculate the value of  $z_1^{s,M}$  from

$$z_1^{s,M} = \rho \left( \sum_{i=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \right) \left( \sum_{i=1}^n i Q_i (\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r (\lambda/R)^r} \right)^{-1}. \quad (3.57)$$

In summary we have obtained the result

**Theorem 3.2.4.** *The system (3.41) has a unique steady state solution given by (3.53) - (3.57).*

#### 3.2.3 The limiting steady-state solutions for the modified mass-conserving model

We point out that Dreyer and Duderstadt [16] have already discussed the limiting case for the equilibrium solutions in the modified mass-conserving model. In their discussions they concluded that in the limit  $n \rightarrow \infty$  the solution  $\bar{\mathbf{z}}^M$  given by (3.37) exists only if the supersaturation ratio  $S$  satisfies  $S \leq 1/(1 - \varepsilon)$ , where  $\varepsilon := \sum_{i=2}^{\infty} \exp(-\tilde{a}i^{2/3})$  for  $\tilde{a} = \gamma/(kT)$ .

Thus our discussion here concerns only the non-equilibrium distribution (3.53) - (3.57). We consider equation (3.56) in the limit  $n \rightarrow \infty$  as

$$\sum_{r=1}^{\infty} \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \left( 1 - \sum_{i=1}^r R Q_i (\lambda/R)^i \right) = 0$$

In a similar way to the analysis used in Section 3.1.3 we note that, the series  $\sum_{r=1}^{\infty} \frac{1}{a_r Q_r (\lambda/R)^{r-1}}$  is convergent only if  $\lambda/R > 1$ . On the other hand in the limit  $r \rightarrow \infty$ , the sum  $\sum_{i=1}^r R Q_i (\lambda/R)^i$  converges only for  $\lambda/R \leq 1$ . However, this contradicts the first requirement. Therefore there are no non-equilibrium solutions for the infinite system.

### 3.3 Comparison of the steady states from the two models

Here we give a quantitative and qualitative comparison between the equilibrium and non-equilibrium steady-state solutions for the constant free molecule and modified mass-conserving models studied in the previous sections.

### 3.3.1 Equilibrium distributions

The equilibrium distribution  $\bar{\mathbf{z}}^F$  for the constant free molecule model is given in (3.11) and (3.12) as

$$\bar{z}_i^F = Q_i R \bar{N}_D^F \left( \frac{1}{R q^{in}} \right)^i, \quad \text{for } i \geq 2 \quad \text{and} \quad \bar{z}_1^F = \mu,$$

$$\bar{N}_D^F = \frac{\mu}{1 - R \sum_{i=2}^n Q_i (1/R q^{in})^i}, \quad Q_i = \prod_{r=2}^i \frac{a_{r-1}}{b_r}, \quad i \geq 2.$$

By using the last equation in (1.29) this distribution can be written as

$$\bar{z}_i^F = \bar{N}_D^F q_i / (q^{in})^i, \quad \text{for } i \geq 2 \quad \text{and} \quad \bar{z}_1^F = \mu,$$

$$\bar{N}_D^F = \frac{\mu}{1 - \sum_{i=2}^n q_i / (q^{in})^i}, \quad q_i = \exp(-\mathcal{A}_i/kT), \quad i \geq 2,$$

where  $\mathcal{A}_i$  is given by (2.12), that is,  $\mathcal{A}_i = -i \ln S + \gamma i^{2/3}$  and  $q^{in} = \exp(-mg_v(T, p_0)/kT)$ . The constant  $\gamma$  is given by  $\gamma = (36\pi)^{1/3} V_1^{2/3} \sigma$ . We point out that the equilibrium distribution  $\bar{\mathbf{z}}^F$  has a minimum at some  $i^*$  given by

$$i^* = \left( \frac{2\gamma}{3kT \ln(S/q^{in})} \right)^3, \quad (3.58)$$

which is different from the critical cluster predicted by the Thomson formula 2.16.

Similarly, by using the last equation in (1.29), the equilibrium distribution  $\bar{\mathbf{z}}^M$  for the modified mass-conserving model is obtained from (3.38) - (3.40) as

$$\bar{z}_i^M = \bar{z}_1^M \lambda^{i-1} q_i, \quad 1 \leq i \leq n,$$

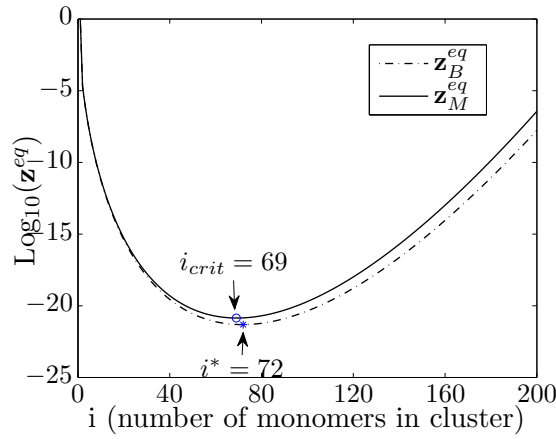
$$\sum_{i=1}^n \lambda^i q_i = 1, \quad q_i = \exp(-\mathcal{A}_i/kT),$$

$$\bar{z}_1^M = \rho \left[ \sum_{i=1}^n i \lambda^{i-1} q_i \right]^{-1}.$$

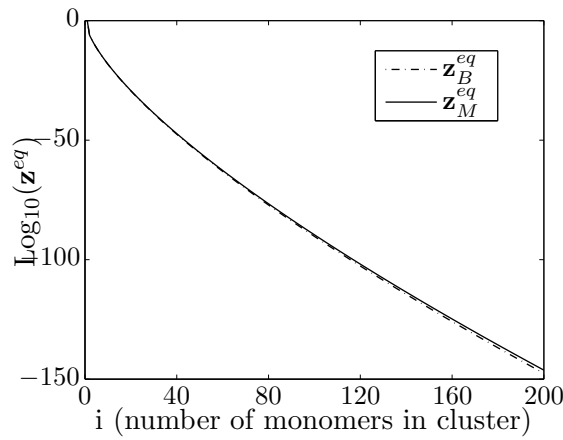
In both models the equilibrium flux is equal to zero. The zero flux truncation is therefore not interesting since it implies zero steady-state nucleation rates. Figure 3.1 shows the equilibrium distributions  $\bar{\mathbf{z}}^F$  and  $\bar{\mathbf{z}}^M$  obtained from the above equations. For the constant free molecule model we have taken  $\mu = \bar{z}^F = 1$  while we have used  $\rho = 1$  for the mass-conserving case. For the different parameter values involved we used the values for water given in Table 3.1 which were taken from steam tables by Wagner and Kretzschmar [66]. We observe that for  $S = 4.0$  the equilibrium distribution  $\bar{\mathbf{z}}^F$  has a minimum at  $i^* = 72$  which is not identical to the value  $i_{crit} = 69$  obtained by the Thomson formula (2.16). For the mass-conserving equilibrium distribution  $\bar{\mathbf{z}}^M$  there exists a minimum exactly at the critical size cluster obtained independently by (2.16). As predicted by the Thomson formula (2.16) the minima of equilibrium distributions depend strongly on the supersaturation ratio  $S$ . The size of the critical cluster increases with a decrease in supersaturation. At  $S = 1$  the critical cluster will have an infinite size. Therefore in this



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(a)



(b)

Figure 3.1: Equilibrium cluster distributions for water vapor at 290K predicted by the two models with zero flux truncation: (a)  $S = 4.0$ , (b)  $S = 0.8$ .

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Table 3.1: Values of various quantities used for calculation of different dependencies for nucleation of water droplets in vapor.

Quantity	T = 290K	T = 300K	T = 310K	T = 320K
m(kg)	$3 \times 10^{-26}$	$3 \times 10^{-26}$	$3 \times 10^{-26}$	$3 \times 10^{-26}$
$v_0(nm^3)$	0.03	0.03	0.03	0.03
$\bar{p}$ (kPa)	1.9	3.5	6.2	10.6
$\sigma$ (mJ/m <sup>2</sup> )	73.2	71.5	69.9	68.3
$\alpha_i$	1	1	1	1

case there will be no nucleation since the new phase is only formed when clusters grow beyond the critical size. For  $S = 0.8$  the equilibrium distributions decrease monotonically with cluster sizes. The results show that there are hardly any bigger clusters in the system at such a low saturation.

### 3.3.2 Non-equilibrium steady-state distributions

The non-equilibrium steady-state distribution for the constant free molecule model is given by (3.24) - (3.26) while equations (3.53) - (3.57) define that for the modified mass-conserving model. By using the last equation in (1.29) to substitute for  $Q_i(1/R)^{i-1}$  in the relevant formulae for the constant free molecule model, we get

$$z_1^{s,F} = \alpha, \quad z_i^{s,F} = J^F q_i / (q^{in})^i \sum_{r=i}^n \frac{1}{a_r q_r / (q^{in})^r}, \quad 2 \leq i \leq n,$$

$$J^F = z_1^{s,F} \left( \frac{1}{a_1} + \bar{\lambda} \sum_{r=2}^n \frac{1}{a_r q_r / (q^{in})^r} \right)^{-1}, \quad \bar{\lambda} = \frac{z_1^{s,F}}{N_D(\mathbf{z}^{s,F})},$$

where  $\bar{\lambda}$  is calculated from

$$\bar{\lambda}^2 \sum_{r=2}^n \frac{1}{a_r q_r / (q^{in})^r} + \bar{\lambda} \left[ \frac{1}{a_1} - \sum_{r=2}^n \frac{1}{a_r q_r / (q^{in})^r} \left( 1 - \sum_{i=2}^r q_i / (q^{in})^i \right) \right] - \frac{1}{a_1} = 0.$$

Similarly, the modified mass-conserving model gives

$$z_i^{s,M} = J^M q_i \lambda^i \sum_{r=i}^n \frac{1}{a_r q_r \lambda^r}, \quad \lambda = \frac{z_1^{s,M}}{N_D(\mathbf{z}^{s,M})},$$

$$J^M = z_1^{s,M} \left( \sum_{i=1}^n \frac{1}{a_r q_r \lambda^{r-1}} \right)^{-1},$$

$$z_1^{s,M} = \rho \left( \sum_{i=1}^n \frac{1}{a_r q_r \lambda^{r-1}} \right) \left( \sum_{i=1}^n i q_i \lambda^i \sum_{r=i}^n \frac{1}{a_r q_r \lambda^r} \right)^{-1}.$$

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For fixed  $S$  and  $n$ , the parameter  $\lambda$  is calculated from

$$f_n(\lambda) := \sum_{r=1}^n \frac{1}{a_r q_r \lambda^r} \left( 1 - \sum_{i=1}^r q_i \lambda^i \right) = 0.$$

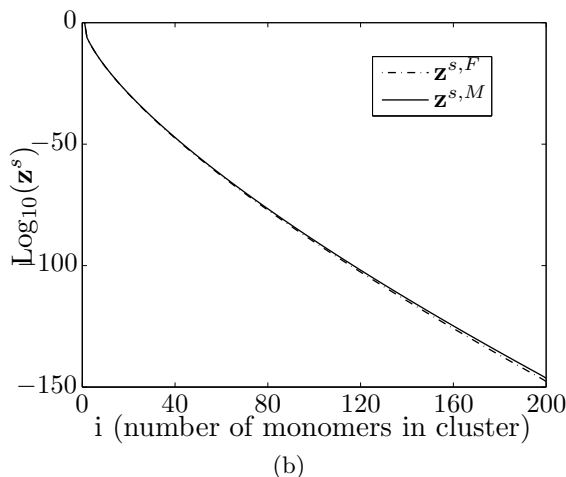
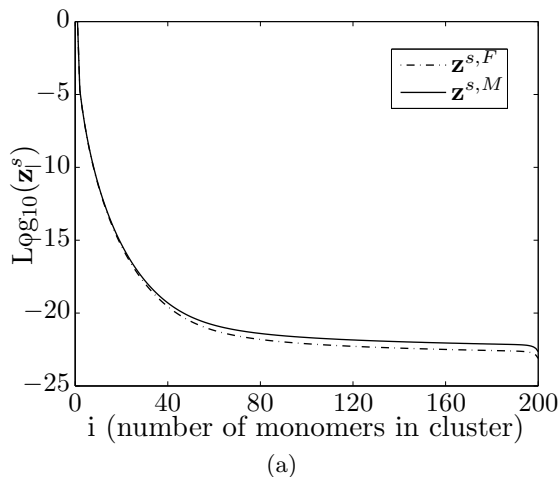


Figure 3.2: Steady-state cluster distributions for water vapor at 290K predicted by the two models with zero particle number truncation: (a)  $S = 4.0$ , (b)  $S = 0.8$ .

Figure 3.2 shows the constant free molecule steady-state distribution  $\mathbf{z}^{s,F}$  and the mass-conserving one  $\mathbf{z}^{s,M}$ . For these plots we have used  $\mu = z_1^{s,F} = 1$ ,  $\rho = 1$  and all other parameters are taken from Table 3.1. We observe from Tables 3.2 and 3.3 that the constant free molecule model predicts slightly lower nucleation rates  $J^F$  than the mass-conserving ones  $J^M$ . Their orders of magnitude differ much more at  $T = 320K$  than at  $T = 290K$ . We also observe that the values of  $\bar{\lambda} = z_1^{s,F}/N(\mathbf{z}^{s,F})$  and  $\lambda = z_1^{s,M}/N(\mathbf{z}^{s,M})$  are very close to 1 for both models. From a physical point of view this actually means that in a steady state there are very few large clusters. The solution is dominated by the free molecules which can also be clearly seen in the logarithmic plots in Figure 3.2. The results show that the nucleation rates are very low for small supersaturations. For under-saturated systems, the nucleation rates are equal to zero. This means

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Table 3.2: Nucleation rates predicted by the two models at  $T = 290K$  for  $z_{1,B}^s = N = 1$ ,  $\nu = 200$

$S$	$i^*$	$i_{crit}$	$\bar{\lambda}$	$\lambda$	$J_B/s^{-1}$	$J_M/s^{-1}$
2	594	554	0.999995	0.999995	$5.72 \times 10^{-60}$	$1.25 \times 10^{-58}$
3	145	139	0.999988	0.999988	$3.64 \times 10^{-27}$	$3.32 \times 10^{-26}$
4	72	69	0.999978	0.999978	$3.35 \times 10^{-14}$	$9.92 \times 10^{-14}$
5	46	44	0.999966	0.999965	$1.50 \times 10^{-08}$	$2.98 \times 10^{-08}$
6	33	32	0.999950	0.999949	$2.13 \times 10^{-05}$	$3.48 \times 10^{-05}$

Table 3.3: Nucleation rates predicted by the two models at  $T = 320K$  for  $z_{1,B}^s = N = 1$ ,  $\nu = 200$

$S$	$i^*$	$i_{crit}$	$\bar{\lambda}$	$\lambda$	$J_B/s^{-1}$	$J_M/s^{-1}$
2	561	335	0.999968	0.999963	$9.95 \times 10^{-49}$	$1.32 \times 10^{-38}$
3	115	84	0.999925	0.999904	$1.11 \times 10^{-17}$	$2.16 \times 10^{-12}$
4	54	42	0.999863	0.999815	$2.03 \times 10^{-07}$	$8.45 \times 10^{-05}$
5	33	27	0.999780	0.999695	$3.95 \times 10^{-03}$	$1.89 \times 10^{-01}$
6	24	19	0.999671	0.999536	$8.66 \times 10^{-01}$	$1.45 \times 10^{+01}$

that the steady-state distributions for both models are actually the equilibria at such saturation. This is depicted by the results in Figures 3.1(b) and 3.2(b).

**Remark 3.3.1.** For finite systems, it would be reasonable to calculate the steady-state concentration  $f_1$  of free molecules for the standard Becker-Döring model by multiplying the second equation in (1.14) by  $i$  and summing the result from 1 to  $n$ . This would lead to

$$\sum_{i=1}^n \frac{1}{a_i Q_i f_1^i} \left( \rho - \sum_{r=1}^i r Q_r f_1^r \right) = 0.$$

However, like in the previous analysis, this equation would not be solvable in the limit  $n \rightarrow \infty$ , since it would lead to contradictory requirements  $f_1 > 1$  and  $f \leq 1$  for the two sums in the equation. This explains why the boundary condition  $f_1 = \mu$  in (1.14) is necessary.

Burton [7] assumed that in a steady state the system has not consumed a sufficient number of free molecules. In his consideration the parameter  $\mu$  represents the initial equilibrium concentration of free molecules. In the two thermodynamically consistent models considered here, Burton's assumption translates into the assumption that  $\bar{\lambda} = \lambda \approx 1$ , which is justified by the results in Tables 3.2 and 3.3.

### 3.4 Nucleation rates for the modified mass-conserving model

Based on the results in Remark 3.3.1 we derive expressions for the nucleation rates from the thermodynamically consistent mass-conserving model. We study the liquid-vapor systems and the crystallization process introduced in Chapter 2.

#### 3.4.1 The liquid-vapor system

We consider the steady-state flux  $J^M$  given in (3.54) and assume that  $\lambda \approx 1$  according to Remark 3.3.1. This gives

$$J^M = z_1^{s,M} \left( \sum_{r=i}^n \frac{1}{a_r Q_r (1/R)^{r-1}} \right)^{-1}.$$

Next we use the last equation in (1.29) to get

$$J_M \approx z_1^s \left[ \sum_{i=1}^n \frac{1}{a_i q_i} \right]^{-1}, \quad q_i = \exp(-\mathcal{A}_i/kT),$$

where  $a_i = C_i$ , with  $C_i$  given in (2.7). Dividing the right-hand side by the total steady-state volume  $V_T$ , the above approximation is exactly equal to  $J$  in (2.25) since  $q_1 = 1$ . In this case  $z_1^s$  has units of concentration. Therefore by following the same simplification steps which were used to derive the classical nucleation rates  $J_{CNT}$  (2.37), we obtain the same formula for the thermodynamically consistent mass-conserving model, i. e.

$$J_M \approx J_{CNT}. \tag{3.59}$$

Next we incorporate an inert gas into the liquid-vapor system.

#### 3.4.2 The liquid-vapor-inert gas system

We recall that in this case the fluxes are given by (2.86) as

$$J_i(\mathbf{z}(t)) = a_i z_i(t) \frac{z_1(t)}{z_1(t) + z_0} - b_{i+1} R \frac{N_D(t)}{z_1(t) + z_0} z_{i+1}(t), \quad N_D(\mathbf{z}(t)) = \sum_{i=0}^n z_i(t),$$

where  $z_0$  represents the inert gas molecules. Now we determine the non-equilibrium steady-state distribution with the above fluxes, starting with  $J_n = a_n z_n^s z_1^s / (z_0 + z_1^s)$ . This has already been done in Section 3.2.2 for the case  $z_0 = 0$ . The steady-state distribution  $\mathbf{z}^s$  is given by

$$z_i^s = J^s \left( \frac{z_1^s + z_0}{z_1^s} \right) Q_i(\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r (\lambda/R)^r} \quad 1 \leq i \leq n, \quad \text{where} \quad \lambda = \frac{z_1^s}{N_D(\mathbf{z}^s)}. \tag{3.60}$$

The steady-state flux is obtained by setting  $i = 1$  and using  $Q_1 = 1$ . This gives

$$J^s = \frac{(z_1^s)^2}{z_1^s + z_0} \left( \sum_{r=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \right)^{-1}. \tag{3.61}$$

### CHAPTER 3. STEADY-STATE SOLUTIONS

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Using the distribution (3.60) and the definition of  $\lambda$ , we note that

$$\lambda N_D(\mathbf{z}^s) = \lambda z_0 + \lambda J^s \left( \frac{z_1^s + z_0}{z_1^s} \right) \sum_{i=1}^n Q_i(\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r(\lambda/R)^r}.$$

By substituting for  $J^s$  we obtain

$$z_1^s = \lambda z_0 + z_1^s \lambda \left( \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} \right)^{-1} \sum_{i=1}^n Q_i(\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r(\lambda/R)^r},$$

which is equivalent to

$$z_1^s \left[ \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} - \lambda \sum_{i=1}^n \sum_{r=i}^n \frac{Q_i(\lambda/R)^i}{a_r Q_r(\lambda/R)^r} \right] = \lambda z_0 \left( \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} \right). \quad (3.62)$$

Using the mass-conservation condition and (3.29) we observe that

$$\rho = z_0 + z_1^s \left( \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} \right)^{-1} \sum_{i=1}^n i Q_i(\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r(\lambda/R)^r}. \quad (3.63)$$

We then substitute for  $z_1^s$  by using (3.62) to obtain

$$\begin{aligned} & \rho \left[ \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} - \lambda \sum_{i=1}^n \sum_{r=i}^n \frac{Q_i(\lambda/R)^i}{a_r Q_r(\lambda/R)^r} \right] \\ &= z_0 \left[ \sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^{r-1}} + \lambda \sum_{i=1}^n \sum_{r=i}^n \frac{(i-1) Q_i(\lambda/R)^i}{a_r Q_r(\lambda/R)^r} \right]. \end{aligned}$$

When  $z_0 = 0$ , this equation and (3.62) lead to the steady state condition

$$\sum_{r=1}^n \frac{1}{a_r Q_r(\lambda/R)^r} - \lambda \sum_{i=1}^n \sum_{r=i}^n \frac{Q_i(\lambda/R)^i}{a_r Q_r(\lambda/R)^{r-1}} = 0,$$

which was already derived in (3.55).

It was shown earlier that the non-equilibrium distribution is only restricted to finite systems. In the limit  $n \rightarrow \infty$ , the steady-state number  $N_D(\mathbf{z}^s)$  is divergent. We therefore use the common assumption that in the steady state the system has not yet consumed a sufficient number of free molecules. In this case the parameter  $\lambda$  becomes

$$\lambda \approx \frac{z_1^s}{z_0 + z_1^s} =: \omega^s. \quad (3.64)$$

We again denote by  $S$  the supersaturation ratio of the vapor in the system. Then by definition we now have

$$S = \frac{p_v}{p(T)} = \frac{\omega^s p_0}{p(T)}. \quad (3.65)$$

### 3.4. NUCLEATION RATES FOR THE MODIFIED MASS-CONSERVING MODEL

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With  $Q_i(1/R)^{i-1} = q_i$ , the steady state flux (3.61) then becomes

$$J^s \approx z_1^s \left[ \frac{1}{a_1} + \sum_{i=2}^{\infty} \frac{1}{a_i q_i} \right]^{-1}, \quad q_i = S^i \exp(-\gamma i^{2/3}/kT). \quad (3.66)$$

Next we follow the simplifying procedure used to derive  $J_{CNT}$  in (2.37). This leads to

$$J^s \approx a_{i_{crit}} \frac{z_1^s}{3} i_{crit}^{-2/3} \left( \frac{\gamma}{kT\pi} \right)^{1/2} \exp \left( \frac{-4\gamma^3}{27k^3 T^3 (\ln S)^2} \right) =: J^{s2} \quad (3.67)$$

With  $a_{i_{crit}} = C_{i_{crit}}$  we use (2.7) and (2.11) to substitute for  $a_{i_{crit}}$  and  $\gamma$  respectively. We obtain

$$J^{s2} = \alpha_{i_{crit}} z_1^s \left( \frac{V_1 p_0}{kT} \right) \left( \frac{2\sigma}{\pi m} \right)^{1/2} \exp \left( \frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln S)^2} \right). \quad (3.68)$$

This approximation gives the number of nuclei formed per second. We can change the units of the nucleation rates by dividing (3.68) by the total volume  $V_T$  in the steady state. Since the system is assumed to be dominated by free molecules together with the inert gas, the total volume is approximately equal the volume of the vapor phase. Therefore we can use (2.56) to approximate the quotient  $z_1^s/V_T$ . This gives

$$J^s \approx \alpha_{i_{crit}} V_1 \omega^s \left( \frac{p_0}{kT} \right)^2 \left( \frac{2\sigma}{\pi m_w} \right)^{1/2} \exp \left( \frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln S)^2} \right) =: J_{SW}.$$

By using  $p_v = \omega^s p_0$ , this approximation can equivalently be written as

$$J_{SW} = \alpha_{i_{crit}} \frac{V_1}{\omega^s} \left( \frac{p_v}{kT} \right)^2 \left( \frac{2\sigma}{\pi m_w} \right)^{1/2} \exp \left( \frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln S)^2} \right) = \frac{1}{\omega^s} J_{CNT}. \quad (3.69)$$

The formula now gives the number of nuclei formed per second per unit volume. Setting  $\omega^s = 1$  yields the classical nucleation rate  $J_{CNT}$ .

It is important to note here that when calculating nucleation rates in the presence of an inert gas, the same formula  $J_{CNT}$  in (2.37) is used in various literature with  $p_0$  replaced by  $p_v$ , see for instance Wölk and Strey [71]. However, we observe that in addition to these changes for pressure, the new formula  $J_{SW}$  in (3.69) multiplies  $J_{CNT}$  by the reciprocal of the vapor fraction  $\omega^s$ . Therefore  $J_{SW}$  gives a correction for  $J_{CNT}$  if  $\omega^s \neq 1$ .

#### 3.4.3 Crystal nucleation process

Here the fluxes are given in (2.87) as

$$J_i(\mathbf{z}(t)) = a_i z_i(t) z_1(t) - b_{i+1} R N_D(t) z_{i+1}(t).$$

The steady-state distribution is given by

$$z_i^s = \frac{J^s}{z_s} Q_i(\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r(\lambda/R)^r} \quad \text{where} \quad \lambda = \frac{z_1^s}{N_D(\mathbf{z}^s)},$$

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with the steady-state flux

$$J^s = (z_1^s)^2 \left( \sum_{r=1}^n \frac{1}{a_r Q_r (\lambda/R)^{r-1}} \right)^{-1}. \quad (3.70)$$

Similar to the discussions in the previous section, we can use the approximation

$$\lambda \approx \omega^s = \frac{z_1^s}{z_0 + z_1^s}.$$

Then with  $Q_i(1/R)^{i-1}$ , the steady state flux  $J^s$  in (3.70) becomes

$$J^s = z_1^s (z_1^s + z_0) \left[ \frac{1}{a_1} + \sum_{i=2}^n \frac{1}{a_i q_i} \right]^{-1}, \quad q_i = \bar{S}^i \exp(-\gamma i^{2/3}/kT). \quad (3.71)$$

The supersaturation ratio  $\bar{S}$  is now given by

$$\bar{S} := \omega^s \exp\left(\frac{m_c \Delta T \Delta h}{kT T_e}\right). \quad (3.72)$$

An approximation for (3.71) similar to the derivation of (3.69), is given by

$$J^s \approx \alpha_i \frac{(z_1^s)^2}{\omega^s} \left(\frac{2V_1 D}{d_1}\right) \left(\frac{\sigma}{kT}\right)^{1/2} \exp\left(\frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln \bar{S})^2}\right) =: J_{CRY}. \quad (3.73)$$

We can use the molecular volumes  $V_1$  and  $V_w$  of solute and solvent molecules respectively to approximate the concentration of free molecules via

$$[z_1^s] = \frac{z_1^s}{V_T} \approx \frac{z_1^s}{z_1^s V_1 + z_w V_w} = \frac{1}{V_1 + \frac{z_w}{z_1^s} V_w},$$

where the square brackets represent the concentration. By using  $\omega^s = z_1^s/(z_w + z_1^s)$  we can eliminate the quotient  $z_w/z_1^s$  to get

$$[z_1^s] \approx \frac{1}{V_1 + \left(\frac{1}{\omega^s} - 1\right) V_w}. \quad (3.74)$$

A similar approximation was used by Kashchiev [27, p. 153] for crystallization in melts, where  $\omega^s = 1$ . Furthermore, by assuming a spherical shape for free molecules we can write

$$d_1 \approx \left(\frac{6V_1}{\pi}\right)^{1/3}.$$

The nucleation rate  $J_{CRY}$  in (3.73) then becomes

$$J_{CRY} \approx \frac{\alpha_{i,crit}}{1 + \left(\frac{1}{\omega^s} - 1\right) \frac{V_w}{V_1}} \left(\frac{D}{\omega^s V_1}\right) \left(\frac{4\pi}{3V_1}\right)^{1/3} \left(\frac{\sigma}{kT}\right)^{1/2} \exp\left(\frac{-4\vartheta^3 V_1^2 \sigma^3}{27k^3 T^3 (\ln \bar{S})^2}\right). \quad (3.75)$$

For  $\omega^s = 1$ , a similar equation was reported in Kashchiev and Rosmalen [28] for interface controlled condensation rates. With  $\bar{S}$  from (3.72), the flux  $J_{CRY}$  in (3.75) is equivalent to

$$J_{CRY} \approx \frac{\alpha_{i,crit}}{1 + \left(\frac{1}{\omega^s} - 1\right) \frac{V_w}{V_1}} \left(\frac{D}{\omega^s V_1}\right) \left(\frac{4\pi}{3V_1}\right)^{1/3} \left(\frac{\sigma}{kT}\right)^{1/2} \exp\left(\frac{-4\vartheta^3 V_1^2 T_e^2 \sigma^3}{27kT(m_c \Delta T \Delta h)^2}\right). \quad (3.76)$$



### 3.5 Comparison with experiments

Here we compare the nucleation rates derived in the previous section with some of the available experimental data. We include results for homogeneous nucleation in liquid-vapor-inert gas systems as well as crystallization in melts. In all the examples we assume that clusters have a spherical shape so that we use  $\vartheta = (36\pi)^{1/3}$  in all the relevant formulas.

#### 3.5.1 The liquid-vapor-inert gas system

In this section we consider the nucleation of liquid droplets in vapor in the presence of an inert gas. We use two examples one of which concerns water vapor nucleation and the other on nucleation of Argon.

##### Homogeneous nucleation of water vapor

Here we set  $\alpha_{i_{crit}} = 1$  and compare the nucleation rates  $J_{CNT}$  obtained by using (2.37),  $J_C$  from (2.38),  $J_{GC}$  from (2.39) and  $J_{SW}$  from (3.69) with experimental data taken from Wölk and Strey [71] and from Brus et al. [6]. Figure 3.3 shows nucleation rates for light water in Argon at different temperatures as functions of supersaturation. We observe that  $J_C$  and  $J_{GC}$  give similar values which are both lower than  $J_{CNT}$ . On the other hand, the new nucleation rate  $J_{SW}$  gives higher values than any of the other three formulae. The values of  $J_{CNT}$  are the closest ones to the experimental data. A nearly perfect agreement of  $J_{CNT}$  with the experiment is found near 240K. At 220K, the rates  $J_{CNT}$ ,  $J_C$  and  $J_{GC}$  all give lower values than the experimental data while  $J_{SW}$  predicts higher values. We observe in Figure. 3.4 at higher temperatures that all the different formulae predict higher values than the experimental data.

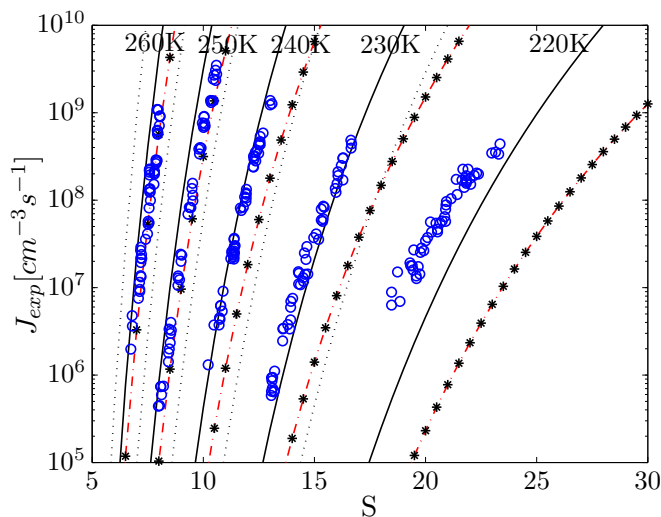


Figure 3.3: Comparison of the experimental nucleation rates  $J_{exp}$  (circles) for light water with prediction of nucleation theory, data obtained from Wölk and Strey [71]. Star (\*):  $J_C$  using formula (2.38) calculated for temperatures of 260, 250, 240, 220 and 220K. Solid lines represent  $J_{CNT}$  in (2.37), which is equivalent to  $J_M$  in (3.59). Dotted lines represent  $J_{SW}$  from formula (3.69) while dashed dotted lines are for  $J_{GC}$  from (2.39), calculated at the same temperatures.

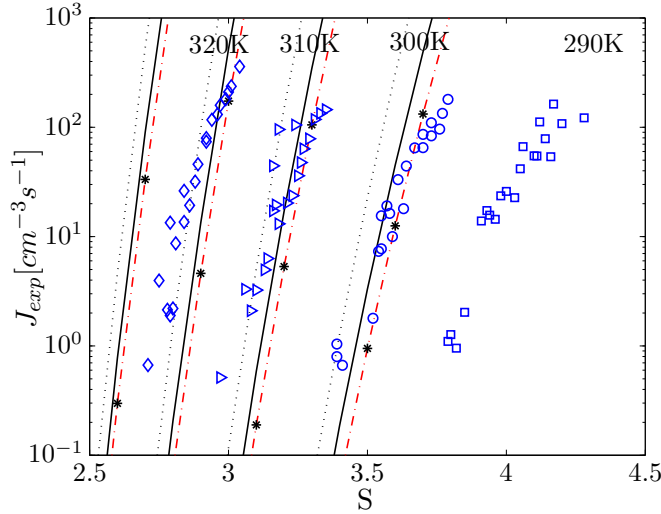


Figure 3.4: Experimental nucleation rates  $J_{exp}$  as a function of saturation ratio  $S$  for water, obtained from Brus et al. [6]. Symbols, from left to right: diamonds - 320K, triangles - 310K, circles - 300K, and squares - 290K. Star (\*):  $J_C$  from formula (2.38), calculated for the temperatures of 320, 310, 300 and 290K. Solid lines:  $J_{CNT}$  from (2.37), which is equivalent to  $J_M$  in (3.59). Dotted lines:  $J_{SW}$ , given by formula (3.69). Dashed dotted lines:  $J_{GC}$ , from formula (2.39).

Based on Figures 3.3 and 3.4, our new formula  $J_{SW}$  predicts higher nucleation rates than the experiments at all the temperatures considered. To correct this we require a multiplicative factor which is less than one. A physically meaningful candidate is a sticking coefficient  $\alpha_{i_{crit}} \in ]0, 1]$ . Here  $\alpha_{i_{crit}} < 1$  reflects the possibility that not all collisions of free molecules with a given cluster result in its growth. Moreover for the experimental data we considered, only our new formula allows correction with a sticking coefficient at all temperatures. The other formulae predict lower rates than the experiments at 220K so that a sticking coefficient would even lower them further. We first consider the case where this coefficient depends only on the temperature  $T$  so that we may write the general formula as

$$J_{SW} = \alpha_{i_{crit}}(T) \frac{1}{\omega_s} J_{CNT}. \quad (3.77)$$

We point out that we have not found experimental values of sticking coefficients for vapor to liquid transitions. There are few substances whose sticking rates were measured experimentally. For instance, Kashchiev [27, p. 266] reported sticking coefficient values for ice ( $2 \times 10^{-3}$ ) and  $\text{NaPO}_3$  crystal nuclei ( $2 \times 10^{-6}$ ). In Stoyanova et al. [62], values of  $\alpha_{i_{crit}}$  less than  $10^{-6}$  were reported for freezing of water droplets.

We therefore determine values of  $\alpha_{i_{crit}}$  by making a least squares fit of  $J_{SW}$  to the experimental data. Table 3.4 shows the values of  $\alpha_{i_{crit}}$  obtained at different temperatures. For the experimental data obtained from Wölk and Strey [71], the values of  $\alpha$  are of orders of  $10^{-3}$ . On the hand, for the data from Brus et al. [6],  $\alpha_{i_{crit}}$  has orders of  $10^{-5}$  and  $10^{-6}$ . Figures 3.5 and 3.6 show the fitted results, with dotted lines, for the two different data sets. However the slope of the experimental data is not well represented by the fitted values. For this

### 3.5. COMPARISON WITH EXPERIMENTS

Table 3.4: Temperature dependence of the sticking coefficient  $\alpha_{i_{crit}}$

T/K	$\alpha_{i_{crit}}$	T/K	$\alpha_{i_{crit}}$
220	$8.5 \times 10^{-3}$	290	$1.3 \times 10^{-5}$
230	$6.3 \times 10^{-3}$	300	$3.5 \times 10^{-6}$
240	$4.6 \times 10^{-3}$	310	$1.7 \times 10^{-5}$
250	$3.8 \times 10^{-3}$	320	$5.6 \times 10^{-5}$
260	$5.1 \times 10^{-3}$		

(a)

(b)

reason we now consider a dependence of the sticking coefficients on both the temperature  $T$  and the size  $i_{crit}$  of the critical cluster. According to the Thomson formula (2.16), the size of the critical cluster depends on the temperature  $T$ . For simplicity we assume that

$$\alpha_{i_{crit}} := \beta_2 i_{crit}^{\beta_1}, \quad (3.78)$$

where the constants  $\beta_1$  and  $\beta_2$  are to be determined from the experimental data. The nucleation rates then become

$$J_{SW} = \beta_2 i_{crit}^{\beta_1} \frac{1}{\omega^s} J_{CNT}. \quad (3.79)$$

Figures 3.7 and 3.8 show the variation of sticking coefficients with the critical size for data taken from Wölk and Strey and from Brus et al. respectively. We observe that for each temperature the sticking coefficient increases with increase in the the size of the critical cluster which seems reasonable. In Figure 3.7, there is in general a decrease in sticking coefficients with increase in temperature except for  $T = 260K$ . The same trend is observed in Figure 3.8 from 290 to 300K. Moreover the values of the sticking coefficients lie between  $10^{-7}$  and  $10^{-1}$ , just like in Table 3.4. With the new dependence of the sticking coefficients on size, we observe from Figures 3.5 and 3.6 that the slope of the experimental nucleation rates is now well captured, see the solid lines.

#### Homogeneous nucleation of Argon

We set  $\alpha_{i_{crit}} = 1$  and compare the results of  $J_{CNT}$  and  $J_{SW}$  with experimental data from Sinha et al. [57]. Argon nucleation rates of  $10^{16} - 10^{18} \text{ cm}^3\text{s}^{-1}$  were registered from experiments. Figure 3.9 shows a Wilson plot for the experimental data and theory. We observe that  $J_{CNT}$  predicts higher pressure values than the experiments for the above nucleation rates. Put in a different way, we observe that  $J_{CNT}$  predicts lower nucleation rates of  $10^0 - 10^9 \text{ cm}^3\text{s}^{-1}$  for the experimental values of pressure and temperature. By using our new corrected rates  $J_{SW}$ , we obtain a slight improvement on the discrepancy between experiment and theory. The pressure-temperature region is now closer to the experimental values.

#### 3.5.2 Crystallization process

Here we consider an example of melt crystallization where  $\omega^s = 1$ . Usually the solid-liquid interfacial energy  $\sigma$  is not known for crystallization processes. Therefore most experiments are

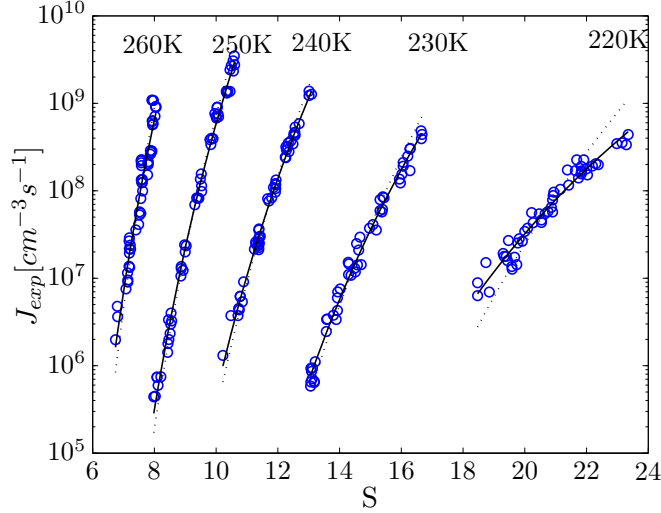


Figure 3.5: Experimental nucleation rates  $J_{exp}$  (circles) as a function of saturation ratio  $S$  for light water, obtained from Wölk and Strey [71]. Dotted lines represent fitted values for  $J_{SW}$  from formula (3.77) calculated at the given temperatures. Fit parameters are given in Table 3.4 (a). Solid lines represent fitted values of  $J_{SW}$  using formula (3.79) for size dependent sticking coefficients shown in Figure 3.7.

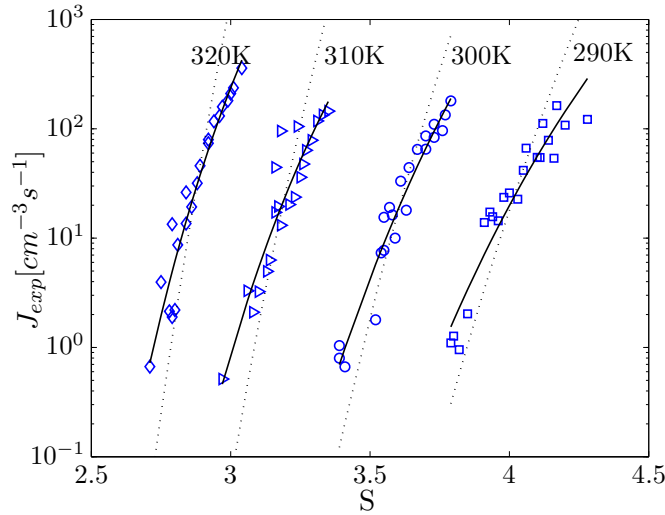


Figure 3.6: Experimental nucleation rates  $J_{exp}$  as a function of saturation ratio  $S$  for water, obtained from Brus et al. [6]. Symbols, from left to right: diamonds - 320K, triangles - 310K, circles - 300K, and squares - 290K. Dotted lines represent fitted values for  $J_{SW}$  from formula (3.77) calculated at the given temperatures. Fit parameters are given in Table 3.4 (b). Solid lines represent fitted values of  $J_{SW}$  using formula (3.79) for size dependent sticking coefficients shown in Figure 3.8

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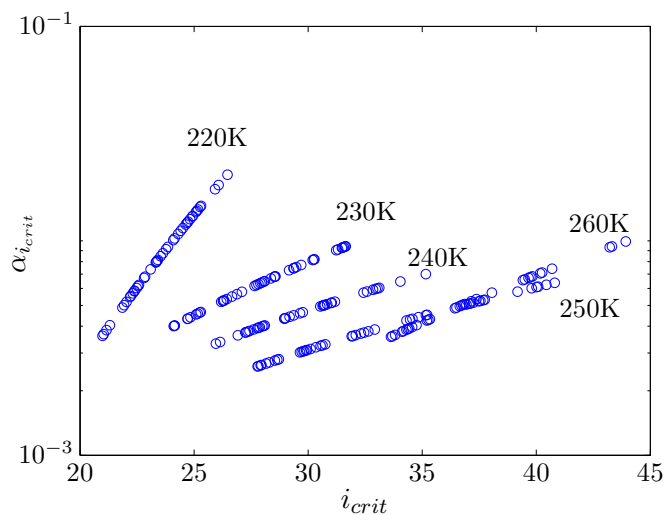


Figure 3.7: Sticking coefficient as a function of the critical cluster size using formula (3.78), data from Wölk and Strey [71].

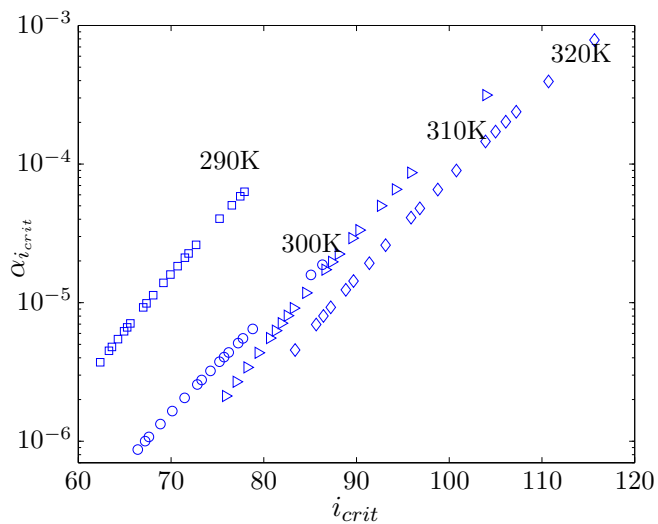


Figure 3.8: Sticking coefficient as a function of the critical cluster size from formula (3.78), data from Brus et al. [6]. Symbols: diamonds - 320K, triangles - 310K, circles - 300K, and squares - 290K.

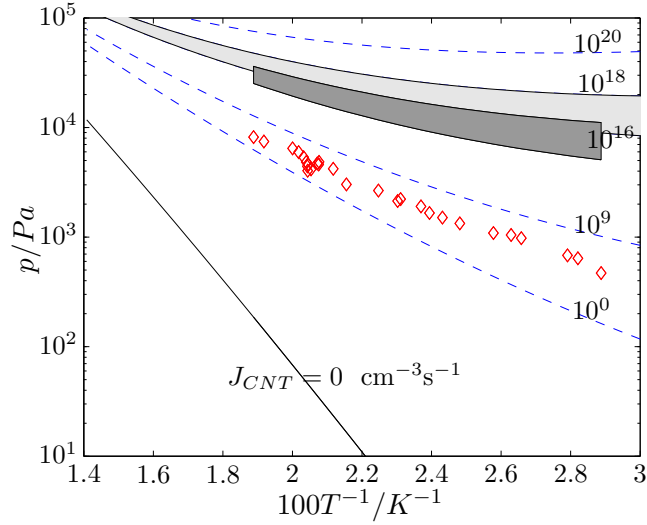


Figure 3.9: The data from Sinha et al. [57] (diamonds) is compared with the prediction of  $J_{CNT}$  from formula (2.37) and  $J_{SW}$  given by formula (3.69). The dashed lines correspond to the indicated constant nucleation rates calculated by using  $J_{CNT}$ . The light shaded region corresponds to the pressure and temperature predicted by  $J_{CNT}$  for the estimated nucleation rates of the experiments. The dark shaded region corresponds to pressure and temperature predicted by  $J_{SW}$  for the given experimental rates.

carried out in order to determine its value together with the pre-exponential factor

$$A := \left( \frac{D}{V_1} \right) \left( \frac{4\pi}{3V_1} \right)^{1/3} \left( \frac{\sigma}{kT} \right)^{1/2} \quad (3.80)$$

which appears in the nucleation rate formula (3.76). We compare the nucleation rates  $J_{CRY}$  in (3.76), for  $\omega^s = 1$ , with experimental nucleation data for Gallium taken from Miyazawa and Pound [38]. By considering two sets of experiments at  $T = -68.5, -69.5, -70.0$  and  $-71.3^\circ C$ , they obtained the following composite nucleation rate formula

$$J_{exp} = 10^{39.8} \exp \left( -\frac{1.54}{T(\Delta T)^2} \times 10^8 \right) cm^{-3}s^{-1}. \quad (3.81)$$

They reported a value of  $\sigma = 0.0677 Nm^{-1}$ . We use this value and Table 3.5 to determine the pre-exponential factor predicted by (3.80), with  $D$  calculated from (2.83). The experimental temperatures lead to an average value of  $A = 10^{32.5}$ . Therefore for Gallium, the nucleation rate (3.76) becomes

$$J_{CRY} = 10^{32.5} \exp \left( -\frac{1.54}{T(\Delta T)^2} \times 10^8 \right) cm^{-3}s^{-1}. \quad (3.82)$$

It is clear that the experimental nucleation rate  $J_{exp}$  in (3.81) exceeds  $J_{CRY}$  by a factor of about  $10^7$ . Kelton [29, p. 122] reported a similar discrepancy for Mercury.

### 3.5. COMPARISON WITH EXPERIMENTS

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Table 3.5: Values of various quantities used for calculation of different dependencies for Gallium nucleation. Data taken from Gale and Totemeir [20].

Quantity	Value
$m_c(kg)$	$1.16 \times 10^{-25}$
$T_e(K)$	302.9
$\Delta h(Jkg^{-1})$	$8.02 \times 10^4$
$\rho(kgm^{-3})$	$6.10 \times 10^3 - 0.56 * (T - T_e)$
$\eta$	$0.4359 \times \exp(4.0 \times 10^3 / (8.314T))$

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## Chapter 4

# Existence and uniqueness of solutions

In this chapter we study the existence and uniqueness of solutions for the general thermodynamically consistent mass-conserving Becker-Döring model (2.85) - (2.88) which includes a parameter  $z_0$  representing the number of molecules of some inert substance. The important point to note here is that the reciprocal  $(z_0 + z_1)^{-1}$  appears in the flux (2.86). Therefore we have a finite or infinite system of ordinary differential equations with a singularity in the right-hand side. It must be shown that under appropriate initial conditions this singularity is avoided by the solutions. It is clear that there is no singularity in the fluxes if  $z_0 > 0$ . We discuss the solutions for two different cases. One is the case  $z_0 > 0$  which shows that there is an inert substance in the given system. The second case  $z_0 = 0$  was solved by Hermann et al. [24] by using the fluxes in (2.87). They transformed the model with fluxes in (2.86) to the one with those in (2.87) by using the time scale  $\tau$ , defined here as,  $\tau(t) := \int_0^t z_1(s) ds$ . However, this transformation gives a solution for the desired flux case (2.86) for all times  $t > 0$  only if the following three conditions are satisfied

$$z_1(t) > 0 \quad \text{for all } t < \infty, \quad \tau(0) = 0, \quad \text{and} \quad \tau(t) \rightarrow \infty \quad \text{for } t \rightarrow \infty. \quad (4.1)$$

The solutions constructed by Hermann et al. [24] satisfy the first two conditions. The third one requires the existence of a uniform lower bound on  $z_1(t)$  or knowledge of the decay of  $z_1(t)$  as  $t \rightarrow \infty$ . In particular,  $z_1(t)$  must not go to zero faster than  $1/t$ . They showed that under some conditions, the solution  $\mathbf{z}(t)$  tends to zero as  $t \rightarrow \infty$ . Unfortunately, they did not discuss the behavior of the decay of  $z_1(t)$ . For this reason we include the existence and uniqueness of solutions to the model for  $z_0 = 0$  and fluxes given by (2.86). In Section 4.1 we introduce the appropriate functional spaces and state some of the results which are essential for the following sections. Section 4.2 contains the existence of solutions. We distinguish between the two cases  $z_0 = 0$  and  $z_0 > 0$ . We discuss the uniqueness of solutions for the two cases in Section 4.3. Finally, in Section 4.4 we discuss the existence of equilibria for the model.

### 4.1 Function spaces

We are interested in solutions for which the total mass remains finite for all time. Let  $\mathbb{N}_0$  denote the set of natural numbers including zero, that is,  $\mathbb{N}_0 := \mathbb{N} \cup \{0\}$ . Like Ball et al. [4] we introduce



the Banach sequence space

$$\mathbf{X} = \{\mathbf{z} = (z_i)_{i \in \mathbb{N}_0} \subseteq \mathbb{R} : \|\mathbf{z}\| < \infty\}, \quad \text{where} \quad \|\mathbf{z}\| = |z_0| + \sum_{i=1}^{\infty} i|z_i|. \quad (4.2)$$

We write  $\mathbf{z} \geq 0$  if  $z_i \geq 0$  for all  $i \in \mathbb{N}_0$ . We choose  $\rho \geq 0$  and set

$$\mathbf{X}^+ = \{\mathbf{z} \in \mathbf{X} : \mathbf{z} \geq 0\} \quad \text{and} \quad \mathbf{X}_\rho^+ = \{\mathbf{z} \in \mathbf{X}^+ : \|\mathbf{z}\| = \rho\}. \quad (4.3)$$

**Theorem 4.1.1.** *The Banach space  $\mathbf{X}$  can be identified with the dual space  $\mathbf{Y}^*$  of the space*

$$\mathbf{Y} = \{\mathbf{y} = (y_i)_{i \in \mathbb{N}_0} \subseteq \mathbb{R} : \lim_{i \rightarrow \infty} \frac{y_i}{i} = 0\}, \quad \text{with norm} \quad \|\mathbf{y}\|_{\mathbf{Y}} = \max_{i \geq 1} \left\{ |y_0|, \frac{|y_i|}{i} \right\}. \quad (4.4)$$

The duality pairing of  $\mathbf{X}$  and  $\mathbf{Y}$  is defined as

$$\langle \mathbf{y}, \mathbf{z} \rangle = \sum_{i=0}^{\infty} z_i y_i. \quad (4.5)$$

The proof of this theorem can be done similarly to the results by Naldzhieva [42] by making the transformation  $z_i \rightarrow z_{i+1}$  and noting that

$$\|\mathbf{z}\|_{\mathbf{X}} = |z_1| + \sum_{i=2}^{\infty} (i-1)|z_i| \quad \text{and} \quad \|\mathbf{z}\|_{\mathbf{Y}} = \max_{i \geq 2} \left\{ |y_1|, \frac{|y_i|}{i-1} \right\}. \quad (4.6)$$

The details of the proof are given in Appendix C.1.

**Lemma 4.1.2** (Ball, Carr and Penrose). *A sequence  $\mathbf{z}^{(n)}$  of elements of  $\mathbf{X}$  converges weak\* to  $\mathbf{z} \in \mathbf{X}$ , we write  $\mathbf{z}^{(n)} \rightharpoonup^* \mathbf{z}$ , if and only if*

- (i)  $z_i^{(n)} \rightarrow z_i$  as  $n \rightarrow \infty$  for each  $i \in \mathbb{N}_0$  and
- (ii)  $\sup_{n \in \mathbb{N}_0} \|\mathbf{z}^{(n)}\|_{\mathbf{X}} < \infty$ .

The proof can be constructed by using the transformation  $z_i \rightarrow z_{i+1}$  and the norms in (4.6). We can easily adapt the results in Naldzhieva [42] to construct the proof. This is done in Appendix C.1

**Definition 4.1.3** (Ball, Carr and Penrose). *Let  $\mathbf{E} \subset \mathbf{X}$ . A function  $\theta : \mathbf{E} \rightarrow \mathbb{R}$  is sequentially weak\* continuous if for  $\mathbf{z}^{(n)}, \mathbf{z} \in \mathbf{E}$  with  $\mathbf{z}^{(n)} \rightharpoonup^* \mathbf{z}$ ,  $\theta(\mathbf{z}^{(n)}) \rightharpoonup^* \theta(\mathbf{z})$ .*

**Lemma 4.1.4** (Ball, Carr and Penrose). *For  $\mathbf{z} \in \mathbf{X}^+$  and  $\mathbf{y} \in \mathbf{Y}$  the functional  $B(\mathbf{z})$  defined by  $B(\mathbf{z}) := \sum_{i=0}^{\infty} y_i z_i$  is well defined and sequentially weak\* continuous. In particular*

$$N_D(\mathbf{z}) = \sum_{i=0}^{\infty} z_i$$

*is sequentially weak\* continuous.*

The proof of Lemma 4.1.4 follows directly from the results in Lemma 4.1.2 and the fact that the constant sequence  $(1, 1, \dots) \in \mathbf{Y}$ .

## 4.2 Existence of solutions

Here we prove existence of solutions to the model for the two different cases  $z_0 = 0$  and  $z_0 > 0$ . In both cases we solve the problem with  $J_i$  given by (2.86). For  $z_0 = 0$  the case for  $J_i$  in (2.87) was solved by Herrmann et al. [24], see the remarks leading to (4.1). By using (1.24) and (1.27), the flux equation (2.86) is equivalent to

$$J_i(\mathbf{z}(t)) = a_i \left( z_i(t) \frac{z_1(t)}{z_1(t) + z_0} - \frac{q_i}{q_{i+1}} \frac{N_D(t)}{z_1(t) + z_0} z_{i+1}(t) \right). \quad (4.7)$$

We make the following assumptions on the kinetic coefficients and initial data.

### Assumption 4.2.1.

(i) The kinetic coefficients  $a_i$  in the fluxes satisfy

$$a_i = \xi i^\alpha \quad \text{for } \alpha \in [0, 1[ \quad \text{and } \xi > 0. \quad (4.8)$$

(ii) For  $i \geq 1$  and  $q_i > 0$  we define  $\Delta_i$  by  $\Delta_i := q_i/q_{i+1}$ . The positive coefficients  $a_i$  and  $\Delta_i$  must be chosen such that  $\kappa := \inf_{i \geq 1} \{\frac{\Delta_i a_i}{a_{i+1}}, 1\}$  and  $\nu := \sup_{i \geq 1} \Delta_i$  both exist and are nonzero. It is also assumed that

$$M := \sup_{i \geq 2} (a_{i-1} \Delta_{i-1} - a_i \Delta_i) < \infty \quad \text{and} \quad 0 < R = \lim_{i \rightarrow \infty} \frac{q_i}{q_{i+1}} < \infty, \quad (4.9)$$

which implies that  $1/R = \lim_{i \rightarrow \infty} q_i^{1/i}$ .

(iii) The initial data  $\mathbf{z}(0) \in \mathbf{X}^+$  must satisfy  $z_0 + z_1(0) > 0$ .

For  $z_0 = 0$ , Assumption 4.2.1 (iii) is physically reasonable for nucleation of condensed phases since free molecules must exist in the old phase before nucleation can take place. As a consequence, this assumption implies that the initial total mass  $\rho(0) := \sum_{i=1}^{\infty} i z_i(0)$  in the system is strictly positive.

**Definition 4.2.2.** A function  $\mathbf{z} : [0, T[ \rightarrow \mathbf{X}^+$  is a solution of (2.85) on  $[0, T[$ ,  $0 \leq T \leq \infty$  if for given initial data  $\mathbf{z}(0) \in \mathbf{X}^+$  with  $z_0(0) + z_1(0) > 0$  the following conditions are satisfied.

(i)  $\mathbf{z} \geq 0$  on  $[0, T[$ .

(ii)  $\sup_{t \in [0, T[} \|\mathbf{z}(t)\| < \infty$ , where  $\|\mathbf{z}(t)\| := z_0 + \sum_{i=1}^{\infty} i z_i(t)$ .

(iii)  $\mathbf{z}$  solves (2.85), that is, each  $z_i : [0, T[ \rightarrow \mathbb{R}$  is differentiable.

Section 4.2.1 contains the existence results for  $z_0 = 0$  while the solution for  $z_0 > 0$  is discussed in Section 4.2.2.

### 4.2.1 Existence for the case $z_0 = 0$

For this case, it is convenient to divide the space  $\mathbf{X}^+$  into two disjoint subspaces  $\mathbf{A}$  and  $\mathbf{B}$  which are chosen such that

$$\mathbf{A} := \{\mathbf{z} \in \mathbf{X}^+ : z_1 < \frac{\kappa}{2} \sum_{i=2}^{\infty} z_i\} \quad \text{and} \quad \mathbf{B} := \{\mathbf{z} \in \mathbf{X}^+ : z_1 \geq \frac{\kappa}{2} \sum_{i=2}^{\infty} z_i\}, \quad (4.10)$$

with  $\kappa$  from Assumption 4.2.1 (ii). We analyze the existence and uniqueness properties of solutions whose initial data are taken from one of the subspaces above. The solution is constructed in three steps. First we prove the existence of solutions to the finite dimensional system of size  $n \in \mathbb{N}$  obtained by using the truncation  $J_n(\mathbf{z}^{(n)}) = 0$  and  $z_i = 0$  for all  $i \geq n + 1$ . The results are summarized in Lemmas 4.2.3 and 4.2.5. Secondly we construct an admissible limiting sequence via Lemma 4.2.7. Finally we show that the constructed admissible sequence is consistent with the infinite system. This is a standard procedure used by Ball et al. [4]. The existence result is stated in Theorem 4.2.8.

#### Finite system

Here we prove existence of a unique solution  $\mathbf{z}^{(n)}$  to the following finite dimensional system of size  $n \in \mathbb{N}$  obtained by using  $J_n(\mathbf{z}^{(n)}) = 0$  and  $z_i = 0$  for all  $i \geq n + 1$ . It is given by

$$\begin{aligned} \dot{z}_1^{(n)}(t) &= -J_1(\mathbf{z}^{(n)}(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}^{(n)}(t)), \\ \dot{z}_i^{(n)}(t) &= J_{i-1}(\mathbf{z}^{(n)}(t)) - J_i(\mathbf{z}^{(n)}(t)) \quad \text{for } 2 \leq i \leq n-1, \\ \dot{z}_n^{(n)}(t) &= J_{n-1}(\mathbf{z}^{(n)}(t)). \end{aligned} \quad (4.11)$$

The system is solved for initial data obtained as truncations of the data  $\mathbf{z}(0) \in \mathbf{X}^+$  satisfying Assumption 4.2.1 (iii). We set  $z_{0i} := z_i(0) \geq 0$  for  $1 \leq i \leq n$  and note that  $z_{01} > 0$  by assumption. We consider the initial conditions

$$z_i^{(n)}(0) = z_{0i} \quad \text{for } 1 \leq i \leq n. \quad (4.12)$$

Further we introduce  $\rho^{(n)}(t) := \sum_{i=1}^n i z_i^{(n)}(t)$  and note that  $\rho^{(n)}(0) > 0$ . In system (4.11), the total number of clusters and free molecules is given by  $N_D^{(n)}(t) := \sum_{i=1}^n z_i^{(n)}(t)$ , while the fluxes are obtained from (4.7), with  $z_0 = 0$ , as

$$J_i(\mathbf{z}^{(n)}(t)) = a_i \left( z_i^{(n)}(t) - \Delta_i \frac{N_D^{(n)}(t)}{z_1^{(n)}(t)} z_{i+1}^{(n)}(t) \right). \quad (4.13)$$

Now suppose that the initial data  $\mathbf{z}(0)$  belong to subspace  $\mathbf{B}$  defined in (4.10). Then

$$z_{01} \geq \frac{\kappa}{2} \sum_{i=2}^n z_{0i}. \quad (4.14)$$

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Define  $f^{(n)}(t) := z_1^{(n)}(t) - \kappa/2 \sum_{i=2}^n z_i^{(n)}(t)$ . Then (4.12) and (4.14) together imply that  $f^{(n)}(0) \geq 0$ . By using (4.11) we have

$$\begin{aligned} \dot{f}^{(n)}(t) &= \dot{z}_1^{(n)}(t) - \frac{\kappa}{2} \sum_{i=2}^n \dot{z}_i^{(n)}(t) \\ &= -J_1(\mathbf{z}^{(n)}(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}^{(n)}(t)) - \frac{\kappa}{2} J_1(\mathbf{z}^{(n)}(t)). \end{aligned} \quad (4.15)$$

**Lemma 4.2.3.** *The system (4.11) - (4.13) with initial data in  $\mathbf{B}$  has a unique solution for  $t \geq 0$ . At every  $t$  the solution satisfies the conditions  $z_1(t) > 0$ ,  $z_i(t) \geq 0$  for all  $2 \leq i \leq n$  and  $f^{(n)}(t) \geq 0$ . Furthermore, the mass in the system is conserved, that is,  $\rho^{(n)}(t) := \sum_{i=1}^n iz_i(t) = \sum_{i=1}^n iz_i(0)$ .*

*Proof.* For  $\varepsilon > 0$  consider the following system obtained by adding  $\varepsilon$  to each of the right-hand side terms of (4.11) for  $2 \leq i \leq n$

$$\dot{z}_i^\varepsilon(t) = \begin{cases} J_{i-1}(\mathbf{z}^\varepsilon(t)) - J_i(\mathbf{z}^\varepsilon(t)) + \varepsilon; & \text{for } 2 \leq i \leq n-1, \\ J_{n-1}(\mathbf{z}^\varepsilon(t)) + \varepsilon, & \text{for } i = n. \end{cases} \quad (4.16)$$

with initial conditions

$$z_i^\varepsilon(0) := z_i^{(n)}(0) + \varepsilon > 0, \quad 2 \leq i \leq n. \quad (4.17)$$

In order to satisfy (4.14) the initial number of free molecules is transformed into

$$z_1^\varepsilon(0) = z_1^{(n)}(0) + \varepsilon + \frac{\kappa}{2}(n-1)\varepsilon > 0. \quad (4.18)$$

For the solution to remain in the set  $\mathbf{B}$ , the free molecules equation becomes

$$\dot{z}_1^\varepsilon(t) = -J_1(\mathbf{z}^\varepsilon(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}^\varepsilon(t)) + \varepsilon + \frac{\kappa}{2}(n-1)\varepsilon. \quad (4.19)$$

We have the mass

$$\rho^\varepsilon(0) = \rho^{(n)}(0) + \left( \frac{n(n+1)}{2} + \frac{\kappa(n-1)}{2} \right) \varepsilon > 0.$$

Note that for this system the mass increases linearly in time. To see this we differentiate  $\rho^\varepsilon$  with respect to  $t$  and use (4.16) together with (4.19) to obtain

$$\begin{aligned} \frac{d}{dt} \rho^\varepsilon(t) &= \sum_{i=1}^n i \dot{z}_i^\varepsilon(t), \\ &= -J_1(\mathbf{z}^\varepsilon(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}^\varepsilon(t)) + \varepsilon + \frac{\kappa}{2}(n-1)\varepsilon \\ &\quad + \sum_{i=2}^n i \left( J_{i-1}(\mathbf{z}^\varepsilon(t)) - J_i(\mathbf{z}^\varepsilon(t)) + \varepsilon \right), \\ &= \varepsilon \left( 1 + \frac{\kappa}{2}(n-1) + \sum_{i=2}^n i \right) > 0. \end{aligned} \quad (4.20)$$

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With  $f^{(\varepsilon)}(t) := z_1^{(\varepsilon)}(t) - \kappa/2 \sum_{i=2}^n z_i^{(\varepsilon)}(t)$ , the analogous equation to (4.15) becomes

$$\dot{f}^{(\varepsilon)}(t) = -J_1(\mathbf{z}^{(\varepsilon)}(t)) - \sum_{i=1}^{n-1} J_i(\mathbf{z}^{(\varepsilon)}(t)) - \frac{\kappa}{2} J_1(\mathbf{z}^{(\varepsilon)}(t)) + \varepsilon. \quad (4.21)$$

We note from the definition of the fluxes that the right-hand sides of each of (4.16) and (4.19) are continuous functions of  $\mathbf{z}^{(\varepsilon)}$  for  $z_1^{(\varepsilon)}(t) > 0$ . Moreover they are even continuously differentiable functions if  $z_1^{(\varepsilon)}(t) > 0$ . Since the mass in the system is increasing we may deduce from  $f^{(\varepsilon)}(t) \geq 0$  that  $z_1^{(\varepsilon)}(t) > 0$ . Suppose  $\tau_\varepsilon$  is the first time at which  $f^{(\varepsilon)}(\tau_\varepsilon) = 0$ . Then  $z_1^{(\varepsilon)}(t) > 0$  on  $[0, t]$  for any  $t \in ]0, \tau_\varepsilon[$  so that the right-hand sides of (4.16) and (4.19) are locally Lipschitz continuous with respect to  $\mathbf{z}^{(\varepsilon)}$  on the interval  $[0, t]$ . The Lipschitz constant can be constructed from the Jacobian matrix of the right-hand side functions as the maximum value of its rows. Thus local existence of solution is guaranteed by using the Picard-Lindelöf theorem.

To prove positivity of the solution we note that the initial conditions (4.17) and (4.18) are strictly positive for  $1 \leq i \leq n$ . Moreover by assumption, the inequality  $f^{(\varepsilon)}(t) > 0$  holds on the interval  $[0, \tau_\varepsilon[$  of existence. Suppose  $s \in ]0, \tau_\varepsilon[$  is the first time for which one of the components  $z_i^{(\varepsilon)}$  becomes zero. That is, there exists  $m : 2 \leq m \leq n$  such that  $z_m^{(\varepsilon)}(s) = 0$ . We exclude the possibility for  $m = 1$  since  $f^{(\varepsilon)}(s) > 0$ , that is,  $z_1$  cannot become zero. At  $s$  we must have

$$\dot{z}_m^{(\varepsilon)}(s) \leq 0 \quad (4.22)$$

and

$$z_i^{(\varepsilon)}(s) \geq 0, \quad \text{for all } 1 \leq i \leq n.$$

After substituting (4.13) for the fluxes  $J_i$  in (4.16) and using  $a_i = \xi i^\alpha$  we have

$$\dot{z}_m^{(\varepsilon)}(s) = \begin{cases} (m-1)^\alpha \xi z_{m-1}^{(\varepsilon)}(s) + \xi m^\alpha \frac{N_D(s)}{z_1^{(\varepsilon)}(s)} \Delta_m z_{m+1}^{(\varepsilon)}(s) + \varepsilon; & \text{if } 2 \leq m \leq n-1, \\ (n-1)^\alpha \xi z_{n-1}^{(\varepsilon)}(s) + \varepsilon & \text{if } m = n. \end{cases} \quad (4.23)$$

Thus  $\dot{z}_m^{(\varepsilon)}(s) > 0$  for all  $2 \leq m \leq n$ . This is a contradiction to the inequality in (4.22) and therefore proves that  $z_i^{(\varepsilon)}(\cdot) > 0$  on  $[0, t]$  for any  $t \in ]0, \tau_\varepsilon[$  and all  $1 \leq i \leq n$ .

Next we show that the solution can be extended to the whole interval  $[0, \tau_\varepsilon]$  by proving that it is bounded up to  $\tau_\varepsilon < \infty$ . For this we integrate (4.20) to obtain

$$0 < z_i^{(\varepsilon)}(t) \leq \sum_{i=1}^n i z_i^{(\varepsilon)}(t) = \sum_{i=1}^n i z_i^{(\varepsilon)}(0) + t\varepsilon \left( 1 + \frac{\kappa}{2}(n-1) + \sum_{i=2}^n i \right). \quad (4.24)$$

Thereby the solution is bounded for all  $t \in ]0, \tau_\varepsilon[$ .

Finally to prove global existence we show that for the above  $\tau_\varepsilon$  we have  $\tau_\varepsilon = \infty$ . Suppose that  $\tau_\varepsilon < \infty$ . Then due to the condition  $f^{(\varepsilon)}(0) > 0$  and continuity of  $f^{(\varepsilon)}(t)$  we must have

$$\dot{f}^{(\varepsilon)}(\tau_\varepsilon) \leq 0 \quad (4.25)$$

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and

$$z_i^{(\varepsilon)}(\tau_\varepsilon) \geq 0, \quad \text{for all } 1 \leq i \leq n. \quad (4.26)$$

Now we substitute for the fluxes according to (4.13) into (4.21) and rearrange to obtain

$$\begin{aligned} \dot{f}^{(\varepsilon)}(t) &= \varepsilon - \left(2 + \frac{\kappa}{2}\right) a_1 z_1^{(\varepsilon)} + \left(1 + \frac{\kappa}{2}\right) \frac{N_D}{z_1^{(\varepsilon)}} z_2^{(\varepsilon)} a_1 \Delta_1 + a_n z_n^{(\varepsilon)} \\ &\quad + \sum_{i=2}^n \left( \frac{N_D}{z_1^{(\varepsilon)}} \frac{a_{i-1} \Delta_{i-1}}{a_i} - 1 \right) a_i z_i^{(\varepsilon)}, \\ &> \varepsilon - \left(2 + \frac{\kappa}{2}\right) a_1 z_1^{(\varepsilon)} + \sum_{i=2}^n \left( \frac{N_D}{z_1^{(\varepsilon)}} \kappa - 1 \right) a_i z_i^{(\varepsilon)}, \end{aligned} \quad (4.27)$$

since  $z_i^{(\varepsilon)}(t) > 0$  for all  $1 \leq i \leq n$  on  $[0, \tau_\varepsilon]$ . We note that

$$\frac{N_D^{(\varepsilon)}(t)}{z_1^{(\varepsilon)}(t)} = 1 + \frac{1}{z_1^{(\varepsilon)}(t)} \sum_{i=2}^n z_i^{(\varepsilon)}(t). \quad (4.28)$$

Using this relation and  $f^{(\varepsilon)}(\tau_\varepsilon) = z_1^{(\varepsilon)}(\tau_\varepsilon) - \kappa/2 \sum_{i=2}^n z_i^{(\varepsilon)}(\tau_\varepsilon) = 0$  we have

$$\dot{f}^{(\varepsilon)}(\tau_\varepsilon) > \varepsilon - \frac{\kappa}{2} \left(2 + \frac{\kappa}{2}\right) a_1 \sum_{i=2}^n z_i^{(n)}(\tau_\varepsilon) + (1 + \kappa) \sum_{i=2}^n a_i z_i^{(n)}(\tau_\varepsilon).$$

Next we use the condition  $a_i > a_1$  on condensation rates and rearrange the results to obtain

$$\dot{f}^{(\varepsilon)}(\tau_\varepsilon) > \varepsilon + a_1 \left(1 - \frac{\kappa^2}{4}\right) \sum_{i=2}^n z_i^{(n)}(\tau_\varepsilon)$$

Since  $\kappa \leq 1$ , the above inequality implies that  $\dot{f}^{(\varepsilon)}(\tau_\varepsilon) > 0$ . This contradicts (4.25) for  $\tau_\varepsilon < \infty$ . Therefore  $\tau_\varepsilon = \infty$  and the solution exists for all  $t \in [0, \infty[$  due to the bound in (4.24). To conclude the proof of Lemma 4.2.3 we take the limit  $\varepsilon \rightarrow 0$  to obtain  $\mathbf{z}^{(n)}(t) = \lim_{\varepsilon \rightarrow 0} \mathbf{z}^{(\varepsilon)}(t) \geq 0$ . We note that the above convergence is uniform, see Hartmann [23, p. 5 & 25]. In particular, the condition  $f^{(n)}(t) \geq 0$  is satisfied. Mass conservation is obtained by taking  $\varepsilon = 0$  in (4.20). This leads to the following uniform upper bound on the solution

$$z_i^{(n)}(t) \leq i^{-1} \rho^{(n)}(0) \quad (4.29)$$

for each  $i$ . □

**Remark 4.2.4.** We point out that we can use the condition  $f^{(n)}(t) \geq 0$  to obtain an upper bound on the quotient  $N_D^{(t)}/z_1^{(n)}(t)$  via

$$\frac{N_D^{(n)}(t)}{z_1^{(n)}(t)} \leq 1 + \frac{2}{\kappa}. \quad (4.30)$$

However, the condition  $f^{(n)}(t) \geq 0$  does not explicitly give a time independent lower bound on the number  $z_1^{(n)}(t)$  of free molecules. To construct a uniform lower bound on  $z_1^{(n)}(t)$  we note that the mass

$$\rho^n(t) = \sum_{i=1}^n i z_i(t) \leq n \sum_{i=1}^n z_i(t) = n N_D^{(n)}(t).$$

Thus by using mass conservation we have

$$N_D^{(n)}(t) \geq \frac{\rho^{(n)}(0)}{n}. \quad (4.31)$$

It follows from (4.30) and (4.31) that

$$z_1^{(n)}(t) \geq \frac{\kappa}{(\kappa + 2)} \frac{\rho^{(n)}(0)}{n}. \quad (4.32)$$

Therefore (4.32) acts as a uniform lower bound on the number of free molecules for a fixed  $n$  on  $[0, \infty[$ .

Now we consider the existence and uniqueness of solutions for the finite system (4.11) with initial data taken from  $\mathbf{A}$ . The result is summarized in Lemma 4.2.5.

**Lemma 4.2.5.** *The system (4.11) - (4.13) with initial data in  $\mathbf{A}$  has a unique solution for all  $t \geq 0$  with  $z_1(t) > 0$  and  $z_i(t) \geq 0$  for  $2 \leq i \leq n$ . There exists a finite time  $t_{\mathbf{A}}$  such that the time derivative  $\dot{z}_1^{(n)}(t)$  of  $z_1^{(n)}(t)$  satisfies  $\dot{z}_1^{(n)}(t) > 0$  on  $[0, t_{\mathbf{A}}]$ . In particular,  $t_{\mathbf{A}}$  is the time it takes for the solution to enter region  $\mathbf{B}$  from  $\mathbf{A}$ . Furthermore, the mass in the system is conserved, that is,  $\rho^{(n)}(t) = \rho^{(n)}(0)$ .*

*Proof.* The existence, uniqueness and mass conservation can be proved analogously to the results in Lemma 4.2.3. For the existence of the time  $t_{\mathbf{A}}$  it is sufficient to show that if  $\mathbf{z}^{(n)}(t) \in \mathbf{A}$  at time  $t$ , then  $\dot{z}_1^{(n)}(t) > 0$ . Consider the free molecule equation in (4.11) and substitute the fluxes according to (4.13). Then following the same procedure as in the derivation of (4.27) we obtain

$$\dot{z}_1^{(n)}(t) > -2a_1 z_1^{(n)} + \sum_{i=2}^n \left( \frac{N_D^{(n)}}{z_1^{(n)}} \kappa - 1 \right) a_i z_i^{(n)},$$

or equivalently

$$\dot{z}_1^{(n)}(t) > -2a_1 z_1^{(n)} + \sum_{i=2}^n \left( \kappa + \frac{\sum_{i=2}^n z_i^{(n)}}{z_1^{(n)}} \kappa - 1 \right) a_i z_i^{(n)}.$$

Recall that  $\mathbf{z}^{(n)}(t) \in \mathbf{A}$  implies that  $z_1^{(n)}(t) < \kappa/2 \sum_{i=2}^n z_i^{(n)}$ . Now using this condition together with  $a_i > a_1$  for all  $2 \leq i \leq n$  we obtain

$$\dot{z}_1^{(n)}(t) > \frac{2}{\kappa} a_1 z_1^{(n)}(t). \quad (4.33)$$

The assumption  $z_1^{(n)}(0) > 0$  implies that the right-hand side of the above inequality is greater than zero for all  $t \in [0, t_{\mathbf{A}}]$ . To prove the finiteness of  $t_{\mathbf{A}}$  we note that (4.33) implies that

$$z_1^{(n)}(t) > z_1^{(n)}(0) \exp\left(\frac{2}{\kappa} a_1 t\right).$$

The conservation of mass means that after a finite time  $t_m$ , with

$$t_m < (\kappa/2a_1) \ln\left(\rho^{(n)}(0)/z_1^{(n)}(0)\right),$$

all the mass will be contained in the free molecules. It is clear that at  $t_m$  the solution will already be in region  $\mathbf{B}$ . The proof ends by noting that there exists a time  $t_{\mathbf{A}}$  with  $t_{\mathbf{A}} < t_m$ .  $\square$

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**Remark 4.2.6.** On  $[0, t_{\mathbf{A}}]$  the value of  $z_1^{(n)}(t)$  is bounded below by  $z_1^{(n)}(0)$ . Thus we can use mass conservation to bound the quotient  $N_D^{(n)}/z_1^{(n)}$  by

$$\frac{N_D^{(n)}(t)}{z_1^{(n)}(t)} \leq \frac{\rho^{(n)}(0)}{z_1^{(n)}(0)} \quad (4.34)$$

on  $[0, t_{\mathbf{A}}]$ .

### Admissible solution

In the second step we construct an admissible solution which is a limit of a sub-sequence  $\mathbf{z}^{(n_k)}(\cdot)$  of solutions  $\mathbf{z}^{(n)}(\cdot)$  as  $k \rightarrow \infty$ . To construct the admissible solution we apply the Arzela-Ascoli theorem by showing that for each  $1 \leq i \leq n$  the sequence of solutions  $z_i^{(n)}$  is uniformly bounded and equicontinuous. Uniform boundedness follows directly from (4.29) while for equicontinuity it is sufficient to show that the derivatives  $\dot{z}_i^{(n)}(t)$  are uniformly bounded in  $i$  and  $t$ . We use the bounds (4.30) and (4.34) to define a constant  $K$  by

$$K := \max \left\{ 1 + \frac{2}{\kappa}, \frac{\rho^{(n)}}{z_1^{(n)}(0)} \right\}, \quad (4.35)$$

so that for all initial conditions taken from  $\mathbf{X}^+$  the solution satisfies

$$\frac{N_D^{(n)}}{z_1^n} \leq K. \quad (4.36)$$

From (4.11) we have

$$|\dot{z}_i^{(n)}(t)| \leq \begin{cases} |J_{i-1}(\mathbf{z}^{(n)}(t))| + |J_i(\mathbf{z}^{(n)}(t))|; & \text{if } 2 \leq i \leq n, \\ |J_1(\mathbf{z}^{(n)}(t))| + |\sum_{i=1}^n J_i(\mathbf{z}^{(n)}(t))| & \text{if } i = 1. \end{cases} \quad (4.37)$$

Using Assumption 4.2.1 (i) the fluxes satisfy

$$\begin{aligned} |J_i(\mathbf{z}^{(n)}(t))| &\leq \sum_{i=1}^n |J_i(\mathbf{z}^{(n)}(t))|, \\ &\leq \xi \sum_{i=1}^n \left( i^\alpha z_i^{(n)}(t) + i^\alpha z_{i+1}^{(n)}(t) \frac{N_D^{(n)}(t)}{z_1^{(n)}(t)} \Delta_i \right). \end{aligned}$$

Next we use the conditions  $\alpha \in [0, 1[$ ,  $\nu = \sup_{i \geq 1} \Delta_i < \infty$ , and (4.36) together with the mass-conservation property for finite systems to obtain

$$|J_i(\mathbf{z}^{(n)}(t))| \leq \sum_{i=1}^n |J_i(\mathbf{z}^{(n)}(t))| \leq \left( 1 + K\nu \right) \xi \rho^{(n)}(0). \quad (4.38)$$

Hence we have

$$|\dot{z}_i^{(n)}(t)| \leq 2 \left( 1 + K\nu \right) \xi \rho^{(n)}(0), \quad (4.39)$$

for all  $1 \leq i \leq n$  and for all  $t \in [0, \infty[$ . If the mass  $\rho^{(n)}(0)$  is bounded independently of  $n$  then  $z_i^{(n)}(t)$  and  $\dot{z}_i^{(n)}(t)$  are uniformly bounded in  $n$ ,  $i$  and  $t$ , giving the equicontinuity of the sequence.



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**Lemma 4.2.7** (Admissible solution for  $z_0 = 0$ ). *Let  $\mathbf{z}(0) = (z_{0i})_{i \in \mathbb{N}_0} \in \mathbf{X}_\rho^+$  with  $z_{00} = 0$  and  $z_{01} > 0$ . Now for every  $n \in \mathbb{N}$  let  $\mathbf{z}^{(n)} \in C([0, \infty[; \mathbb{R}^n)$  be the unique solution of (4.11) for the initial data defined by*

$$z_{0i}^{(n)} = \begin{cases} \frac{\rho}{\sum_{k=1}^n k z_{0k}} z_{0i}; & \text{for } 1 \leq i \leq n, \\ 0 & \text{otherwise.} \end{cases} \quad (4.40)$$

*Then there exists a sub-sequence  $(\mathbf{z}^{(n_k)})_{k \in \mathbb{N}}$  of  $(\mathbf{z}^{(n)})_{n \in \mathbb{N}}$  and a function  $\mathbf{z} : [0, \infty[ \rightarrow \mathbf{X}$  such that*

(i) *For every  $i \in \mathbb{N}_0$ ,  $z_i$  is continuous and  $z_i^{(n_k)} \xrightarrow{k \rightarrow \infty} z_i$  uniformly on compact subsets of  $[0, \infty[$ .*

(ii) *The total number  $N_D(\mathbf{z})$  of clusters and free molecules is continuous and we have  $N_D(\mathbf{z}^{(n_k)}) \xrightarrow{k \rightarrow \infty} N_D(\mathbf{z})$  uniformly on compact subsets of  $[0, \infty[$ .*

*Proof.* We note that the choice (4.40) of initial conditions implies that the mass  $\rho^{(n)}(0)$  is such that  $\rho^{(n)}(0) = \rho$  for all  $n \in \mathbb{N}$ . Therefore from (4.29) and (4.39) the sequence  $z_i^{(n)}(t)$  is uniformly bounded and equicontinuous for each  $i \in \mathbb{N}_0$ . Thus by the Arzela Ascoli theorem there exists a sub-sequence  $z_1^{(n_k)}$  and a function  $z_1$  such that  $z_1^{(n_k)}$  converges uniformly to  $z_1$  on compact subsets of  $[0, \infty[$  as  $k \rightarrow \infty$ . Similarly there exists a sub-sequence  $z_2^{(n_k)}$  converging uniformly to  $z_2$  on compact subsets of  $[0, \infty[$  as  $k \rightarrow \infty$ . This procedure is repeated for  $z_3^{(n)}, z_4^{(n)}, \dots$  and so on. By using the diagonalization method we can extract a sequence  $\mathbf{z}^{(n_k)}$  so that  $z_i^{(n_k)} \xrightarrow{k \rightarrow \infty} z_i$  uniformly for every  $i \in \mathbb{N}_0$  on compact subsets of  $[0, \infty[$ . Since for every  $n_k$ , we have  $z_i^{n_k} \in C([0, \infty[)$  and  $z_i^{n_k}(t) \geq 0$ , then due to uniform convergence we must have  $z_i \in C([0, \infty[)$  and  $z_i(t) \geq 0$  for all  $t \in [0, \infty[$ .

Furthermore since  $N_D$  is weak\* continuous due to Lemma 4.1.4, then  $N_D(\mathbf{z}^{(n_k)})$  converges point-wise in time to  $N_D(\mathbf{z})$  for  $k \rightarrow \infty$ . Besides we have

$$|\dot{N}_D(\mathbf{z}^{(n_k)})| = \left| - \sum_{i=1}^{n_k} J_i(\mathbf{z}^{(n_k)}) \right|.$$

Using (4.38) then gives

$$|\dot{N}_D(\mathbf{z}^{(n_k)})| \leq \left(1 + K\nu\right) \xi \rho.$$

Similarly it is clear from mass conservation that  $N_D(\mathbf{z}^{(n_k)}) \leq \rho$ . Therefore by the Arzela Ascoli theorem there exists a sub-sequence still denoted by  $\mathbf{z}^{(n_k)}$  such that the sequence  $N_D(\mathbf{z}^{(n_k)})$  converges to some  $N_D$  uniformly on compact subsets of  $[0, \infty[$ . Due to the uniqueness of the limit we must have  $N_D(t) = N_D(\mathbf{z}(t)) = \sum_{i=1}^{\infty} i z_i(t)$  for all  $t \geq 0$ . □

Up to this point we have constructed an admissible solution  $\mathbf{z}$  to (1.2) via Lemma 4.2.7. In the following section we prove that this solution is consistent with the infinite system (1.2).

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### Consistency

Here we show that the admissible solution constructed above actually solves (2.85).

**Theorem 4.2.8** (Existence for  $z_0 = 0$ ). *Let the conditions of Lemma 4.2.7 be fulfilled. Then  $\mathbf{z}$  is a solution of (2.85) on  $[0, \infty[$  for initial data  $\mathbf{z}(0) = (z_{0i})_{i \in \mathbb{N}_0}$ . In particular  $z_i \in C([0, \infty[)$  for every  $i \in \mathbb{N}_0$ .*

*Proof.* For the sub-sequence  $\mathbf{z}^{(n_k)}$  we note by (4.8) and (4.13) that

$$\begin{aligned} \lim_{k \rightarrow \infty} J_i(\mathbf{z}^{(n_k)}(t)) &= \lim_{k \rightarrow \infty} \xi i^\alpha \left( z_i^{(n_k)}(t) - \Delta_i z_{i+1}^{(n_k)}(t) \frac{N_D(\mathbf{z}^{(n_k)}(t))}{z_1^{(n_k)}} \right) \\ &= \xi i^\alpha \left( z_i(t) - \Delta_i z_{i+1}(t) \frac{N_D(\mathbf{z}(t))}{z_1} \right) \\ &= J_i(\mathbf{z}(t)), \end{aligned} \quad (4.41)$$

with the convergence being uniform on compact subsets of  $[0, \infty[$ . Thus  $J_i(\mathbf{z}) \in C([0, \infty[)$ . Since from (4.38)  $J_i(\mathbf{z}^{(n_k)}(t))$  is uniformly bounded, then by using the Lebesgue dominated convergence theorem we observe that

$$\lim_{k \rightarrow \infty} \int_0^t J_i(\mathbf{z}^{(n_k)}(s)) ds = \int_0^t J_i(\mathbf{z}(s)) ds. \quad (4.42)$$

Besides, the continuity of  $J_i(\mathbf{z})$  in time implies that the fundamental theorem of calculus can be applied to give

$$\frac{d}{dt} \int_0^t J_i(\mathbf{z}(s)) ds = J_i(\mathbf{z}(t)). \quad (4.43)$$

The convergence of the term  $\sum_{i=1}^{n_k} J_i(\mathbf{z}^{(n_k)}(t))$  which appears in the differential equation for the free molecules is more involved. First of all we have to show that it is uniformly bounded and converges point-wise towards a finite limit  $\sum_{i=1}^{\infty} J_i(\mathbf{z}(t))$  as  $k \rightarrow \infty$ . Secondly we must also show that the series  $\sum_{i=1}^{\infty} J_i(\mathbf{z}(t))$  is uniformly convergent so as to guarantee its continuity. For each  $n_k$  we regard the solution  $\mathbf{z}^{n_k}$  to the finite system as an element of the space  $\mathbf{X}$  defined in (4.2) by setting  $z_i^{n_k} = 0$  for all  $i > n_k$ . Then we can use the mass conservation property of these solutions to write

$$\sum_{i=1}^{n_k} i z_i^{n_k}(t) = \sum_{i=1}^{\infty} i z_i^{n_k}(t) = \sum_{i=1}^{n_k} i z_i^{n_k}(0) \leq \sum_{i=1}^{\infty} i z_i(0) = \rho.$$

Therefore, for a fixed  $m \in \mathbb{N}$  we have

$$\sum_{i=1}^{m-1} i z_i^{n_k}(t) + \sum_{i=m}^{\infty} i z_i^{n_k}(t) \leq \rho.$$

By taking the limit  $k \rightarrow \infty$  we note that both terms on the left-hand side of this inequality have finite limits, due to the bound on the right. In the first one we use  $\lim_{k \rightarrow \infty} z_i^{n_k}(t) = z_i(t)$ . Next we take the limit  $m \rightarrow \infty$  to obtain

$$\sum_{i=1}^{\infty} i z_i(t) \leq \rho. \quad (4.44)$$

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It can easily be seen from (4.36) and the uniform convergence of both  $N_D(\mathbf{z}^{n_k}(t)) \rightarrow N_D(\mathbf{z}(t))$  and  $z_1^{n_k}(t) \rightarrow z_1(t)$  for  $k \rightarrow \infty$ , that

$$\frac{N_D(\mathbf{z}(t))}{z_1(t)} \leq K. \quad (4.45)$$

Now we use (4.44), (4.45) and Assumption 4.2.1 (ii),  $\alpha < 1$  to get

$$\begin{aligned} \left| \sum_{i=m}^n J_i(\mathbf{z}(t)) \right| &\leq \sum_{i=m}^n \xi i^\alpha \left( z_i(t) + \Delta_i z_{i+1}(t) \frac{N_D(\mathbf{z}(t))}{z_1(t)} \right) \\ &\leq \sum_{i=m}^n \xi \frac{i}{i^{1-\alpha}} \left( z_i(t) + \Delta_i z_{i+1}(t) \frac{N_D(\mathbf{z}(t))}{z_1(t)} \right) \\ &\leq \frac{\xi}{m^{1-\alpha}} (1 + K\nu) \rho. \end{aligned}$$

The bound is independent of  $n$  and  $t$ . This implies that the series  $\sum_{i=1}^{\infty} J_i(\mathbf{z}(t))$  is uniformly convergent. Continuity of the series follows from continuity of each  $J_i(\mathbf{z})$ . Analogously, for  $m < n_k$ , we can derive the following estimate for the finite system

$$\left| \sum_{i=m}^{n_k} J_i(\mathbf{z}^{(n_k)}) \right| \leq \frac{\xi}{m^{1-\alpha}} (1 + K\nu) \rho.$$

This means that for each fixed  $m < n_k$ , the sequence  $S_m^{n_k} := |\sum_{i=m}^{n_k} J_i(\mathbf{z}(t))|$  is uniformly bounded and hence convergent. We can choose  $m$  large enough to have

$$\left| \sum_{i=m}^{n_k} J_i(\mathbf{z}^{(n_k)}) \right| \leq \frac{\varepsilon}{3} \quad \text{and} \quad \left| \sum_{i=m}^{\infty} J_i(\mathbf{z}(t)) \right| \leq \frac{\varepsilon}{3}.$$

Now these results together with the uniform convergence  $z_i^{n_k}(t) \rightarrow z_i(t)$  lead to

$$\begin{aligned} \left| \sum_{i=1}^{n_k} J_i(\mathbf{z}^{(n_k)}(t)) - \sum_{i=1}^{\infty} J_i(\mathbf{z}(t)) \right| &\leq \left| \sum_{i=1}^{m-1} (J_i(\mathbf{z}^{(n_k)}(t)) - J_i(\mathbf{z}(t))) \right| + \left| \sum_{i=m}^{n_k} J_i(\mathbf{z}^{(n_k)}(t)) \right| \\ &\quad + \left| \sum_{i=m}^{\infty} J_i(\mathbf{z}(t)) \right| \leq \frac{\varepsilon}{3} + \frac{\varepsilon}{3} + \frac{\varepsilon}{3}. \end{aligned}$$

Therefore

$$\lim_{k \rightarrow \infty} \sum_{i=1}^{n_k} J_i(\mathbf{z}^{(n_k)}) = \sum_{i=1}^{\infty} J_i(\mathbf{z}) < \infty. \quad (4.46)$$

By the Lebesgue dominated convergence theorem we have

$$\lim_{k \rightarrow \infty} \int_0^t \sum_{i=1}^{n_k} J_i(\mathbf{z}^{(n_k)}(s)) ds = \int_0^t \sum_{i=1}^{\infty} J_i(\mathbf{z}(s)) ds. \quad (4.47)$$

Then we can still apply the fundamental theorem of calculus to write

$$\frac{d}{dt} \int_0^t \sum_{i=1}^{\infty} J_i(\mathbf{z}(s)) ds = \sum_{i=1}^{\infty} J_i(\mathbf{z}(t)). \quad (4.48)$$

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Next we consider the convergence for the initial data in the limit  $k \rightarrow \infty$ . This gives

$$z_{0i}^{(n_k)} \xrightarrow{k \rightarrow \infty} z_{0i} \quad (4.49)$$

for  $i \in \mathbb{N}$  because  $\rho / \sum_{i=1}^{(n_k)} z_{0i} \xrightarrow{k \rightarrow \infty} 1$ . Finally we write (4.11) in integral form as

$$\begin{aligned} z_1^{(n_k)}(t) &= z_1^{(n_k)}(0) - \int_0^t J_1(\mathbf{z}^{(n_k)}(s)) ds - \int_0^t \sum_{i=1}^{n_k-1} J_i(\mathbf{z}^{(n_k)}(s)) ds, \\ z_i^{(n_k)}(t) &= z_i^{(n_k)}(0) + \int_0^t J_{i-1}(\mathbf{z}^{(n_k)}(s)) ds - \int_0^t J_i(\mathbf{z}^{(n_k)}(s)) ds \quad \text{for } 2 \leq i \leq n, \\ z_n^{(n)}(t) &= z_n^{(n)}(0) + \int_0^t J_{n-1}(\mathbf{z}^{(n_k)}(s)) ds. \end{aligned} \quad (4.50)$$

Taking the limit as  $k \rightarrow \infty$  in the above system and using (4.42), (4.47) and (4.49) we obtain

$$\begin{aligned} z_1(t) &= z_1(0) - \int_0^t J_1(\mathbf{z}(s)) ds - \int_0^t \sum_{i=1}^{\infty} J_i(\mathbf{z}(s)) ds, \\ z_i(t) &= z_i(0) + \int_0^t J_{i-1}(\mathbf{z}(s)) ds - \int_0^t J_i(\mathbf{z}(s)) ds \quad \text{for } i \geq 2. \end{aligned}$$

To conclude the proof we note that the right-hand sides of the above system are continuously differentiable in  $t$ . Thus the left-hand sides must also be continuously differentiable. We can then differentiate both sides with respect to  $t$  and use (4.43) together with (4.48) to show that the solution  $\mathbf{z}$  solves (2.85) in strong sense.  $\square$

**Remark 4.2.9.** *We point out that the solution which was constructed by Herrmann et al. [24, Equation (A2) and the remark on P. 121] was weak in the sense that the continuity of the series in (4.48) could not be established for the class of condensation rates they considered. Although they considered a bigger class of rates, we are not aware of any applications with rates other than those of the form in (4.8).*

### 4.2.2 Existence for the case $z_0 > 0$

Here we briefly discuss the existence of solutions to (2.85) - (2.88) in the presence of an inert substance. The solution can be constructed analogously to the results in the previous section. In this case the quotients  $z_1^{(n)}(t)/(z_0 + z_1^{(n)}(t))$  and  $N_D^{(n)}(t)/(z_0 + z_1^{(n)}(t))$ , which appear in the flux (4.7) for finite systems, are such that

$$\frac{z_1^{(n)}(t)}{z_0 + z_1^{(n)}(t)} \leq 1 \quad \text{and} \quad \frac{N_D^{(n)}(t)}{z_0 + z_1^{(n)}(t)} \leq \frac{\rho}{z_0}. \quad (4.51)$$

The existence result is summarized in the following theorem.

**Theorem 4.2.10** (Existence for  $z_0 > 0$ ). *Let  $\mathbf{z}(0) = (z_{0i})_{i \in \mathbb{N}_0} \in \mathbf{X}_\rho^+$  with  $z_{00} = z_0 > 0$ . Suppose that the fluxes are given by (4.7) and let the conditions of Assumption 4.2.1 be fulfilled. Then there exists a solution  $\mathbf{z}(t)$  to (2.85) in the sense of Definition 4.2.2.*

A general existence and uniqueness result with fluxes from (2.87) is stated later in Theorem 4.3.6.

### 4.3 Uniqueness of solutions and Mass conservation

In this section we prove uniqueness of the solution by following an idea introduced by Laurençot and Mischler [34]. There, the authors assumed that the coefficients  $a_i$  satisfy

$$0 \leq a_i \quad \text{and} \quad a_{i+1} - a_i \leq K \quad (4.52)$$

for some positive constant  $K$ . Clearly the choice  $a_i = \xi i^\alpha$ ,  $\alpha \in [0, 1[$  made in Section 4.2 satisfies this condition with  $K = \xi$ . In addition, by Assumptions 4.2.1 (ii), we have

$$\sup_{i \geq 1} (a_i \Delta_i - a_{i+1} \Delta_{i+1}) = M < \infty.$$

We consider the case where the fluxes are given by (4.7). For  $z_0 = 0$ , the case where  $J_i$  is given by (2.87) was studied by Herrmann et al. [24]. In the case  $z_0 > 0$ , the systems obtained by using the two different flux expressions are mathematically equivalent. Solutions of one can be deduced from the other through an appropriate time scaling.

Let  $\mathbf{z}$  be a solution of (2.85) in the sense of Definition 4.2.2. Define a sequence  $\mathbf{F} = (F_i)_{i \in \mathbb{N}_0}$  by

$$F_i(t) := \sum_{j=i}^{\infty} z_j(t). \quad (4.53)$$

Then  $\mathbf{F}$  is a solution to the system

$$\dot{F}_i(t) = J_{i-1}(\mathbf{F}(t)), \quad i \geq 2, \quad (4.54)$$

$$\dot{F}_0(t) = \dot{F}_1(t) = - \sum_{i=1}^{\infty} J_i(\mathbf{F}(t)), \quad (4.55)$$

where the fluxes are derived from (4.7), with  $\Delta_i = q_i/q_{i+1}$ , by using the substitution  $z_i = F_i - F_{i+1}$  for  $i \geq 0$ . They are given by

$$J_i(\mathbf{F}(t)) = \xi i^\alpha \left[ \left( F_i - F_{i+1} \right) \frac{F_1 - F_2}{F_0 - F_2} - \frac{\Delta_i F_0}{F_0 - F_2} \left( F_{i+1} - F_{i+2} \right) \right]. \quad (4.56)$$

**Definition 4.3.1.** *A function  $\mathbf{F} : [0, T[ \rightarrow l^1(\mathbb{R})$  is a solution of (4.54) - (4.56) on  $[0, T[$ ,  $0 < T \leq \infty$  if*

- (i)  $F_i(t) \geq F_{i+1}(t) \geq 0$  on  $[0, T[$  for all  $i \in \mathbb{N}_0$ .
- (ii)  $\sup_{t \in [0, T[} \sum_{i=1}^{\infty} i(F_i(t) - F_{i+1}(t)) < \infty$ .
- (iii)  $\lim_{n \rightarrow \infty} n F_{n+1}(t) = 0$  for all  $t \in [0, T[$ .
- (iv)  $\mathbf{F}$  solves (4.54) - (4.56).

**Claim:** If  $\mathbf{z}$  solves (2.85) then  $\mathbf{F}$  solves (4.54) - (4.56). On the other hand if  $\mathbf{F}$  solves (4.54) - (4.56) then the sequence  $\mathbf{z} = (z_i)_{i \in \mathbb{N}_0}$  defined by  $z_i = F_i - F_{i+1}$  solves (2.85). The proof of this claim can be done analogously to the results in Naldzhieva [42, Section 4]. For the first part, the idea is to write (2.85) as a system of integral equations and then use (4.53) with infinity replaced by a finite value, say  $n$ . The next step is to take the limit  $n \rightarrow \infty$ , noting that due to (4.46)  $J_n \rightarrow 0$  in this limit. For the second part one has to first show the existence of solutions for (4.54) - (4.56) by following the same procedure used in Section 4.2. Then with  $z_i = F_i - F_{i+1}$  the solution to (2.85) can be constructed.

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**Lemma 4.3.2.** *Let  $\mathbf{F}$  be a solution of (4.54) - (4.56). Then  $\sum_{i=1}^{\infty} F_i(t) = \sum_{i=1}^{\infty} F_i(0)$  for all  $t \geq 0$ .*

*Proof.* With  $z_i = F_i - F_{i+1}$  we note that

$$\sum_{i=1}^n iz_i(t) = \sum_{i=1}^n i(F_i(t) - F_{i+1}(t)) = \sum_{i=1}^n F_i(t) - nF_{n+1}(t).$$

Next we take the limit  $n \rightarrow \infty$ , while using Definition 4.3.1 (iii) and Definition 4.2.2 (ii) to obtain

$$\sum_{i=1}^{\infty} F_i(t) = \sum_{i=1}^{\infty} iz_i(t) < \infty.$$

For  $n \geq 2$  we have

$$\sum_{i=2}^n F_i(t) - \sum_{i=2}^n F_i(0) = \int_0^t \sum_{i=2}^n J_{i-1}(\mathbf{F}(s)) ds = \int_0^t \sum_{i=1}^n J_i(\mathbf{F}(s)) ds.$$

Next we take the limit  $n \rightarrow \infty$  while noting that  $\sum_{i=1}^{\infty} J_i(\mathbf{F}(s))$  is convergent due to  $|J_i(\mathbf{F}(t))| \leq \text{const} \cdot i(F_i(t) - F_{i+1}(t))$  and Definition 4.3.1 (ii). We therefore get the following result from (4.55)

$$\sum_{i=2}^{\infty} F_i(t) - \sum_{i=2}^{\infty} F_i(0) = \int_0^t \sum_{i=1}^{\infty} J_i(\mathbf{F}(s)) ds = -F_1(t) + F_1(0).$$

The proof is accomplished by collecting like terms. □

**Remark 4.3.3.** *Mass conservation of solutions for (2.85) is therefore equivalent to the conservation property for (4.54) and (4.55) proved in Lemma 4.3.2, since  $\rho(t) = z_0 + \sum_{i=1}^{\infty} iz_i(t) = z_0 + \sum_{i=1}^{\infty} F_i(t)$ .*

**Theorem 4.3.4** (Uniqueness). *Let  $\mathbf{F}$  and  $\hat{\mathbf{F}}$  be two solutions for (4.54) - (4.56) such that  $\mathbf{F}(0) = \hat{\mathbf{F}}(0)$  for the initial data taken from  $\mathbf{X}^+$ .*

(i) *Suppose  $z_0 > 0$  and  $\alpha \in [0, 1[$ ,*  
*or*

(ii) *Suppose  $z_0 = 0$  and  $\alpha = 0$ ,*  
*Then  $\mathbf{F}(t) = \hat{\mathbf{F}}(t)$  for all  $t \geq 0$ .*

*Proof.* For the two solutions we have corresponding solutions  $\mathbf{z}$  and  $\hat{\mathbf{z}}$  for (2.85). Define  $\mathbf{E} := \mathbf{F} - \hat{\mathbf{F}}$ . Then for  $i \geq 2$  we have by (4.56)

$$\begin{aligned} \frac{d}{dt} E_i(t) &= \frac{d}{dt} F_i(t) - \frac{d}{dt} \hat{F}_i(t) = J_{i-1}(\mathbf{F}(t)) - J_{i-1}(\hat{\mathbf{F}}(t)), \\ &= \xi(i-1)^\alpha \left[ \frac{z_1(F_{i-1} - F_i)}{z_0 + z_1} - \frac{\Delta_{i-1} F_0(F_i - F_{i+1})}{z_0 + z_0} - \frac{\hat{z}_1(\hat{F}_{i-1} - \hat{F}_i)}{z_0 + \hat{z}_1} + \frac{\Delta_{i-1} \hat{F}_0(\hat{F}_i - \hat{F}_{i+1})}{z_0 + \hat{z}_1} \right]. \end{aligned}$$

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We add and subtract the term  $\xi (i-1)^\alpha [(\hat{F}_{i-1} - \hat{F}_i)z_1/(z_0 + z_1) + \Delta_{i-1}(\hat{F}_i - \hat{F}_{i+1})F_0/(z_0 + z_1)]$  to obtain

$$\begin{aligned} \frac{d}{dt}E_i(t) = & \xi (i-1)^\alpha \left[ \frac{z_1(E_{i-1} - E_i)}{z_0 + z_1} - \frac{\Delta_{i-1}F_0(E_i - E_{i+1})}{z_0 + z_1} + (\hat{F}_{i-1} - \hat{F}_i) \left( \frac{z_1}{z_0 + z_1} - \frac{\hat{z}_1}{z_0 + \hat{z}_1} \right) \right. \\ & \left. + \Delta_{i-1}(\hat{F}_i - \hat{F}_{i+1}) \left( \frac{\hat{F}_0}{z_0 + \hat{z}_1} - \frac{F_0}{z_0 + z_1} \right) \right]. \end{aligned}$$

Next we add and subtract the term  $\xi (i-1)^\alpha [(\hat{F}_{i-1} - \hat{F}_i)z_1/(z_0 + \hat{z}_1) + \Delta_{i-1}(\hat{F}_i - \hat{F}_{i+1})F_0/(z_0 + \hat{z}_1)]$  and then use  $\hat{z}_i = \hat{F}_i - \hat{F}_{i+1}$ . This gives

$$\begin{aligned} \frac{d}{dt}E_i(t) = & \xi (i-1)^\alpha \left[ \frac{z_1(E_{i-1} - E_i)}{z_0 + z_1} - \frac{\Delta_{i-1}F_0(E_i - E_{i+1})}{z_0 + z_1} + \frac{\hat{z}_{i-1}}{z_0 + \hat{z}_1} \left( z_1 \frac{\hat{z}_1 - z_1}{z_0 + z_1} + E_1 - E_2 \right) \right. \\ & \left. + \Delta_{i-1} \frac{\hat{z}_i}{z_0 + \hat{z}_1} \left( \frac{F_0(z_1 - \hat{z}_1)}{z_0 + z_1} - E_1 \right) \right]. \end{aligned}$$

We then apply  $z_1 - \hat{z}_1 = (F_1 - F_2) - (\hat{F}_1 - \hat{F}_2) = E_1 - E_2$  to get

$$\begin{aligned} \frac{d}{dt}E_i(t) = & \xi (i-1)^\alpha \left[ \frac{z_1(E_{i-1} - E_i)}{z_0 + z_1} - \frac{\Delta_{i-1}F_0(E_i - E_{i+1})}{z_0 + z_1} - \frac{\Delta_{i-1}\hat{z}_i}{z_0 + \hat{z}_1} E_1 \right. \\ & \left. + \left( \frac{\hat{z}_{i-1}}{z_0 + \hat{z}_1} - \frac{\hat{z}_{i-1}}{z_0 + \hat{z}_1} \frac{z_1}{z_0 + z_1} + \frac{\Delta_{i-1}\hat{z}_i}{z_0 + \hat{z}_1} \frac{F_0}{z_0 + z_1} \right) (E_1 - E_2) \right]. \end{aligned}$$

Multiplying this equation by  $\text{sign}(E_i)$  and simplifying the result, we obtain

$$\begin{aligned} \frac{d}{dt}|E_i(t)| \leq & \xi (i-1)^\alpha \left[ \frac{z_1(|E_{i-1}| - |E_i|)}{z_0 + z_1} - \frac{\Delta_{i-1}F_0(|E_i| - |E_{i+1}|)}{z_0 + z_1} \right. \\ & \left. + \left( \frac{z_0\hat{z}_{i-1}}{z_0 + \hat{z}_1} + \frac{\Delta_{i-1}\hat{z}_i F_0}{z_0 + \hat{z}_1} \right) \frac{|E_2|}{z_0 + z_1} + \left( \frac{z_0\hat{z}_{i-1}}{z_0 + z_1} + \frac{\Delta_{i-1}\hat{z}_i F_2}{z_0 + z_1} \right) \frac{|E_1|}{z_0 + \hat{z}_1} \right]. \end{aligned}$$

For  $n \geq 3$  we sum this inequality from 2 to  $n$  and simplify the result to get

$$\frac{d}{dt} \sum_{i=2}^n |E_i(t)| \leq \sum_{i=1}^{n+1} \beta_i |E_i|. \quad (4.57)$$

The coefficients  $\beta_i$  are now given by

$$\beta_i = \begin{cases} \frac{\xi z_1}{z_0 + z_1} + \frac{\xi}{z_0 + \hat{z}_1} \sum_{i=2}^n (i-1)^\alpha \left( \frac{z_0\hat{z}_{i-1} + \Delta_{i-1}\hat{z}_i F_2}{z_0 + z_1} \right) & \text{for } i = 1, \\ \frac{\xi}{z_0 + z_1} [2^\alpha z_1 - (z_1 + \Delta_1 F_0)] + \frac{\xi}{z_0 + \hat{z}_1} \sum_{i=2}^n (i-1)^\alpha \left( \frac{z_0\hat{z}_{i-1} + \Delta_{i-1} F_0 \hat{z}_i}{z_0 + z_1} \right) & \text{for } i = 2, \\ \frac{\xi z_1}{z_0 + z_1} [i^\alpha - (i-1)^\alpha] + \frac{\xi F_0}{z_0 + z_1} [(i-2)^\alpha \Delta_{i-2} - (i-1)^\alpha \Delta_{i-1}] & \text{for } 3 \leq i \leq n-1, \\ \frac{\xi F_0}{z_0 + z_1} [(n-2)^\alpha \Delta_{n-2} - (n-1)^\alpha \Delta_{n-1}] - \frac{\xi z_1}{z_0 + z_1} (n-1)^\alpha & \text{for } i = n, \\ \frac{\xi F_0}{z_0 + z_1} (n-1)^\alpha \Delta_{n-1} & \text{for } i = n+1. \end{cases}$$

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Now we turn our attention to part (i) of the uniqueness theorem, the case where  $z_0 > 0$ . We show that the coefficients  $\beta_i$  are bounded independently of  $i$ . We note that

$$\frac{1}{z_0 + \hat{z}_1} \leq \frac{1}{z_0}, \quad \frac{z_1}{z_0 + z_1} \leq 1 \quad \text{and} \quad F_i \leq \rho, \quad \text{for} \quad i \geq 0. \quad (4.58)$$

By using the above inequalities, we can construct upper bounds for the coefficients  $\beta_1$  and  $\beta_2$  via

$$\beta_1 \leq \xi \left( 1 + \frac{z_0 \hat{\rho} + \nu \hat{\rho} \rho}{z_0^2} \right) \quad \text{and} \quad \beta_2 \leq \xi \left( 1 + \frac{z_0 \hat{\rho} + z_0 \nu \rho + \nu \hat{\rho} \rho}{z_0^2} \right),$$

where  $\nu$  is defined in Assumption 4.2.1 (ii) and  $\rho, \hat{\rho}$  are the masses for the corresponding systems. We can also construct upper bounds for  $\beta_i$ ,  $3 \leq i \leq n$ , if the terms  $[i^\alpha - (i-1)^\alpha]$  and  $[(i-2)^\alpha \Delta_{i-2} - (i-1)^\alpha \Delta_{i-1}]$  are bounded uniformly in  $n$ . This has been done in [42] for the Gallium Arsenide example. For the other two examples, we use the condition  $M < \infty$  in Assumption 4.2.1 (ii). Finally we show that  $\lim_{n \rightarrow \infty} \beta_{n+1} |E_{n+1}(t)| = 0$  for all  $t \geq 0$ . For this we have

$$\begin{aligned} \beta_{n+1} |E_{n+1}| &\leq \beta_{n+1} |F_{n+1}| + \beta_{n+1} |\hat{F}_{n+1}| \\ &\leq \beta_{n+1} \sum_{i=n+1}^{\infty} z_i + \beta_{n+1} \sum_{i=n+1}^{\infty} \hat{z}_i \\ &\leq \frac{\xi \nu \rho}{z_0} n^\alpha \sum_{i=n+1}^{\infty} i z_i / i + \frac{\xi \nu \rho}{z_0} n^\alpha \sum_{i=n+1}^{\infty} i \hat{z}_i / i \\ &\leq \frac{\xi \nu \rho}{z_0} \left( \frac{\rho + \hat{\rho}}{n^{1-\alpha}} \right). \end{aligned}$$

The right-hand side goes to zero as  $n \rightarrow \infty$ . Equation (4.57) can be written in integral form as

$$\sum_{i=2}^n |E_i(t)| \leq \sum_{i=2}^n |E_i(0)| + \int_0^t \left( \beta_1 |E_1(s)| + \sum_{i=2}^{n+1} \beta_i |E_i(s)| \right) ds. \quad (4.59)$$

Note that

$$\sum_{i=1}^{\infty} |E_i(t)| \leq \sum_{i=1}^{\infty} |F_i(t)| + \sum_{i=1}^{\infty} |\hat{F}_i(t)| < \infty, \quad (4.60)$$

and

$$\begin{aligned} |E_1(t)| &= |F_1(t) - \hat{F}_1| = \left| \sum_{i=1}^{\infty} F_i(t) - \sum_{i=2}^{\infty} F_i(t) - \sum_{i=1}^{\infty} \hat{F}_i(t) + \sum_{i=2}^{\infty} \hat{F}_i(t) \right| \\ &\leq \sum_{i=2}^{\infty} |E_i(t)| + \sum_{i=1}^{\infty} |E_i(0)|, \end{aligned} \quad (4.61)$$

the last line being due to Lemma 4.3.2. Using (4.60) and (4.61) we can take the limit  $n \rightarrow \infty$  in (4.59) and apply the Lebesgue dominated convergence theorem to obtain

$$\sum_{i=2}^{\infty} |E_i(t)| \leq (1 + \beta_1 t) \sum_{i=2}^{\infty} |E_i(0)| + 2 \max_{i \in \mathbb{N}} \beta_i \int_0^t \sum_{i=2}^{\infty} |E_i(s)| ds. \quad (4.62)$$



### 4.3. UNIQUENESS OF SOLUTIONS AND MASS CONSERVATION

Then the application of Gronwall's Lemma gives the desired result that  $E_i(t) = 0$  for all  $i \geq 1$  and for all  $t \geq 0$  and hence uniqueness.

For part (ii) we use  $z_0 = 0$ , so that the coefficients  $\beta_i$  become

$$\beta_i = \begin{cases} \xi + \frac{F_2}{z_1} \sum_{i=2}^n \xi (i-1)^\alpha \Delta_{i-1} \frac{\hat{z}_i}{\hat{z}_1} & \text{for } i = 1, \\ \xi \left[ 2^\alpha - \left( 1 + \Delta_1 \frac{F_1}{z_1} \right) \right] + \left[ \sum_{i=2}^n \xi (i-1)^\alpha \Delta_{i-1} \frac{\hat{z}_i}{\hat{z}_1} \right] \frac{F_1}{z_1} & \text{for } i = 2, \\ \xi [i^\alpha - (i-1)^\alpha] + \xi [(i-2)^\alpha \Delta_{i-2} - (i-1)^\alpha \Delta_{i-1}] \frac{F_1}{z_1} & \text{for } 3 \leq i \leq n-1, \\ \xi [(n-2)^\alpha \Delta_{n-2} - (n-1)^\alpha \Delta_{n-1}] \frac{F_1}{z_1} - \xi (n-1)^\alpha & \text{for } i = n, \\ \xi (n-1)^\alpha \Delta_{n-1} \frac{F_1}{z_1} & \text{for } i = n+1. \end{cases} \quad (4.63)$$

The bound (4.45) is equivalent to  $F_1/z_1 \leq K$ , where  $K$  is defined in (4.35). Since we have not constructed a time independent lower bound on  $z_1(t)$  the coefficients  $\beta_1$  and  $\beta_2$  can only be bounded uniformly in  $n$  if  $\alpha = 0$ . Then we have

$$\begin{aligned} \beta_1 &\leq \xi + \xi \left( F_1/z_1 - 1 \right) \frac{\hat{F}_2}{\hat{z}_1} \nu \\ &\leq \xi [1 + (K+1)K\nu]. \end{aligned}$$

Similarly, for  $\beta_2$  we have

$$\beta_2 \leq \xi (1+K)K\nu.$$

For  $3 \leq i \leq n-1$  we obtain

$$\beta_i \leq 2\xi K\nu,$$

while

$$\beta_n \leq \xi (1+2K\nu).$$

The uniqueness result can be completed analogously to the proof of part (i).  $\square$

**Remark 4.3.5.** *If it is known a priori that the initial data are taken from  $\mathbf{A}$  then up to the time  $t_{\mathbf{A}}$  introduced in Section 4.2 we have a lower bound on  $z_1$  given by (4.34). We can therefore prove uniqueness locally for  $\alpha \in [0, 1[$  and  $t \in [0, t_{\mathbf{A}}]$ , since we saw in the proof of part (i) that the terms  $[i^\alpha - (i-1)^\alpha]$  and  $[(i-2)^\alpha \Delta_{i-2} - (i-1)^\alpha \Delta_{i-1}]$  are bounded uniformly in  $n$ .*

We now show how to construct the solutions to (2.85) when the fluxes are given by (2.87) and  $z_0 > 0$ . We multiply both sides of these equations by the nonzero term  $z_0 + z_1(t)$  to obtain

$$\begin{aligned} \dot{z}_0(t) &= 0 \\ (z_0 + z_1(t))\dot{z}_1(t) &= -J_1(\mathbf{z}(t)) - \sum_{i=1}^{\infty} J_i(\mathbf{z}(t)), \\ (z_0 + z_1(t))\dot{z}_i(t) &= J_{i-1}(\mathbf{z}(t)) - J_i(\mathbf{z}(t)) \quad \text{for } i \geq 2. \end{aligned} \quad (4.64)$$

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The fluxes are now given by

$$J_i(\mathbf{z}(t)) = a_i(z_1(t)z_i(t) - \Delta_i N_D(\mathbf{z}(t))z_{i+1}(t)),$$

which correspond to the (2.87). We introduce a new time scale  $\tau$  and define  $z_i(\tau) = z_i(t)$  for all  $i \geq 1$ . With  $\dot{t}(\tau) = (z_0 + z_1(t))$  we can transform (4.64) into

$$\begin{aligned} \dot{z}_0(\tau) &= 0 \\ \dot{z}_1(\tau) &= -J_1(\mathbf{z}(\tau)) - \sum_{i=1}^{\infty} J_i(\mathbf{z}(\tau)), \\ \dot{z}_i(\tau) &= J_{i-1}(\mathbf{z}(\tau)) - J_i(\mathbf{z}(\tau)) \quad \text{for } i \geq 2, \end{aligned} \tag{4.65}$$

where the differentiation is now with respect to  $\tau$ . The fluxes are now written in the new time scale as

$$J_i(\mathbf{z}(\tau)) = a_i \left( z_i(\tau)z_1(\tau) - \Delta_i N_D(\mathbf{z}(\tau))z_{i+1}(\tau) \right). \tag{4.66}$$

It is now very clear that solutions to (2.85) with  $J_i$  in (4.7) solve (4.65) and (4.66) in a different time scale  $\tau$  defined by

$$\tau(t) := \int_0^t \frac{1}{z_0 + z_1(s)} ds. \tag{4.67}$$

Since

$$0 < \frac{1}{z_0 + \rho} \leq \frac{1}{z_0 + z_1(t)} \leq \frac{1}{z_0},$$

there is a one to one correspondence between  $t$  and  $\tau$ . In addition, the time scale  $\tau$  satisfies

$$\tau(0) = 0 \quad \text{and} \quad \tau(t \rightarrow \infty) = \infty. \tag{4.68}$$

We summarize the result in the following theorem.

**Theorem 4.3.6** (Existence and Uniqueness for  $z_0 > 0$  and  $J_i$  given by (2.87)). *Let  $\mathbf{z}(t)$  be the unique solution to (2.85) and (4.7) for  $\mathbf{z}(0) \in \mathbf{X}^+$ . For the same initial data, the solution  $\mathbf{z}(\tau)$  solves (4.65) and (4.66) uniquely in a time scale defined by (4.67).*

**Remark 4.3.7.** *If  $\mathbf{z}(\tau)$  is the unique solution to (4.65) and (4.66) for initial data  $\mathbf{z}(0) \in \mathbf{X}^+$ , then for the same initial data,  $\mathbf{z}(t)$  solves (2.85) and (4.7) uniquely in a time scale defined by*

$$t(\tau) := \int_0^\tau z_0 + z_1(s) ds. \tag{4.69}$$

### 4.4 Equilibrium distribution

An equilibrium state of the Becker-Döring system is a state  $\bar{\mathbf{z}} \in \mathbf{X}^+$  such that all fluxes  $J_i$  vanish in  $\bar{\mathbf{z}}$  and  $\bar{z}_0 = z_0$ . In this section we discuss equilibrium solutions to (2.85) for the case where  $z_0 > 0$ . The case  $z_0 = 0$  was discussed already by Herrmann et al. [24]. For convenience we repeat the definitions in (1.24) as

$$R := \lim_{i \rightarrow \infty} \frac{q_i}{q_{i+1}}, \quad \tilde{q}_i := R^i q_i \quad \tilde{f}(\mu) := \sum_{i=1}^{\infty} \tilde{q}_i \mu^i \quad \text{and} \quad \tilde{g}(\mu) := \sum_{i=1}^{\infty} i \tilde{q}_i \mu^i,$$

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#### 4.4. EQUILIBRIUM DISTRIBUTION

**Theorem 4.4.1** (Herrmann et al. [24]). *Let  $z_0 = 0$ . For any given mass  $\bar{\rho} > 0$ , there exists an equilibrium state  $\bar{\mathbf{z}}$  with  $\rho(\bar{\mathbf{z}}) = \bar{\rho}$  if and only if*

$$\tilde{f}(1) > 1, \quad \text{or} \quad \tilde{f}(1) = 1 \quad \text{and} \quad \tilde{g}(1) < \infty. \quad (4.70)$$

Moreover, if (4.70) is satisfied, then

(a) *there exists a unique value  $\bar{\mu} \in ]0, 1]$  such that  $\tilde{f}(\bar{\mu}) = 1$ .*

(b) *the equilibrium solution is given by*

$$\bar{z}_i = N_D(\bar{\mathbf{z}}) \tilde{q}_i \bar{\mu}^i, \quad \text{for } i \geq 1 \quad \text{and} \quad N_D(\bar{\mathbf{z}}) = \frac{\bar{\rho}}{\tilde{g}(\bar{\mu})}.$$

Now we turn our attention to the case where  $z_0 > 0$ . It is clear that  $\mathbf{z} = (z_0, 0, 0, \dots)$  is an equilibrium solution with mass  $z_0$ . We study equilibrium states with  $\bar{z}_0 = z_0$  and prescribed fixed positive total mass  $\rho > z_0$ . By setting the fluxes  $J_i$  in (4.7) or (4.66) to zero and using  $\Delta_i = q_i/q_{i+1}$ , we obtain

$$\bar{z}_{i+1} = \left( \frac{\bar{z}_1}{\bar{N}_D} \right) \frac{q_{i+1}}{q_i} \bar{z}_i = \left( \frac{\bar{z}_1}{R\bar{N}_D} \right) \frac{\tilde{q}_{i+1}}{\tilde{q}_i} \bar{z}_i, \quad i \geq 1. \quad (4.71)$$

With  $\bar{\mu} := \bar{z}_1/(R\bar{N}_D)$  this equation gives

$$\bar{z}_i = \left( \frac{\bar{z}_1}{R\bar{N}_D} \right)^{i-1} \frac{\tilde{q}_i}{\tilde{q}_1} \bar{z}_1 = \bar{N}_D \tilde{q}_i \bar{\mu}^i = \bar{N}_D q_i (R\bar{\mu})^i, \quad \text{for } i \geq 1. \quad (4.72)$$

The condition  $\bar{N}_D = N_D(\bar{\mathbf{z}})$  and the constraint  $\rho(\bar{\mathbf{z}}) = \bar{\rho}$  require that

$$z_0 + \bar{N}_D \tilde{f}(\bar{\mu}) = \bar{N}_D \quad \text{and} \quad \bar{N}_D \tilde{g}(\bar{\mu}) = \bar{\rho} - z_0, \quad (4.73)$$

where  $\tilde{f}$  and  $\tilde{g}$  are defined above. Note that both series have the same radius of convergence  $\mu_s = 1$  and are strictly increasing on  $[0, 1]$ . We summarize the existence of equilibrium solutions in the following theorem.

**Theorem 4.4.2** (Equilibria). *For any given mass  $\rho$ , with  $0 < \rho < \infty$ , let  $0 \leq z_0/(\rho - z_0) < \infty$ . Then there exists an equilibrium state  $\bar{\mathbf{z}}$  with mass  $\rho$  if and only if*

$$\tilde{f}(1) + \frac{z_0 \tilde{g}(1)}{\rho - z_0} \geq 1. \quad (4.74)$$

Equivalently, this condition implies existence of equilibria if

$$\tilde{f}(1) \geq 1 \quad \text{or} \quad \rho \leq z_0 (1 + \tilde{g}(1)), \quad (4.75)$$

or if

$$0 < \frac{\tilde{g}(1)}{1 - \tilde{f}(1)} < \infty \quad \text{and} \quad z_0 (1 + \tilde{g}(1)) < \rho \leq z_0 \left( 1 + \frac{\tilde{g}(1)}{1 - \tilde{f}(1)} \right). \quad (4.76)$$

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Moreover, if (4.74) is satisfied then there exists a unique value  $\bar{\mu}$  such that

$$\bar{\rho} = z_0 \left( 1 + \frac{\tilde{g}(\bar{\mu})}{1 - \tilde{f}(\bar{\mu})} \right). \quad (4.77)$$

The equilibrium solution is given by

$$\bar{z}_0 = z_0, \quad \bar{N}_D = \frac{\bar{\rho} - z_0}{\tilde{g}(\bar{\mu})}, \quad \text{and} \quad \bar{z}_i = \bar{N}_D \tilde{q}_i \bar{\mu}^i \quad \text{for} \quad i \geq 1. \quad (4.78)$$

This theorem shows that in the presence of an inert substance, there are more possibilities for existence of equilibrium solutions than the condition (4.70) which was obtained by Herrmann et al. [24] for  $z_0 = 0$ . In fact one can obtain the results of Theorem 4.4.1 by setting  $z_0 = 0$  in (4.74). The only case where equilibria of the form (4.78) do not exist, is the negation of (4.76), given by

$$0 < \frac{g(1)}{1 - f(1)} < \infty \quad \text{and} \quad z_0 \left( 1 + \frac{g(1)}{1 - f(1)} \right) < \rho. \quad (4.79)$$

We conclude this section by showing how the results in Theorem 4.4.2 apply to the different systems studied in Chapter 2. With  $\bar{S} = p_0/\bar{p}(T)$  or  $\bar{S} = \exp(\eta\Delta T/kT)$ , the liquid-vapor-inert gas and crystallization in solution systems are equivalent. In both cases the existence of an equilibrium state  $\bar{z}$  with  $z_0 > 0$  does not only depend on the values of  $\bar{S}$  and  $\gamma/kT$ , but also on the mass in the system. In particular, the existence of equilibria fails for large values of  $\bar{S}$ ,  $\gamma/kT$  and for a mass that satisfies (4.79). This is different from the case  $z_0 = 0$  where the existence of an equilibrium solution doesnot depend on the mass. In the Gallium Arsenide Example 1.2.2, the presence of an inert substance doesnot change the results discussed by Herrmann et al. [24]. In particular, we have  $R = \exp(+\beta) > 1$ , for  $\beta > 0$ , so that the first inequality in (4.75) always holds.

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## Chapter 5

# Metastability

The aim of this chapter is to show the existence of a metastable class of solutions for the thermodynamically consistent model. In Section 5.1 we introduce the concepts on metastability as used in the standard Becker-Döring models. Section 5.2 contains the existence of metastable solutions for the modified Becker-Döring model.

### 5.1 Introduction

According to Penrose and Lebowitz [48], a metastable state is characterized by the following conditions.

- (i) Only one thermodynamic phase is present although the intensive thermodynamic parameters have values such that the equilibrium state would consist of more than one phase or possibly a single but different phase.
- (ii) The metastable state has a very long lifetime.
- (iii) Escape from the metastable state is an irreversible process, that is, once the system has left the metastable state, it is very unlikely to return.

We assume that the kinetic coefficients  $a_i$  and  $b_i$  satisfy the following conditions, cf. [46], for all  $i \in \mathbb{N}$ :

#### Assumption 5.1.1.

- (i) *there exist positive constants  $A, A'$  and  $\alpha \in ]0, 1[$  such that  $0 < A' < a_i < Ai^\alpha$ .*
- (ii)  $\lim_{i \rightarrow \infty} \frac{b_{i+1}}{b_i} = 1$ .
- (iii)  $\frac{b_{i+1}}{a_{i+1}} \leq \frac{b_i}{a_i}$  and  $\lim_{i \rightarrow \infty} \frac{b_i}{a_i} = \mu_s > 0$ .
- (iv) *there exist  $G, G', \gamma, \gamma' > 0$ ,  $\gamma \in ]0, 1[$  such that  $\mu_s \exp(Gi^{-\gamma}) < \frac{b_i}{a_i} < \mu_s \exp(G'i^{-\gamma'})$ .*

The following lemma will be useful for our results.

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**Lemma 5.1.2** (Penrose [46]). *For each  $\mu > \mu_s$  the second order difference equation for the steady-state solutions*

$$a_{i-1}\mu f_{i-1}(\mu) - (b_i + a_i\mu)f_i(\mu) + b_{i+1}f_{i+1}(\mu) = 0, \quad i \geq 2 \quad (5.1)$$

*with the end conditions  $f_1(\mu) = \mu$  and  $\lim_{i \rightarrow \infty} f_i(\mu) < \infty$  implies a constant quantity  $J(\mu)$  defined by*

$$J(\mu) := a_i\mu f_i(\mu) - b_{i+1}f_{i+1}(\mu). \quad (5.2)$$

*The unique positive solution to difference equation is given by*

$$f_i(\mu) = J(\mu)Q_i\mu^i \sum_{r=i}^{\infty} \frac{1}{a_r Q_r \mu^{r+1}}, \quad (5.3)$$

*with the steady-state flux*

$$J(\mu) = \left[ \sum_{i=1}^{\infty} \frac{1}{a_i Q_i \mu^{i+1}} \right]^{-1}.$$

*Further*

- (i) *for a fixed  $\mu > \mu_s$  and all  $i \in \mathbb{N}$ ,  $a_{i+1}f_{i+1}(\mu) \leq a_i f_i(\mu)$ .*
- (ii) *for a fixed  $i$ ,  $\frac{f_i(\mu)}{\mu} \leq \frac{f_i(\mu')}{\mu'}$  if  $\mu \leq \mu'$ . This implies that  $f_i(\mu) \leq f_i(\mu')$  if  $\mu \leq \mu'$ .*
- (iii)  *$f_i(\mu) \leq Q_i\mu^i \leq \frac{a_1}{a_i}\mu_s \left(\frac{\mu}{\mu_s}\right)^i \exp\left[-G\left(\frac{i^{1-\gamma} - 2^{1-\gamma}}{1-\gamma}\right)\right]$  for  $i \in \mathbb{N}$ .*
- (iv)  *$\lim_{\mu \rightarrow \mu_s} f_i(\mu) = Q_i\mu_s^i$  for all  $i \in \mathbb{N}$ .*

We point out that the exponential term in part (iii) differs from the one used by Penrose [46] and Kreer [30]. We have introduced the term  $2^{1-\gamma}$  instead of 1 which they used. This is because the argument used by Penrose to obtain the estimate before [46, Equation (9.3)], is not correct. It works only if the lower limit  $m$  of the integral there is replaced by  $m + 1$ , see (5.32). Thus the above change is necessary.

The original theory of metastability applies to the version of the kinetic equations with  $z_1$  constant and the situation where  $z_1 = \mu > \mu_s$ . Becker and Döring [5] solved for the *steady-state solutions* of this version where the fluxes  $J_i$  are independent of  $i$  but not zero. We denote the non-equilibrium steady-state solutions by  $\mathbf{f}(\mu) := (f_i(\mu))_{i \in \mathbb{N}}$ , given in Lemma 5.1.2. The common value of fluxes denoted by  $J(\mu)$  is called the *nucleation rate* and it gives the rate per unit volume at which clusters are acquiring new particles in the steady state. Becker and Döring showed that for moderately small values of supersaturations, say  $\delta := (\mu - \mu_s)/\mu_s$ , the nucleation rate  $J(\mu)$  can be very small. This makes it possible to think of the steady state as representing a metastable state in which large clusters are being formed extremely slowly. Penrose [46] went beyond the Becker-Döring steady state consideration and proved that, subject to some further conditions on the kinetic coefficients  $a_i$  and  $b_i$ , there is a class of time dependent *metastable solutions* of the equations with  $\delta = (\mu - \mu_s)/\mu_s$  positive and small which take an exponentially long time to decay to their asymptotic steady states. Kreer [30] later considered the standard constant free molecule model and extended the class of allowed initial conditions for the existence

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of metastable solutions. He proved existence of such solutions with lifetimes proportional to  $\exp(C\delta^{-\omega})$ , for some constants  $C, \omega > 0$ . With some additional assumptions on the kinetic coefficients, Kreer also constructed time scales for equilibration towards the metastable state, provided that the initial state contains an exponentially small mass of super-critical clusters. Duncan and Dunwell [18] showed that metastability for the truncated standard constant free molecule model can be explained in terms of the eigensystem of the resulting linear ordinary differential system. In particular they showed that there is an eigenvalue which is so small compared to the rest of the spectrum.

### 5.2 Metastability in the modified mass-conserving model

With careful choices of the relevant parameters we will show here that the metastability results by Penrose [46] also extend to the thermodynamically consistent models. Define  $\tilde{\mu}(t)$  by

$$\tilde{\mu}(t) := \frac{z_1(t)}{RN_D(\mathbf{z}(t))}. \quad (5.4)$$

Here the existence of metastable solutions depends on the initial value of the quantity  $\tilde{\mu}$  defined above. This is in contrast to the standard mass conserving model where metastability directly depends on the concentration of free molecules. We are interested in cases where a given mass cannot be contained in an equilibrium solution. This situation arises only if one has a negation of (4.76), that is the situation of a supersaturated system. We assume that the function  $\tilde{\mu}(t)$  defined in (5.4) satisfies  $\mu > \tilde{\mu}(0) > \mu_s = 1$ , where  $\mu$  is given in Lemma 5.1.2. This requirement means that the constant  $R$  defined in (4.9) must satisfy  $R < 1$ . Herrmann et al. [24] showed that in the Gallium Arsenide example which was introduced by Dreyer and Duderstadt [16], the parameter  $R$  is such that  $R > 1$ . This means that there is no metastability in this case.

Before we state the theorems on metastability, we introduce some important definitions.

#### Definition 5.2.1.

- (i) The critical cluster size  $i^*$  is the value of  $i$  that minimizes the quantity  $a_i Q_i \mu^i$ .
- (ii) The  $r^{\text{th}}$  moment  $M_r(t)$  of super-critical clusters at time  $t$  is defined as

$$M_r(t) := \sum_{i=i^*+1}^{\infty} i^r z_i(t) \quad r = 0, 1. \quad (5.5)$$

- (iii) Finally we introduce the constants  $\beta, t_0$  and  $J^*$  defined by

$$\beta := \frac{2 - \alpha}{1 - \alpha}, \quad t_0 := \frac{i^* + 1}{A}, \quad J^* := \Lambda a_{i^*} Q_{i^*} \mu^{i^*}. \quad (5.6)$$

**Lemma 5.2.2.** For a given  $\mu > \mu_s$  suppose that  $\mu \in [b_i/a_i, b_{i+1}/a_{i+1}]$ . Then  $i = i^*$ . In addition, the limit  $\mu \rightarrow \mu_s$  implies that  $i^* \rightarrow \infty$ .

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*Proof.* Definition 5.2.1 (i) obviously implies that

$$a_i^* Q_i^* \mu^{i^*} \leq a_{i^*-1} Q_{i^*-1} \mu^{i^*-1} \quad \text{and} \quad a_i^* Q_i^* \mu^{i^*} \leq a_{i^*+1} Q_{i^*+1} \mu^{i^*+1}.$$

Using these inequalities together with the first equation in (1.29) we obtain

$$\frac{b_{i^*}}{a_{i^*}} \geq \mu \geq \frac{b_{i^*+1}}{a_{i^*+1}}, \quad (5.7)$$

with the convention  $b_1 = \infty$  to take care of the case where  $\mu > b_2/a_2$ . The statement for the limit follows using Assumption 5.1.1 (iii).  $\square$

The following theorem is a modification of the result stated by Kreer [30, Lemma II] for the standard constant free molecule model. It gives the existence and uniqueness of solutions to (2.85) and (2.86). We will make a specific choice of  $\mu$  in (5.9) which is very useful in the proof of some bounds in Theorem 5.2.3.

**Theorem 5.2.3** (Existence and bounds). *Assume that  $M = \sup_{i \geq 1} (b_i - b_{i+1}) < \infty$ . Let  $z_0(0) = z_0 \geq 0$  and  $\rho(0) = z_0 + \sum_{i=1}^{\infty} i z_i(0)$  be the initial mass in the system. For  $\tilde{f}(\mu)$  and  $\tilde{g}(\mu)$  defined in (1.24) suppose that*

$$0 < \frac{\tilde{g}(\mu_s)}{1 - \tilde{f}(\mu_s)} < \infty \quad \text{and} \quad \rho_s = z_0 \left[ 1 + \frac{\tilde{g}(\mu_s)}{1 - \tilde{f}(\mu_s)} \right] < \rho(0) = \rho < \infty. \quad (5.8)$$

Define  $\Lambda := \max\{1, R\rho(0)\}$  and choose

$$\mu = \frac{\rho(0) - z_0}{R\rho(0)}. \quad (5.9)$$

For  $\tilde{\mu}$  in (5.4), suppose that the initial data in a solution of (2.85) and (2.86) satisfy  $\tilde{\mu}(0) > \mu_s = 1$  together with

$$0 \leq z_i(0) \leq \Lambda f_i(\mu), \quad \text{for all } i \geq 1, \quad \text{and that} \quad \sum_{i=1}^{\infty} i^2 z_i(0) < \infty, \quad (5.10)$$

where  $\mathbf{f}(\mu) = (f_i(\mu))_{i \in \mathbb{N}}$  is the steady-state sequence defined in Lemma 5.1.2. Then there exists a unique solution defined for all  $t \geq 0$ . It satisfies

$$\tilde{\mu}(t) \leq \mu, \quad (5.11)$$

$$0 \leq z_i(t) \leq \Lambda f_i(\mu) \quad \text{for all } i \geq 1, \quad (5.12)$$

$$M_0(t) \leq M_0(0) + J^* t, \quad (5.13)$$

$$M_1(t) \leq 2^{\beta-2} \left\{ M_1(0) + t_0 J^* + t_0 J^* \left( \frac{i^* + 1}{\beta} \right)^{\beta-1} \left( 1 + \frac{M_0(0)}{t_0 J^*} + \frac{t}{t_0} \right)^{\beta} \right\}. \quad (5.14)$$

where  $M_r(t)$ ,  $\beta$ ,  $t_0$  and  $J^*$  are given in Definition 5.2.1.



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We point out that in order to prove uniqueness of the solution of the standard model (1.2) - (1.7), Ball et al. [4] made a stronger assumption on the initial data viz  $\sum_{i=1}^{\infty} i^2 z_i(0) < \infty$ . Laurençot and Mischler [34] showed later that for uniqueness the condition can be relaxed to  $\sum_{i=1}^{\infty} i z_i(0) < \infty$  if the kinetic coefficients satisfy  $a_{i+1} - a_i \leq K$ , consequently  $a_i \leq i \cdot \max\{K, a_1\}$ , and  $b_i - b_{i+1} \leq K$  for some positive constant  $K$ . Therefore to guarantee the uniqueness of the solution it suffices to use the relaxed condition and to add the extra requirement  $b_i - b_{i+1} \leq K$  to Assumption 5.1.1. Although we can solve the uniqueness problem by making such extra requirements, the use of the strong assumption cannot be avoided. Penrose [46] used it to show that the series  $\sum_{i=1}^{\infty} J_i(\mathbf{z}(t))$  is convergent for all  $t \in [0, \infty[$  and also in the proof of the bounds (5.13) and (5.14).

We construct the solution of (2.85) and (2.86) by considering an auxiliary  $n$ -dimensional system obtained by truncating the infinite system at  $i = n$  and setting  $z_i = 0$  for all  $i > n$ . This technique was used by Penrose [46] to solve the standard Becker-Döring model. It leads to the following system of equations

$$\begin{aligned} \dot{z}_i^{(n)}(t) &= J_{i-1}(\mathbf{z}^{(n)}(t)) - J_i(\mathbf{z}^{(n)}(t)) \quad \text{for } 2 \leq i \leq n, \\ \dot{z}_1^{(n)}(t) &= -J_1(\mathbf{z}^{(n)}(t)) - \sum_{i=1}^n J_i(\mathbf{z}^{(n)}(t)), \\ \dot{z}_0^{(n)} &= 0. \end{aligned} \tag{5.15}$$

The fluxes are given in (2.86), with  $z_i = 0$  for all  $i > n$ . The following lemma gives the existence and uniqueness of solution for the finite system.

**Lemma 5.2.4.** *Define  $z_i^n(0) := z_i(0)$ , where  $z_i(0)$  fulfills the conditions in Theorem 5.2.3. Then there exists a unique solution  $\mathbf{z}^{(n)}$  of (5.15) defined for all  $t \geq 0$ . It satisfies*

$$z_i^{(n)}(t) \geq 0 \quad \text{for all } i \geq 1 \text{ and } t \in [0, \infty[ , \tag{5.16}$$

$$\frac{z_1^{(n)}(t)}{z_0 + \sum_{i=1}^n z_i^{(n)}(t)} \leq \mu R, \tag{5.17}$$

$$z_i^{(n)}(t) \leq \sum_{i=1}^n i z_i^{(n)}(t) \leq \rho(0) - z_0, \tag{5.18}$$

$$\frac{z_0 + \sum_{i=1}^n z_i^{(n)}(t)}{z_0 + z_1^{(n)}(t)} \leq \max \left\{ 1 + \frac{2}{\kappa}, \frac{\rho(0)}{z_0 + z_1(0)} \right\}, \tag{5.19}$$

$$\sum_{i=1}^n i^2 z_i^{(n)}(t) \leq \sigma \exp \left( \frac{2A\rho(0)}{z_0 + \rho(0)} t \right), \tag{5.20}$$

where  $\kappa := \min\{\mu_s, 1\}$ . In addition

$$\lim_{k \rightarrow \infty} z_i^{(n_k)} = z_i(t) \quad \text{for all } i \geq 1 \text{ and } t \in [0, \infty[ . \tag{5.21}$$

The results in (5.16), (5.18), (5.20), and (5.21) are analogous to those for the finite dimensional system studied by Penrose [46]. Inequality (5.17) is essential for the proof of (5.11), while (5.19)

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is useful for the proof of existence and uniqueness of solutions, in particular for  $z_0 = 0$ . It is intended to show that the quotient  $N_D(\mathbf{z}(t))/z_1(t)$ , which appears in the fluxes (2.86), is bounded for all  $t \geq 0$ . For  $z_0 > 0$ , one may or may not use (5.19) to prove the existence and uniqueness of solutions since the denominator on the left-hand side is bounded from below by  $z_0 > 0$ . In this case the term on the left-hand side is bounded from above by the quotient  $\rho(0)/z_0$ , which follows directly from (5.18) and the lower bound on  $z_0 + z_1(t)$ . For the proof of (5.19), the reader is referred to Section 4.2.1. There we proved the inequality for  $z_0 = 0$ . The case for  $z_0 > 0$  can be showed in a similar way. Therefore we prove only inequality (5.17) in the following way. The positivity of the solution implies that

$$\frac{z_1^{(n)}(t)}{z_0 + \sum_{i=1}^n z_i^{(n)}(t)} \leq \frac{z_1^{(n)}(t)}{z_0 + z_1^{(n)}(t)}.$$

Next we use (5.9) and (5.18) to obtain

$$\frac{z_1^{(n)}(t)}{z_0 + \sum_{i=1}^n z_i^{(n)}(t)} \leq \frac{\rho(0) - z_0}{\rho(0)} = \mu R.$$

We are now ready to prove Theorem 5.2.3.

*Proof.* (Theorem 5.2.3)

Apart from the inequality (5.11), all other parts of the theorem can be proved by following Penrose [46]. We include the proof in order to justify the choices  $\Lambda = \max\{1, R\rho(0)\}$  and  $\mu$  in (5.9). Additionally we want to demonstrate the need for inequality (5.11) and to derive the relevant changes introduced to the different bounds in the theorem.

The bound in (5.11) follows by taking the limit  $n \rightarrow \infty$  and using (5.21) together with the bounded convergence theorem.

To prove (5.12) the idea is to show that it holds for a system obtained by subtracting a term  $\varepsilon z_i(t)$  from the right-hand side of the differential equation for  $z_i$ ,  $i \geq 2$  in the  $n$ -dimensional system. For this system, positivity of solutions is guaranteed and hence the left-hand inequality in (5.12) is satisfied. Now for any integer  $n$ , let  $\mathbf{z}^{(n)}(t)$  be the solution of the modified equations. Suppose that the right-hand inequality is not true for some values of  $i$  and  $t$ . We shall show that this hypothesis leads to a contradiction.

Note that by (5.10) the right-hand side of (5.12) holds at  $t = 0$ . Let  $T > 0$  be the first time at which the inequality is violated, say for  $i = I$ . Then there exists a time  $T^+$ , with  $T^+ > T$ , such that

$$0 \leq z_i^{(n)}(T) \leq \Lambda f_i(\mu) \quad \text{for all } i \geq 1, \quad z_I^{(n)}(T) = \Lambda f_I(\mu), \quad (5.22)$$

and

$$z_I^{(n)}(t) > \Lambda f_I(\mu) \quad T < t < T^+.$$

This inequality means that

$$\dot{z}_I^{(n)}(T) \geq 0. \quad (5.23)$$

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In the remainder of the proof we show that this cannot be true. Suppose that  $I = 1$ , so that  $z_1(T) = \Lambda f_1(\mu) = \Lambda\mu$ . Then by omitting the superscript  $n$  for easy reading and using  $z_{n+1} = 0$ , from (2.86) and (5.15) we have

$$\dot{z}_1(T) = -a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + b_2 \frac{RN_D}{z_0 + \Lambda\mu} z_2(T) - a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + \sum_{i=2}^n \frac{(b_i RN_D - a_i \Lambda\mu)}{z_0 + \Lambda\mu} z_i(T).$$

Next we use (5.18) to get  $N_D \leq z_0 + \sum_{i=1}^n i z_i(t) \leq \rho(0)$ . Now since  $\Lambda = \max\{1, R\rho(0)\}$ , this implies that  $RN_D \leq \Lambda$  so that the above equation becomes

$$\dot{z}_1(T) \leq -a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + b_2 \frac{RN_D}{z_0 + \Lambda\mu} z_2(T) - a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + \sum_{i=2}^n \frac{(b_i - a_i \mu)}{z_0 + \Lambda\mu} \Lambda z_i(T).$$

By Assumption 5.1.1 (iii) and (5.7) the coefficients of  $z_i(T)$  are non-negative for  $i \leq i^*$  but negative for larger  $i$ . Define  $i^{**} := \min\{n, i^*\}$ . Then by using (5.22) and (5.22) we obtain

$$\begin{aligned} \dot{z}_1(T) &\leq -a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + b_2 \frac{\Lambda^2 f_2(\mu)}{z_0 + \Lambda\mu} - a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + \sum_{i=2}^{i^{**}} \frac{(b_i - a_i \mu)}{z_0 + \Lambda\mu} \Lambda^2 f_i(\mu), \\ &\leq -a_1 \frac{(\Lambda\mu)^2}{z_0 + \Lambda\mu} + b_2 \frac{\Lambda^2 f_2(\mu)}{z_0 + \Lambda\mu} - \sum_{i=1}^{i^{**}-1} \left( a_i \frac{\Lambda^2 \mu f_i(\mu)}{z_0 + \Lambda\mu} - b_{i+1} \frac{\Lambda^2 f_{i+1}(\mu)}{z_0 + \Lambda\mu} \right) - a_{i^{**}} \frac{\Lambda^2 \mu f_{i^{**}}(\mu)}{z_0 + \Lambda\mu}, \\ &= -i^{**} \frac{\Lambda^2}{z_0 + \Lambda\mu} J(\mu) - a_{i^{**}} \frac{\Lambda^2 \mu f_{i^{**}}(\mu)}{z_0 + \Lambda\mu}. \end{aligned}$$

Since  $J(\mu)$  and  $f_{i^{**}}(\mu)$  are both positive, we have a contradiction to (5.23). Now suppose that  $I > 1$ . Subtracting  $\varepsilon z_i(T)$  from (5.15) for  $I > 1$  and using (2.86) we have

$$\dot{z}_I(T) = a_{I-1} \frac{z_1(T)}{z_0 + z_1(T)} z_{I-1}(T) - \frac{b_I RN_D + a_I z_1(T)}{z_0 + z_1(T)} z_I(T) + \frac{b_{I+1} RN_D}{z_0 + z_1(T)} z_{I+1}(T) - \varepsilon z_I(T).$$

Using (5.22), and  $z_{I+1}(T) = 0$  if  $I = n$ , give

$$\dot{z}_I(T) \leq a_{I-1} \frac{z_1(T)}{z_0 + z_1(T)} \Lambda f_{I-1}(\mu) - \frac{b_I RN_D + a_I z_1(T)}{z_0 + z_1(T)} \Lambda f_I(\mu) + \frac{b_{I+1} RN_D}{z_0 + z_1(T)} \Lambda f_{I+1}(\mu) - \varepsilon \Lambda f_I(\mu).$$

Multiplying (5.1) by  $\Lambda RN_D / (z_0 + z_1(T))$  for  $i = I$  and subtracting the resulting expression for zero from the right-hand side of the above inequality, we get

$$\dot{z}_I(T) \leq \frac{\Lambda}{z_0 + z_1(T)} [z_1(T) - \mu RN_D] [a_{I-1} f_{I-1}(\mu) - a_I f_I(\mu)] - \varepsilon f_I(\mu).$$

By (5.17) the first quantity in square brackets on the right is non-positive, and by Lemma 5.1.2 (i) the second is non-negative. This also gives a contradiction to (5.23). The next step is to take the limit  $\varepsilon \rightarrow 0$  and then use the fact that the solutions of a differential equation depend continuously on parameters in the equation. Finally we take the limit  $n \rightarrow \infty$  for  $z_i^{(n)}$  for each  $i \in \mathbb{N}$  and use (5.21) to obtain the desired result (5.13).

To prove (5.13) we first note that (2.86), (5.20), and Assumption 5.1.1 (i) imply that

$$J_i^{(n)}(\mathbf{z}(t)) \leq \frac{A\sigma}{i^{2-\alpha}} \exp\left(\frac{2A\rho(0)}{z_0 + \rho(0)} t\right), \quad (5.24)$$

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while (2.86), (5.18), (5.20) and Assumption 5.1.1 (iv) give

$$J_i^{(n)}(\mathbf{z}(t)) \geq -\frac{AR\sigma\rho(0)}{z_0 i^{2-\alpha}} \mu_s \exp(G') \exp\left(\frac{2A\rho(0)}{z_0 + \rho(0)}t\right). \quad (5.25)$$

The two inequalities (5.24) and (5.25) lead to

$$|J_i^{(n)}(\mathbf{z}(t))| \leq \frac{K}{i^{2-\alpha}} \exp\left(\frac{2A\rho(0)}{z_0 + \rho(0)}t\right), \quad (5.26)$$

where  $K := A\sigma \max\{1, R\rho(0)\mu_s \exp(G')/z_0\}$ . In fact this inequality shows that due to  $\alpha < 1$  the series  $\sum_{i=1}^{\infty} |J_i^{(n)}(\mathbf{z}(t))|$  is convergent for all  $t \in [0, \infty[$ . Now we note from the fundamental theorem of calculus, the definition of  $M_0$  in (5.5) and (5.15) that

$$M_0(t) - M_0(0) = \lim_{n \rightarrow \infty} \sum_{i=i^*+1}^n \int_0^t (J_{i-1}(\mathbf{z}(s)) - J_i(\mathbf{z}(s))) ds = \lim_{n \rightarrow \infty} \int_0^t (J_{i^*}(\mathbf{z}(s)) - J_n(\mathbf{z}(s))) ds.$$

Due to the bound in (5.26) we have  $\lim_{n \rightarrow \infty} J_n(\mathbf{z}(s)) = 0$  so that we obtain

$$M_0(t) - M_0(0) = \int_0^t J_{i^*}(\mathbf{z}(s)) ds.$$

We use (2.86), (5.12), Lemma 5.1.2 (iii) and (5.6)<sub>3</sub> to obtain

$$J_{i^*}(\mathbf{z}(s)) \leq \Lambda a_{i^*}^* f_{i^*}(\mu) \leq \Lambda a_{i^*}^* Q_{i^*} \mu^{i^*} = J^*, \quad (5.27)$$

and then evaluate the integral to get (5.13).

Analogously it is easy to see, by using (2.85), (5.5), and the bound in (5.26) that

$$\begin{aligned} M_1(t) - M_1(0) &= \lim_{n \rightarrow \infty} \sum_{i=i^*+1}^n \int_0^t \left[ (i^* + 1)J_{i^*}(\mathbf{z}(s)) + \sum_{i=i^*+1}^{n-1} J_i(\mathbf{z}(s)) - nJ_n(\mathbf{z}(s)) \right] ds, \\ &= \int_0^t \left[ (i^* + 1)J_{i^*}(\mathbf{z}(s)) + \sum_{i=i^*+1}^{\infty} J_i(\mathbf{z}(s)) \right] ds. \end{aligned}$$

The series on the right-hand side is a uniformly convergent sum of continuous functions and therefore a continuous function. Differentiating both sides and using (2.86), (5.27) and Assumption 5.1.1 (i) give

$$\begin{aligned} \dot{M}_1(t) &\leq (i^* + 1)J^* + \sum_{i=i^*+1}^{\infty} a_i z_i(t), \\ &\leq (i^* + 1)J^* + A \sum_{i=i^*+1}^{\infty} i^\alpha z_i(t). \end{aligned}$$

We then apply Hölder's inequality to obtain

$$\dot{M}_1(t) \leq (i^* + 1)J^* + AM_0^{1-\alpha}(t)M_1^\alpha(t).$$

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To solve the differential inequality we introduce the following scaled variables using  $t_0$  defined in (5.6)

$$\nu_r(t) := \frac{M_r(t)}{t_0 J^*}, \quad r = 0, 1 \quad \text{and} \quad \tau := t/t_0. \quad (5.28)$$

In the new variables the inequality becomes

$$\frac{d\nu_1}{d\tau} \leq (i^* + 1)(1 + \nu_0^{1-\alpha}(\tau)\nu_1^\alpha(\tau)).$$

We again use the Hölder's inequality to get

$$\frac{d\nu_1}{d\tau} \leq (i^* + 1)(1 + \nu_0(\tau))^{1-\alpha}(1 + \nu_1(\tau))^\alpha,$$

which is equivalent to

$$\frac{d}{d\tau}(1 + \nu_1(\tau))^{1-\alpha} \leq (i^* + 1)(1 - \alpha)(1 + \nu_0(\tau))^{1-\alpha}$$

and hence

$$(1 + \nu_1(\tau))^{1-\alpha} \leq (1 + \nu_1(0))^{1-\alpha} + (i^* + 1)(1 - \alpha) \int_0^\tau (1 + \nu_0(s))^{1-\alpha} ds.$$

Rewriting (5.13) in the present notation gives  $\nu_0(t) \leq \nu_0(0) + \tau$ . Substituting this into the above integral and evaluating the result, we get

$$(1 + \nu_1(\tau))^{1-\alpha} \leq (1 + \nu_1(0))^{1-\alpha} + \frac{(i^* + 1)}{\beta} ((1 + \nu_0(0) + \tau)^{2-\alpha} - (1 + \nu_0(0))^{2-\alpha}),$$

where  $\beta$  is as defined in (5.6). Next we omit the negative term on the right-hand side and then use Hölder's inequality to obtain

$$(1 + \nu_1(\tau))^{1-\alpha} \leq 2^\alpha \left[ 1 + \nu_1(0) + \left( \frac{(i^* + 1)}{\beta} \right)^{1/(1-\alpha)} (1 + \nu_0(0) + \tau)^\beta \right]^{1-\alpha}.$$

This implies that

$$\nu_1(\tau) \leq 2^{\alpha/(1-\alpha)} \left[ 1 + \nu_1(0) + \left( \frac{(i^* + 1)}{\beta} \right)^{1/(1-\alpha)} (1 + \nu_0(0) + \tau)^\beta \right].$$

Finally we use (5.28) to write the inequality in the original variables. This gives the required expression (5.14) and ends the proof of Theorem 5.2.3.  $\square$

We recall the following terminology used by Penrose [46]. For any quantity  $q(\mu)$  depending on  $\mu$ , we say that

- (i)  $q(\mu)$  is exponentially small if for all  $m > 0$  the quotient  $q(\mu)/(\mu - \mu_s)^m$  is bounded as  $\mu \rightarrow \mu_s$ .
- (ii)  $q(\mu)$  is at most algebraically large if for some  $m > 0$  the product  $q(\mu)(\mu - \mu_s)^m$  is bounded as  $\mu \rightarrow \mu_s$ .

## CHAPTER 5. METASTABILITY

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The next theorem contains bounds on the quantities  $i^*$  and  $J^*$  in Theorem 5.2.3. It is intended to show that the number  $M_0(t)$  and mass  $M_1(t)$  of super-critical clusters are exponentially small if the time  $t$  is at most algebraically large.

**Theorem 5.2.5.** *Define  $\delta := (\mu - \mu_s)/\mu_s > 0$ . There exists a constant  $\delta_0 > 0$  such that the following is true*

(i)  $i^*$  is at most algebraically large as  $\delta \rightarrow 0+$ , that is, for  $\delta \in ]0, \delta_0[$  we have

$$0 < i^* < \left( \frac{1}{2G'\delta} \right)^{-1/\gamma'}, \quad (5.29)$$

see Assumption 5.1.1 (iv).

(ii) For  $\Lambda \geq 1$  fixed,  $J^*$  is exponentially small as  $\delta \rightarrow 0+$ , that is, for  $\delta \in ]0, \delta_0[$  the following bound holds

$$0 < J^* < \Lambda a_1 \mu_s \exp \left\{ \frac{G(2^{4-\gamma} + \gamma - \gamma^2)}{8(1-\gamma)} - \frac{\gamma}{1-\gamma} G^{1/\gamma} \left( \frac{1}{\delta} \right)^{(1/\gamma)-1} \right\}. \quad (5.30)$$

Moreover  $J(\mu)$  is also exponentially small since  $J(\mu) \leq J^*$ .

The proof of this theorem is constructed in a similar way to that by Penrose [46]. We pay attention to the parameter  $\Lambda$  and the term  $2^{4-\gamma}$  introduced on the right-hand side of (5.30). These are the only changes to results by Penrose.

*Proof.* To prove part (i) we use Assumption 5.1.1 (iv) and (5.7) to get

$$\mu \leq \frac{b_{i^*}}{a_{i^*}} < \mu_s \exp(G' i^{*\gamma'}).$$

This implies that  $i^* < [G'^{-1} \ln(\mu/\mu_s)]^{-1/\gamma'}$ . By using the mean value theorem, there exists a constant  $\mu' \in ]\mu_s, \mu[$  such that

$$\ln(\mu/\mu_s) = (\mu - \mu_s)/\mu' = \delta\mu_s/\mu' > \delta\mu_s/\mu. \quad (5.31)$$

For  $\delta_0 < 1$  we have  $2\mu_s > \mu$  giving

$$\ln(\mu/\mu_s) > \delta/2.$$

Using this we finally obtain the right inequality in (5.29). The left inequality is trivial.

Next we prove part (ii) of the theorem. The left-hand inequality of (5.30) is clear from the definition of  $J^*$  in (5.6). We note that for any two integers  $m$  and  $n$  satisfying  $1 \leq m < n$ , we have by (1.8)

$$\frac{Q_n}{Q_m} = \left( \frac{a_m}{a_n} \right) \prod_{r=m+1}^n \left( \frac{a_r}{b_r} \right).$$

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Then by using the first inequality in Assumption 5.1.1 (iv) we get,

$$\begin{aligned}
\frac{Q_n}{Q_m} &\leq \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ - \sum_{r=m+1}^n Gr^{-\gamma} \right] \\
&\leq \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ - \int_{m+1}^n Gr^{-\gamma} dr \right] \\
&= \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ -G \left( \frac{n^{1-\gamma} - (m+1)^{1-\gamma}}{1-\gamma} \right) \right].
\end{aligned} \tag{5.32}$$

Next we set  $m = 1$ ,  $n = i$  and use  $Q_1 = 1$  to obtain

$$Q_i \mu^i \leq \frac{a_1}{a_i} \mu_s \left( \frac{\mu}{\mu_s} \right)^i \exp \left[ -G \left( \frac{i^{1-\gamma} - 2^{1-\gamma}}{1-\gamma} \right) \right],$$

which implies that

$$a_i Q_i \mu^i \leq a_1 \mu_s \exp \left[ i \ln \left( \frac{\mu}{\mu_s} \right) - G \left( \frac{i^{1-\gamma} - 2^{1-\gamma}}{1-\gamma} \right) \right]. \tag{5.33}$$

The minimum value of the right-hand side, achieved when  $i = [G/\ln(\mu/\mu_s)]^{1/\gamma}$ , is

$$a_1 \mu_s \exp \left[ \frac{2^{1-\gamma} G}{1-\gamma} - \frac{\gamma}{1-\gamma} G^{1/\gamma} \left[ \ln \left( \frac{\mu}{\mu_s} \right) \right]^{-(1-\gamma)/\gamma} \right]. \tag{5.34}$$

Since we are considering the limit  $\mu \rightarrow \mu_s$ , we may take  $\mu$  close enough to  $\mu_s$  to ensure that  $[G/\ln(\mu/\mu_s)]^{1/\gamma} \geq 3/2$ . Then the second derivative  $G\gamma i^{-\gamma-1}$  of the exponent is bounded from above by  $G\gamma$  for all  $i$  in the interval defined by

$$[G/\ln(\mu/\mu_s)]^{1/\gamma} - 1/2 \leq i \leq [G/\ln(\mu/\mu_s)]^{1/\gamma} + 1/2,$$

and so by Taylor's expansion with the second derivative as the remainder term, the exponent itself exceeds its minimum value by at most  $\frac{1}{2}G\gamma(\frac{1}{2})^2$  for all  $i$  in this interval. There is an integer value of  $\hat{i}$  within this interval for which (5.34) makes the right-hand side of (5.33) maximal giving

$$a_{\hat{i}} Q_{\hat{i}} \mu^{\hat{i}} \leq a_1 \mu_s \exp \left[ \frac{2^{1-\gamma} G}{1-\gamma} - \frac{\gamma}{1-\gamma} G^{1/\gamma} \left[ \ln \left( \frac{\mu}{\mu_s} \right) \right]^{-(1-\gamma)/\gamma} + \frac{1}{2} G\gamma \left( \frac{1}{2} \right)^2 \right]. \tag{5.35}$$

Since also  $a_{i^*} Q_{i^*} \mu^{i^*} \leq a_i Q_i \mu^i$  for all  $i \in \mathbb{N}$ , this inequality leads to

$$J^* = \Lambda a_{i^*} Q_{i^*} \mu^{i^*} \leq \Lambda a_1 \mu_s \exp \left[ \frac{2^{1-\gamma} G}{1-\gamma} - \frac{\gamma}{1-\gamma} G^{1/\gamma} \left[ \ln \left( \frac{\mu}{\mu_s} \right) \right]^{-(1-\gamma)/\gamma} + \frac{G\gamma}{8} \right].$$

Finally we use (5.31) and  $\mu > \mu_s$  to obtain

$$J^* \leq \Lambda a_1 \mu_s \exp \left[ \frac{G(2^{4-\gamma} + \gamma - \gamma^2)}{8(1-\gamma)} - \frac{\gamma}{1-\gamma} G^{1/\gamma} \left( \frac{1}{\delta} \right)^{\frac{1}{\gamma}-1} \right],$$

which is the required expression (5.30). □

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It is important to note here that we have proved two of the metastability conditions stated in Section 5.1. Following the custom of identifying the sub-critical clusters,  $i \leq i^*$ , with the old phase and the super-critical ones,  $i > i^*$ , with the new phase, the results in Theorems 5.2.7 and 5.2.5 show that if  $t$  is at most algebraically large then the number of super-critical clusters is exponentially small. Within this time the system is said to be in a metastable phase where only the initial phase is present. We introduce the lifetime  $t_M$  of the metastable phase as the time after which the right-hand side of (5.13) is  $O(1)$ . Using (5.13) and (5.30) give

$$t_M \approx \frac{1}{J^*} > \frac{1}{\Lambda a_1 \mu_s} \exp \left\{ \frac{-G(2^{4-\gamma} + \gamma - \gamma^2)}{8(1-\gamma)} + \frac{\gamma}{1-\gamma} G^{1/\gamma} \left( \frac{1}{\delta} \right)^{(1/\gamma)-1} \right\}, \quad (5.36)$$

which is a large quantity in the limit  $\delta \rightarrow 0$ .

**Remark 5.2.6.** For any given mass  $\rho > 0$  the structure of the fluxes in (2.87) allows for a scaling of the model (1.2) so that the resulting system has a unit mass. In this case we interpret  $z_i(t)$  as the number of clusters of size  $i$  per unit mass at time  $t$ . We recall from the introductory paragraph of Section 5.2 that we require that  $R < 1$ . Now coupling these results we obtain  $\Lambda = \max\{1, R\rho(0)\} = 1$  for the scaled system.

This remark shows that all the results of Theorems 5.2.3 and 5.2.5 hold with  $\Lambda = 1$ . The following theorem is intended to show the last of the three conditions in Section 5.1 which characterize the metastable state.

**Theorem 5.2.7.** For  $\Lambda = 1$ , let the requirements of Theorem 5.2.3 be fulfilled. Again let  $\mathbf{f}(\mu) = (f_i(\mu))_{i \in \mathbb{N}}$  be the steady-state sequence. With  $z_0 \geq 0$  consider any initial data for which

$$0 = M_1(0) \quad \text{and} \quad 0 \leq [f_i(\mu) - z_i(0)], \quad 1 \leq i \leq i^*$$

are exponentially small at  $\mu_s$ . Then the unique solution for the modified model (1.2) and (2.87) has an exponentially long lifetime in the sense that for each fixed  $i$  the following two results hold in the limit  $\mu \rightarrow \mu_s$ , which implies  $i^* \rightarrow \infty$ :

(i) If  $t$  is at most algebraically large, then  $[f_i(\mu) - z_i(t)]$  is exponentially small.

(ii)  $\lim_{t \rightarrow \infty} [f_i(\mu) - z_i(t)]$  is not exponentially small.

The statement of the theorem is similar to that by Penrose [46]. The difference lies only in the choice of initial conditions. Here we allow for an exponentially small deviation of the initial distribution of sub-critical clusters from those of the steady-state distribution  $\mathbf{f}(\mu)$ . Penrose used initial conditions for which this deviation is equal to zero. The proof of the theorem follows the idea of Penrose [46].

*Proof.* We use (5.5) and the mass conservation property for the modified model as well as the assumption  $M_1(0) = 0$  to obtain

$$\sum_{i=1}^{i^*} i[z_i(0) - z_i(t)] = M_1(t) - M_1(0) = M_1(t). \quad (5.37)$$

We recall from Lemma 5.2.2 that  $\mu \rightarrow \mu_s$  implies that  $i^* \rightarrow \infty$ . Therefore in the limit  $\mu \rightarrow \mu_s$ , for any given fixed value of  $i$  the summation on the left-hand side will eventually include a term



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$i[z_i(0) - z_i(t)]$ . We add and subtract the term  $\sum_{i=1}^{i^*} i f_i(\mu)$  in the left-hand side of (5.37) to obtain

$$\sum_{i=1}^{i^*} i[f_i(\mu) - z_i(t)] = \sum_{i=1}^{i^*} i[f_i(\mu) - z_i(0)] + M_1(t).$$

Our restriction on the initial data allows us to write

$$\begin{aligned} \sum_{i=1}^{i^*} i[f_i(\mu) - z_i(t)] &\leq i^* \sum_{i=1}^{i^*} [f_i(\mu) - z_i(0)] + M_1(t), \\ &\leq i^{*2} \max_{1 \leq i \leq i^*} [f_i(\mu) - z_i(0)] + M_1(t). \end{aligned} \quad (5.38)$$

The inequality (5.12) for  $\Lambda = 1$  shows that the left-hand side of the above inequality consists of non-negative terms for each  $i$ . We can therefore write

$$[f_i(\mu) - z_i(t)] \leq \sum_{i=1}^{i^*} i[f_i(\mu) - z_i(t)] \leq i^{*2} \max_{1 \leq i \leq i^*} [f_i(\mu) - z_i(0)] + M_1(t). \quad (5.39)$$

We recall that the bound (5.14) together with Theorem 5.2.5 imply that  $M_1(t)$  is exponentially small if  $t$  is at most algebraically large. Similarly we proved in Theorem 5.2.5 that  $i^*$  is an at most algebraically large quantity. Thus all the terms on the right-hand side of (5.39) are exponentially small if  $t$  is at most algebraically large. This ends the proof of part (i).

To prove part (ii) we note that it is possible to use the results by Ball et al. [4, Chapter 5] and Herrmann et al. [24, Chapter 4] to show that

$$\lim_{t \rightarrow \infty} z_i(t) = R \bar{N}_D Q_i \mu_s^i \quad \text{where} \quad \bar{N}_D = \frac{\bar{\rho}_s - z_0}{\tilde{g}(\mu_s)} \quad \text{and} \quad \bar{\rho}_s = z_0 \left( 1 + \frac{\tilde{g}(\mu_s)}{1 - \tilde{f}(\mu_s)} \right). \quad (5.40)$$

Clearly for  $z_0 = 0$  this gives the result

$$\lim_{t \rightarrow \infty} z_i(t) = 0,$$

which was proved by Herrmann et al. [24, Theorem 17, (NEQ)]. We note from (1.24) that  $\tilde{f}(\mu_s) < \tilde{g}(\mu_s)$ . Now using this condition and (5.40) we observe that

$$\bar{N}_D = \frac{z_0}{1 - \tilde{f}(\mu_s)} = \frac{z_0[1 - \tilde{f}(\mu_s) + \tilde{f}(\mu_s)]}{1 - \tilde{f}(\mu_s)} < \frac{z_0[1 - \tilde{f}(\mu_s) + \tilde{g}(\mu_s)]}{1 - \tilde{f}(\mu_s)} = \bar{\rho}_s.$$

This result as well as the requirement  $\rho_s < \rho$  in (5.8) imply that for  $i \leq i^*$  we have

$$\begin{aligned} \lim_{t \rightarrow \infty} [f_i(\mu) - z_i(t)] &= f_i(\mu) - R \bar{N}_D Q_i \mu_s^i, \\ &> \frac{f_i(\mu)}{\mu} \mu - R \rho Q_i \mu_s^i. \end{aligned}$$

Next we use Lemma 5.1.2 (ii) and (iv) as well as  $R\rho \leq \Lambda = 1$  to obtain for  $i \leq i^*$

$$\lim_{t \rightarrow \infty} [f_i(\mu) - z_i(t)] > \frac{Q_i \mu_s^i}{\mu_s} \mu - Q_i \mu_s^i = \frac{\mu - \mu_s}{\mu_s} Q_i \mu_s^i, \quad (5.41)$$

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which is positive and  $O(\mu - \mu_s)$ . The latter is not exponentially small. For any fixed  $i$ , one can always achieve the bound  $i \leq i^*$  by choosing  $\mu$  close enough to  $\mu_s$  so that (5.41) holds. This ends the proof of the theorem.  $\square$

The result in Theorem 5.2.7 (ii) as well as inequality (5.38) together with the exponentially small quantities  $f_i(\mu) - z_i(0)$  and  $M_1(0)$  imply that in the limit  $t \rightarrow \infty$  the mass  $M_1(t)$  of super-critical clusters is not exponentially small.

**Remark 5.2.8.** *Herrmann et al. [24] proved that for  $z_0 = 0$  the solution converges weak\* to  $\mathbf{0}$  in the limit  $t \rightarrow \infty$  and all the mass is transferred to larger and larger clusters. In this case we can prove that*

$$\lim_{t \rightarrow \infty} [f_i(\mu) - z_i(t)] \geq \frac{Q_i \mu_s^i}{\mu_s} \mu = \left( \frac{\mu - \mu_s}{\mu_s} + 1 \right) Q_i \mu_s^i, \quad i \leq i^*,$$

*which is not exponentially small.*

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## Chapter 6

# Numerical approximation

In this Chapter we compute numerically the time dependent cluster distribution  $\mathbf{z}(t)$  for finite systems. We point out that due to the large range of parameter values involved in the nucleation problem, care must be taken in order to decide which numerical method is to be used. This problem falls into the class of *stiff* differential systems. For such problems certain implicit methods, in particular BDF, perform better than explicit ones. See Dekker and Verwer [14], Hairer and Wanner [22] as well as Shampine [53] for detailed information on stiff problems. For general numerical methods for ordinary differential equations, one can also see Butcher [8], Shampine et al. [55], Lambert [32] as well as Deuffhard and Bornemann [15].

Carr et al. [9] described an efficient numerical algorithm for solving the standard mass-conserving Becker-Döring model. They reported that higher order stiff solvers do not correctly reproduce the positivity property of the solutions to the model. They observed from their numerical simulations that for small supersaturations, one requires a very large system for the solution to exhibit metastability. Therefore, they exploited the special structure of the equations to speed up the linear algebra required by implicit solvers for the problem. In particular the Jacobian matrix for the system of equations has a tridiagonal arrow head form. However, in the thermodynamically consistent models we cannot obtain such a structure of the Jacobian matrix in a straight forward way. This is because of the presence of the term  $N_D(\mathbf{z}(t))$  in the fluxes, thereby leading to a dense Jacobian matrix. We obtain an efficient algorithm by applying the transformation  $F_i(t) = \sum_{j=i}^n z_j(t)$  which was introduced by Laurençot and Mischler [34]. We have already used it in Section 4.3 to prove the uniqueness of solutions.

### 6.1 Efficient numerical approximation

We consider finite systems of the modified mass-conserving model, which we studied in Chapter 3. There we discussed the zero flux and the zero particle number truncations. These respectively led to equations (3.30) and (3.41).

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### 6.1.1 The zero flux truncation

Here we set  $J_n = 0$  and  $z_i = 0$  for all  $i \geq n$ . For  $F_i(t) = \sum_{j=i}^n z_j(t)$  we use equation (3.30) to get

$$\dot{F}_i(t) = J_{i-1}(\mathbf{F}(t)), \quad i \geq 2, \quad (6.1)$$

$$\dot{F}_0(t) = \dot{F}_1(t) = - \sum_{i=1}^{n-1} J_i(\mathbf{F}(t)), \quad (6.2)$$

where the fluxes are now given by

$$J_i(\mathbf{F}(t)) = a_i \left( F_i(t) - F_{i+1}(t) \right) \frac{F_1(t) - F_2(t)}{F_0(t) - F_2(t)} - \frac{b_{i+1} R F_0(t)}{F_0(t) - F_2(t)} \left( F_{i+1}(t) - F_{i+2}(t) \right). \quad (6.3)$$

This truncation implies that  $F_i = 0$  for all  $i > n$ . We note that the conservation of mass is equivalent to the conservation of the quantity  $z_0 + \sum_{i=1}^n F_i(t)$ , see Remark 4.3.3. Thus the model (4.54) - (4.56) can be written as a differential algebraic system of equations (DAE) in the following way

$$\begin{aligned} z_0(t) &= z_0, \\ 0 &= (\rho - z_0) - \sum_{i=1}^n F_i(t), \\ \dot{F}_i(t) &= J_{i-1}(\mathbf{F}(t)), \quad \text{for } 2 \leq i \leq n. \end{aligned} \quad (6.4)$$

We introduce the vectors

$$\dot{\mathbf{F}}_i(t) := \begin{pmatrix} \dot{F}_1(t) \\ \dot{F}_2(t) \\ \vdots \\ \dot{F}_n(t) \end{pmatrix}, \quad \mathbf{G}(\mathbf{F}) := \begin{pmatrix} (\rho - z_0) - \sum_{i=1}^n F_i(t) \\ J_1(\mathbf{F}(t)) \\ \vdots \\ J_{i-1}(\mathbf{F}(t)) \\ \vdots \\ J_{n-1}(\mathbf{F}(t)) \end{pmatrix}, \quad (6.5)$$

and the  $n$  by  $n$  singular matrix

$$\mathbf{M} = \begin{pmatrix} 0 & 0 & & \dots & & & 0 \\ 0 & 1 & 0 & & & & \\ & 0 & 1 & 0 & & & \\ \vdots & & & \ddots & & & \vdots \\ & & & & 0 & 1 & 0 \\ & & & & 0 & 1 & 0 \\ 0 & & & \dots & & 0 & 1 \end{pmatrix}.$$

Then (6.4) is equivalent to

$$\mathbf{M} \dot{\mathbf{F}}_i(t) = \mathbf{G}(\mathbf{F}). \quad (6.6)$$

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## 6.1. EFFICIENT NUMERICAL APPROXIMATION

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Below we report results obtained by using the Matlab ode15s solver for this system, see Shampine and Reichelt [56] as well as Shampine et al. [54]. At each time step, the solver makes use of the Jacobian of the vector  $\mathbf{G}(\mathbf{F})$ . If not specified, the solver approximates the Jacobian by using finite differences. By providing the exact Jacobian matrix, the accuracy of our computations is improved and since it has a sparse structure, the code is even faster. The Jacobian matrix for the system (6.6) is a tridiagonal arrow head matrix of the form

$$\frac{\partial \mathbf{G}(\mathbf{F})}{\partial \mathbf{F}} = \begin{pmatrix} \cdot & \cdot & \text{---} & & & \\ \cdot & \cdot & \text{---} & & & \\ \vdots & \vdots & \text{---} & & & \\ \vdots & \vdots & \text{---} & \diagdown & & \\ \vdots & \vdots & \text{---} & \diagdown & \diagdown & \\ \vdots & \vdots & \text{---} & \diagdown & \diagdown & \diagdown \end{pmatrix},$$

where the entries at the positions of the dots and along the lines are to be specified. To do this, we introduce various vectors and matrices. Define  $m := 1/(z_0 + F_1 - F_2)$  and let

$$\begin{aligned} v &:= m^2 [a_1(1/m^2 - z_0^2) - b_2R(F_2 - F_3)(z_0 - F_2)], \\ w &:= m^2 [-a_1(1/m^2 - z_0^2) - b_2R(z_0 + F_1)(z_0 + F_1 - F_3)]. \end{aligned}$$

We introduce the  $(n - 2) \times 1$  vectors  $\mathbf{d}$ ,  $\mathbf{e}$  and  $\mathbf{f}$  as

$$\mathbf{d} := mb_2R(z_0 + F_1) \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix},$$

$$\mathbf{e} := m^2 \begin{pmatrix} a_2z_0(F_2 - F_3) - b_3R(F_3 - F_4)(z_0 - F_2) \\ \vdots \\ a_{i-1}z_0(F_{i-1} - F_i) - b_iR(F_i - F_{i+1})(z_0 - F_2) \\ \vdots \\ a_{n-1}z_0(F_{n-1} - F_n) - b_nRF_n(z_0 - F_2) \end{pmatrix},$$

and

$$\mathbf{f} := m^2 \begin{pmatrix} a_2(1/m - z_0)1/m - z_0(F_2 - F_3) - b_3R(z_0 + F_1)(F_3 - F_4) \\ -z_0a_3(F_3 - F_4) - b_4R(z_0 + F_1)(F_4 - F_5) \\ \vdots \\ -z_0a_{i-1}(F_{i-1} - F_i) - b_iR(z_0 + F_1)(F_i - F_{i+1}) \\ \vdots \\ -z_0a_{n-1}(F_{n-1} - F_n) - b_nR(z_0 + F_1)F_n \end{pmatrix}.$$

Lastly, we define the components  $p_1, p_2, \dots, p_{n-2}$  by

$$p_i := a_{i+1} + b_{i+2}R \frac{z_0 + F_1}{F_1 - F_2} = a_{i+1} + b_{i+2}R m \frac{z_0 + F_1}{1 - mz_0},$$

## CHAPTER 6. NUMERICAL APPROXIMATION

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and define an  $(n - 2) \times (n - 2)$  matrix  $\mathbb{T}$  by

$$\mathbb{T} := (1 - mz_0) \begin{pmatrix} -p_1 & (p_1 - a_2) & 0 & \dots & 0 \\ a_3 & -p_2 & (p_2 - a_3) & 0 & 0 \\ 0 & a_4 & -p_3 & (p_3 - a_4) & 0 \\ \vdots & & & & \vdots \\ 0 & & & & 0 \\ 0 & & \dots & a_{n-2} & -p_{n-3} & (p_{n-3} - a_{n-2}) \\ & & & 0 & a_{n-1} & -p_{n-2} \end{pmatrix}.$$

With the above information, the Jacobian matrix is therefore given as

$$\frac{\partial \mathbf{G}(\mathbf{F})}{\partial \mathbf{F}} = \begin{pmatrix} 1 & 1 & \mathbf{u}^T \\ v & w & \mathbf{d}^T \\ \mathbf{e} & \mathbf{f} & \mathbb{T} \end{pmatrix}. \quad (6.7)$$

### 6.1.2 The zero particle number truncation

Here we set  $z_i = 0$  for all  $i \geq n$ . Again we use the transformation  $F_i = \sum_{j=i}^n z_j(t)$  into (3.41). This leads to the following differential algebraic system

$$\begin{aligned} z_0(t) &= z_0, \\ \sum_{i=1}^n F_i(t) &= (\rho - z_0), \\ \dot{F}_i(t) &= J_{i-1}(\mathbf{F}(t)) - J_n(\mathbf{F}(t)), \quad \text{for } 2 \leq i \leq n. \end{aligned} \quad (6.8)$$

We now have an extra non-zero flux  $J_n$  appearing on the right-hand side. For the zero particle number truncation, the vector  $\mathbf{G}$  in (6.5) changes to

$$\mathbf{G}(\mathbf{F}) := \begin{pmatrix} (\rho - z_0) - \sum_{i=1}^n F_i(t) \\ J_1(\mathbf{F}(t)) - J_n(\mathbf{F}(t)) \\ \vdots \\ J_{i-1}(\mathbf{F}(t)) - J_n(\mathbf{F}(t)) \\ \vdots \\ J_{n-1}(\mathbf{F}(t)) - J_n(\mathbf{F}(t)) \end{pmatrix}.$$

With  $J_n(\mathbf{F}(t)) = a_n F_n(t)(F_1(t) - F_2(t))/(z_0 + F_1(t) - F_2(t))$  we have to modify the first, second and  $n$ th column of the Jacobian matrix  $\partial \mathbf{G}(\mathbf{F})/\partial \mathbf{F}$  defined in (6.7). In this case we have additional terms involving  $a_n$  in all the following quantities

$$\begin{aligned} v &= m^2 [a_1(1/m^2 - z_0^2) - b_2 R(F_2 - F_3)(z_0 - F_2) - a_n z_0 F_n], \\ w &= m^2 [-a_1(1/m^2 - z_0^2) - b_2 R(z_0 + F_1)(z_0 + F_1 - F_3) + a_n z_0 F_n]. \end{aligned}$$

The  $(n - 2) \times 1$  vectors  $\mathbf{d}$ ,  $\mathbf{e}$  and  $\mathbf{f}$  are now given by

$$\mathbf{d} = \begin{pmatrix} mb_2R(z_0 + F_1) \\ 0 \\ \vdots \\ 0 \\ -a_n(1 - z_0m) \end{pmatrix},$$

$$\mathbf{e} = m^2 \begin{pmatrix} a_2z_0(F_2 - F_3) - b_3R(F_3 - F_4)(z_0 - F_2) - a_nz_0F_n \\ \vdots \\ a_{i-1}z_0(F_{i-1} - F_i) - b_iR(F_i - F_{i+1})(z_0 - F_2) - a_nz_0F_n \\ \vdots \\ a_{n-1}z_0(F_{n-1} - F_n) - b_nRF_n(z_0 - F_2) - a_nz_0F_n \end{pmatrix},$$

and

$$\mathbf{f} = m^2 \begin{pmatrix} a_2(1/m - z_0)1/m - z_0(F_2 - F_3) - b_3R(z_0 + F_1)(F_3 - F_4) + a_nz_0F_n \\ -z_0a_3(F_3 - F_4) - b_4R(z_0 + F_1)(F_4 - F_5) + a_nz_0F_n \\ \vdots \\ -z_0a_{i-1}(F_{i-1} - F_i) - b_iR(z_0 + F_1)(F_i - F_{i+1}) + a_nz_0F_n \\ \vdots \\ -z_0a_{n-1}(F_{n-1} - F_n) - b_nR(z_0 + F_1)F_n + a_nz_0F_n \end{pmatrix}.$$

Lastly, the  $(n - 2) \times (n - 2)$  matrix  $\mathbb{T}$  now becomes

$$\mathbb{T} = (1 - mz_0) \begin{pmatrix} -p_1 & (p_1 - a_2) & 0 & \dots & & -a_n \\ a_3 & -p_2 & (p_2 - a_3) & 0 & & -a_n \\ 0 & a_4 & -p_3 & (p_3 - a_4) & 0 & -a_n \\ \vdots & & & & & \vdots \\ & & & & & -a_n \\ 0 & & & & a_{n-2} & -p_{n-3} & (p_{n-3} - a_{n-2} - a_n) \\ 0 & & \dots & & 0 & a_{n-1} & -p_{n-2} - a_n \end{pmatrix}.$$

Note that we do not have the tridiagonal arrow head structure any more but the matrix is still sparse.

## 6.2 Numerical example

We use the following parameters

$$a_i = \xi i^\alpha, \quad \tilde{q}_1 = R, \quad \tilde{q}_i = \exp(-\tilde{a} i^{2/3}) \quad \text{for } 2 \leq i \leq n, \quad (6.9)$$

where  $\xi = 1$ ,  $\alpha = 2/3$ ,  $\tilde{a} = 8.4296$  and  $R$  to be determined from the initial conditions. These imply that  $b_{i+1} = a_i \tilde{q}_i / \tilde{q}_{i+1} = \exp(\tilde{a} [(i+1)^{2/3} - i^{2/3}])$ . The initial conditions are given by

$$z_i(0) = \begin{cases} z_0 \geq 0 & \text{for } i = 0, \\ \rho(0) - z_0 = 1 & \text{for } i = 1, \\ 0 & \text{otherwise.} \end{cases} \quad (6.10)$$

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where  $z_0$  is to be specified. The initial data implies that  $N_D(\mathbf{z}(0)) = z_0 + z_1(0) = \rho(0) = \rho$ , so that equations (5.4) and (5.9) give  $\tilde{\mu}(0) = \mu$ .

For a given value of  $z_0 \geq 0$  we choose  $\mu > 0$  and calculate the following

$$R = \frac{\rho - z_0}{\mu\rho}, \quad \tilde{f}(\mu_s) = \sum_{i=1}^{\infty} \tilde{q}_i \mu_s^i, \quad \tilde{g}(\mu_s) = \sum_{i=1}^{\infty} i \tilde{q}_i \mu_s^i, \quad \rho_s = z_0 \left[ 1 + \frac{\tilde{g}(\mu_s)}{(1 - \tilde{f}(\mu_s))} \right], \quad (6.11)$$

where  $\mu_s = 1$ . The value of  $\mu$  must be chosen so that all the assumptions of Theorem 5.2.3 are fulfilled. The main requirements are  $\mu > \mu_s = 1$ ,  $\tilde{f}(\mu_s) < 1$ , and  $\rho > \rho_s$ . It is clear from Tables 6.1 and 6.2 that these requirements are indeed fulfilled.

$\mu = \tilde{\mu}(0)$	$R$	$\tilde{f}(\mu_s)$	$\tilde{g}(\mu_s)$	$\rho_s$	$\bar{z}_1^{n \rightarrow \infty}$	$\bar{z}_1^{\text{plateau}}$	$n^{\text{plateau}}$
3	0.3333	0.33333490	0.33333650	0	0	0.99996972	403
4	0.2500	0.25000157	0.25000316	0	0	0.99994474	187
5	0.2000	0.20000157	0.20000316	0	0	0.99991124	111

Table 6.1: Parameter values for  $z_0 = 0$  giving  $\rho = 1$  and various values for  $\mu$

$\mu = \tilde{\mu}(0)$	$R$	$\tilde{f}(\mu_s)$	$\tilde{g}(\mu_s)$	$\rho_s$	$\bar{z}_1^{n \rightarrow \infty}$	$\bar{z}_1^{\text{plateau}}$	$n^{\text{plateau}}$
3	0.1667	0.16666824	0.16666983	1.20000417	0.2000	0.99993974	401
4	0.1250	0.12500157	0.12500316	1.14286101	0.1429	0.99989000	185
5	0.1000	0.10000157	0.10000316	1.11111482	0.1111	0.99982290	110

Table 6.2: Parameter values for  $z_0 = 1$  giving  $\rho = 2$  and various values for  $\mu$

We point out that a necessary requirement for the condition  $\tilde{f}(\mu_s) < 1$  is that the parameter  $\tilde{a}$  in (6.9) must satisfy  $\tilde{a} > 1.2$ , see the analysis in Section 3.1.3. This explains why the value  $\tilde{a} = 1$ , which was used by Carr et al. [9] and Duncan and Soheili [19] for the numerical solution of the standard mass conserving Becker-Döring model, does not work for the thermodynamically consistent models. Our choice  $\tilde{a} = 8.4296$  corresponds to nucleation of water vapor at a temperature of 25°C.

We recall from Section 4.4 that the equilibrium distribution  $\bar{z}$  is given by

$$\bar{z}_0 = z_0, \quad \bar{N}_D = \frac{\rho - z_0}{\tilde{g}(\bar{\mu})}, \quad \text{and} \quad \bar{z}_i = \bar{N}_D \tilde{q}_i \bar{\mu}^i \quad \text{for} \quad i \geq 1,$$

where  $\bar{\mu}$ , the equilibrium value of  $\tilde{\mu}$ , is the unique solution of

$$\frac{z_0}{\rho - z_0} \tilde{g}(\bar{\mu}) + \tilde{f}(\bar{\mu}) = 1. \quad (6.12)$$

The functions  $\tilde{f}$  and  $\tilde{g}$  are defined in (6.11) with  $\mu_s$  replaced by  $\bar{\mu}$ . For finite systems, we must have  $\tilde{f}(\bar{\mu}) = \sum_i^n \tilde{q}_i \bar{\mu}^i$  and  $\tilde{g}(\bar{\mu}) = \sum_i^n i \tilde{q}_i \bar{\mu}^i$ . In this case, solutions of (6.12) will depend on the



value of  $n$ . For a fixed  $n$ , we use the two different values  $z_0 = 0$  and  $z_0 = 1$  together with (6.10) to determine  $\bar{\mu}$  from (6.12). We then calculate the equilibrium number  $\bar{z}_1$  of free molecules by using

$$\bar{z}_1 = \bar{\mu} R \bar{N}_D = \frac{\rho - z_0}{\tilde{g}(\bar{\mu})} \bar{\mu} R. \quad (6.13)$$

Figure 6.1 shows the variation of the equilibrium number of free molecules with the size  $n$  of the largest cluster.

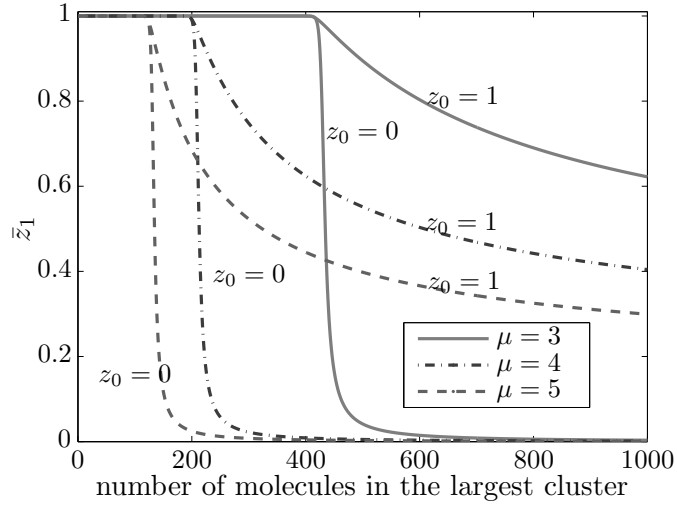


Figure 6.1: Equilibrium number of free molecules calculated from (6.12) and (6.13)

We observe in all cases, that there is an initial plateau where the changes of  $\bar{z}_1$  are minimal. Depending on  $\mu$  there is a maximum size of the largest cluster for which this holds. Exceeding this size, an increase in the size of the largest cluster is compensated by a decrease in the values of  $\bar{z}_1$ . For a fixed value of  $z_0$ , the length of the plateau decreases with an increase in  $\mu$ . For a given  $\mu$ , the values of  $\bar{z}_1$  are lower for higher values of  $z_0$  within the plateau. This trend is reversed when the size of the largest cluster is increased away from the plateau. These observations are evident from Figures 6.1 and 6.2. We believe that the equilibrium number  $\bar{z}_1$  of free molecules converge to values where  $\bar{\mu} = \mu_s$  and  $\rho = \rho_s$  as the size of the largest cluster increases to infinity. Denoted by  $\bar{z}_1^{n \rightarrow \infty}$ , these values are given in Tables 6.1 and 6.2. For  $z_0 = 0$  they are not reached since there is no solution to (6.12) because of the condition  $\tilde{f}(\mu_s) < 1$ . On the other hand if  $z_0 > 0$ , then  $\bar{z}_1^{n \rightarrow \infty}$  solves (6.12) with  $\mu = \mu_s$  and  $\rho = \rho_s$ .

The last two columns of Tables 6.1 and 6.2 indicate the height  $\bar{z}_1^{plateau}$  of the plateau and its right end point  $n^{plateau}$ . For our results, we define the plateau as the region where each value of  $\bar{z}_1$  is within a vertical distance  $1.0 \times 10^{-5}$  of its two neighbors. The heights  $\bar{z}_1^{plateau}$  correspond to the averages of the values of  $\bar{z}_1$  within each plateau. Similar results were reported by Carr et al. [9] on the equilibrium of the standard mass conserving Becker-Döring model.

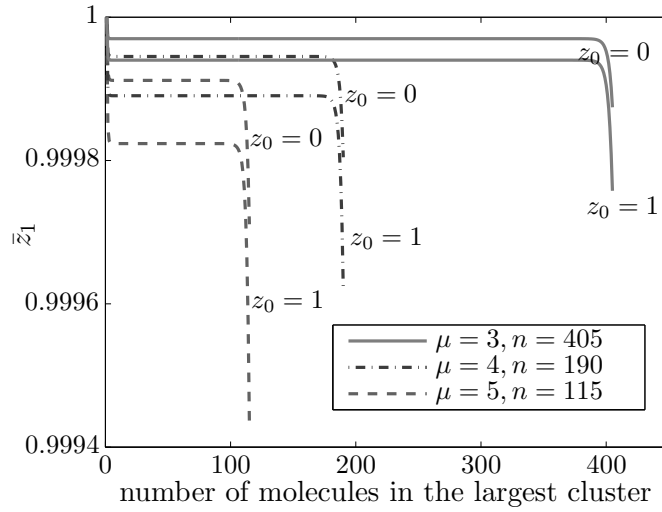


Figure 6.2: Equilibrium number of free molecules calculated from (6.12) and (6.13) with maximum system size  $n$

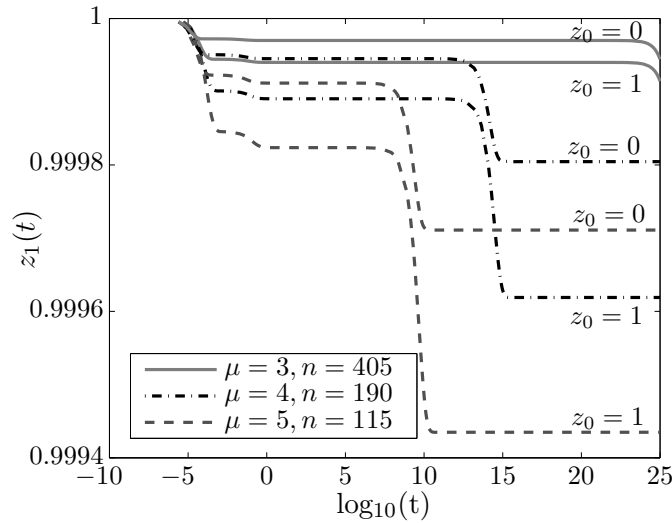


Figure 6.3: Variation of the number of free molecules with time in seconds for  $J_n = 0$

We now turn our attention to the time dependent solutions of the truncated modified mass-conserving model. Figure 6.3 shows the time dependence of the number of free molecules for different values of  $z_0$  and  $\mu$ , with the zero flux truncation. In this case the solution goes through a metastable state before attaining an equilibrium. We observe that the duration of the metastable state depends on the choice of  $\mu$ . For a fixed value of  $z_0$ , there is an increase in the length of the metastable state as one approaches  $\mu_s = 1$  from above. We point out that in order to capture the metastable phase, there is a need to use larger and larger systems as one approaches  $\mu_s$  from above. For instance, using a system of size 115 with  $\mu = 3$  would not show the breakdown of the metastable phase at about  $t = 10^{23}$ s. Instead this phase would continue as if it were an

## 6.2. NUMERICAL EXAMPLE

equilibrium. On the other hand, if one uses  $n = 405$  for  $\mu = 5$ , the duration of the metastable phase will not be affected. Instead the equilibrium number of free molecules will be lower than the values indicated in the figure for the different values of  $z_0$ . In addition, such a computation would take more time. Interestingly, the results of Figure 6.3 are related to those in Figure 6.2 on equilibrium. In both figures, the heights of the plateaus are the same for corresponding values of  $z_0$  and  $\mu$ . To distinguish the metastable phase from an equilibrium, the system size  $n$  must be bigger than the values  $n^{plateau}$  indicated in Tables 6.1 and 6.2. For our choices of  $n$  the equilibrium values of the free molecules are those indicated by the right end points of each of the plots in Figure 6.2.

Table 6.3 shows the information returned by the solver when either the Jacobian matrix is given explicitly or approximated numerically. The aim of the table is to illustrate the computational advantages of using the exact Jacobian matrix. We observe that in all the cases for  $\mu$  and  $n$ , the number of function evaluations as well as the computational time reduce when the Jacobian matrix is specified. A considerable improvement is observed for the case where  $\mu = 3$  and  $n = 405$ .

$\tilde{\mu}(0)$	$n$		numerical Jacobian	exact Jacobian
3	405	Function evaluations	966	151
		Computational time/s	1.7070	0.8297
4	190	Function evaluations	571	182
		Computational time/s	0.8737	0.6487
5	115	Function evaluations	280	171
		Computational time/s	0.6786	0.5557

Table 6.3: Computational information for  $z_0 = 0$  and  $J_n = 0$

Next we consider the case for  $\mu = 4$ ,  $n = 190$ , and compare the results for the two truncations considered. These are shown in Figure 6.4. We observe that for the zero flux truncation, the solution undergoes a long metastable state before converging to an equilibrium. On the other hand, the zero particle number truncation gives a steady-state solution which approximates the metastable state of the zero flux truncation. According to Penrose and Lebowitz [48], a system can remain in its metastable phase if one prevents the growth of the mass of super-critical clusters in a given local region. The zero particle number truncation does exactly this. Therefore the above results are expected.

Figure 6.5 shows the distribution  $\mathbf{z}(t)$  at different time periods for  $\tilde{\mu} = 4.0$  and  $n = 190$ . The initial period ends at about  $t = 10^0$ , while the metastable period goes up to about  $t = 10^{11}$ . They were computed using the zero flux truncation.

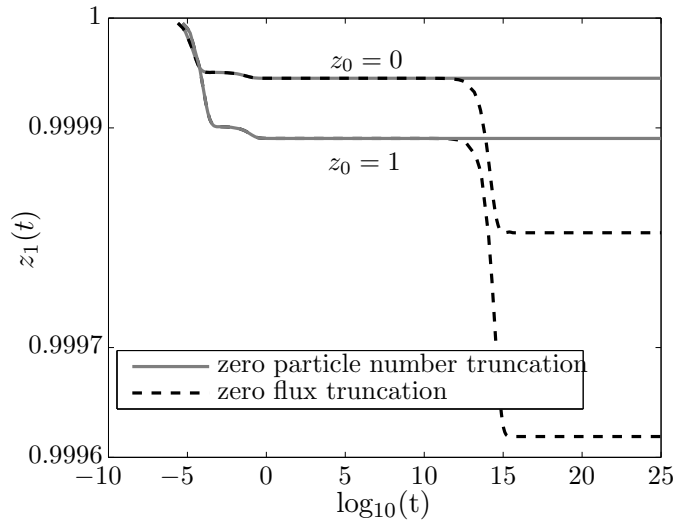


Figure 6.4: Variation of the number of free molecules with time for the different truncations,  $\mu = 4.0$  and  $n = 190$

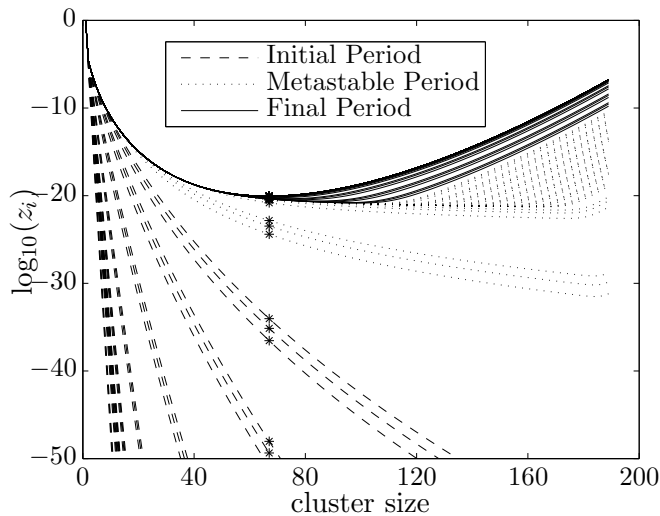


Figure 6.5: Cluster size distribution at different time periods,  $\mu = 4.0$  and  $n = 190$ . The symbols \* represent values of  $\log_{10}(z_{i_{crit}})$  at different times, where  $i_{crit} = 67$  in this case. The initial period ends at about  $10^0$  while the metastable one goes up to about  $10^{11}$ .

Finally Figure 6.6 shows the fluxes for the critical cluster. They are the rates at which supercritical clusters are being formed from the critical ones. We observe that the steady-state formulae  $J^s$  and  $J^{s2}$  are very good approximations to the nucleation rate within the metastable phase. It is clear from the figure that after the metastable phase, the time dependent nucleation rates drop down to zero thereby leading to an equilibrium distribution of clusters. By using

(1.15) and (2.7) we note that the structure of  $a_i$  in (6.9) must imply that

$$\xi = \alpha_i \vartheta V_1^{2/3} \frac{p_0}{kT} \sqrt{\frac{kT}{2\pi m}}.$$

We set the sticking coefficient  $\alpha_i$  to unity and use the two formulae in (2.11) with  $S = 1/R$  to obtain

$$\xi = \frac{\gamma \bar{p}(T)}{\sigma RkT} \sqrt{\frac{kT}{2\pi m}}.$$

We recall from (2.27) that  $\tilde{a} = \gamma/kT$  so that we get

$$\xi = \frac{\tilde{a} \bar{p}(T)}{\sigma R} \sqrt{\frac{kT}{2\pi m}}. \quad (6.14)$$

Our choice  $\xi = 1$  in the numerical computations corresponds to a time scaling of the modified Becker-Döring equations to a new time  $t$  related to the actual time  $\tau$  by

$$t = \xi \tau.$$

This means that the time  $\tau_{lag}$  it takes the nucleation rate  $J_{i_{crit}}$  in Figure 6.6 to reach its metastable value is given by

$$\tau_{lag} = \frac{t_{lag}}{\xi} \approx \frac{10^{2.5}}{\xi}. \quad (6.15)$$

We recall that we have used the value  $\tilde{a} = 8.4296$  corresponding to water vapor at 25°C. At this temperature the steam tables by Wagner and Kretzschmar [66] give  $\sigma = 71.972 \times 10^{-3} Nm^{-1}$ ,  $\bar{p}(T) = 3.170 \times 10^3 Pa$  and  $m = 3.0 \times 10^{-26} kg$ . Using these values and  $R = 1/4$  in (6.14) as well as (6.15) gives  $\tau_{lag} \approx 10^{-6} s$ .

It was not possible to simulate results for  $\mu$  very close to  $\mu_s = 1$ . This is because of the need to use very large systems and also the prolonged duration of the corresponding metastable phase. In other words, after a very long time, the numerical errors accumulate and therefore render the results inaccurate. These difficulties were also reported by Carr et al. [9] for the standard mass conserving model.

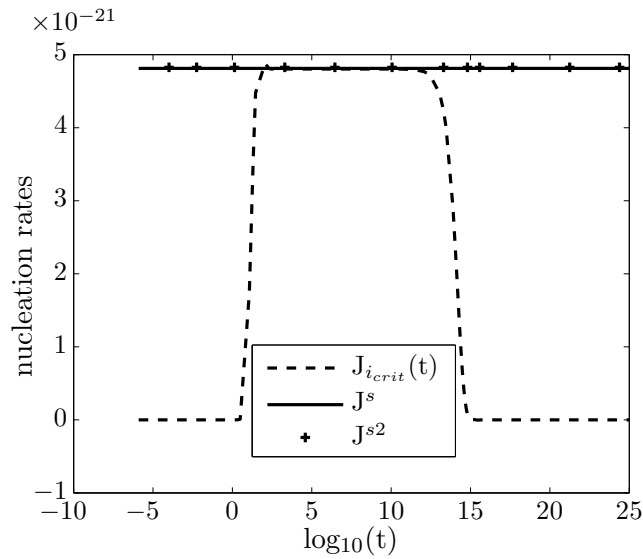


Figure 6.6: Nucleation rates at the critical cluster  $i_{crit} = 67$ , for  $\mu = 4.0$  and  $n = 190$ . Here  $J_{i_{crit}}(t)$  represents the time dependent flux for the critical cluster, computed using (6.3) and the zero flux truncation. The rates  $J^s$  are the steady-state nucleation rates calculated from (3.66), while  $J^{s2}$  is given by (3.67) with  $\gamma/kT = \tilde{a}$  and  $S = 1/R = 4.0$ .

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## Chapter 7

# Conclusions

This thesis was devoted to the dynamics of the Becker-Döring model as used in the nucleation theory. We extended the liquid-vapor system of Dreyer and Duderstadt [16] by incorporating an inert gas. We also derived the expression for the available free energy of a closed crystallization system. Here the solvent was considered as an inert substance in which the free solute particles or molecules are dissolved. From these two examples we stated a general thermodynamically consistent mass-conserving Becker-Döring model with an additional parameter  $z_0$  taking care of the presence of an inert substance. In addition, we studied the existence and uniqueness of steady-state as well as time independent solutions to the model. We showed that under some restrictions on the kinetic coefficients and initial data, there exists a metastable class of solutions for the model. In the following sections we summarize the results of our work.

### Steady-state solutions

We proved the existence and uniqueness of steady-state solutions for the truncated versions of the model. One truncation was the zero flux truncation where we took a system of size  $n$  and set  $J_n$  to zero. With this truncation we obtained only the equilibrium solution where all the fluxes vanish. In the second truncation we set  $z_i = 0$  for all  $i \geq n + 1$ . This truncation led to the non-equilibrium steady-state solutions where all the fluxes have a non-zero common value. For very large systems, that is, in the limit  $n \rightarrow \infty$  we showed that such solutions do not exist for the thermodynamically consistent models. However, by making extra assumptions we were able to construct approximations to the steady states of the infinite models. In this way we were able to derive a new correction of the classical nucleation rates. Our new formula predicts higher nucleation rates than the classical one in the presence of an inert substance. We compared the calculated nucleation rates with those observed in experiments. There was a discrepancy between the predicted rates and the observed ones. We corrected this by accounting for the sticking coefficients which shows that not all collisions of free molecules with a given cluster result into its growth. For water vapor, we obtained sticking coefficients ranging between  $10^{-7} - 10^{-1}$ . However, by considering the Argon data by Sinha et al. [57] we observed that our nucleation rates are lower than those observed in experiments. In this case the sticking coefficient was not enough to correct the discrepancy since it would even lead to lower rates. Therefore more work has to be done in order to improve the nucleation rate prediction of the classical droplet model for general substances.

## CHAPTER 7. CONCLUSIONS

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### Existence and uniqueness of solutions

We observed that for some choices of condensation rates the resulting modified model is singular in  $z_1$ . We showed in Chapter 4 that the singular problem can be solved directly without any need to make a time scaling. This was possible due to the structure of the model. For  $z_0 = 0$ , we showed by making some assumptions on the kinetic coefficients and initial data that the quotient  $N_D(t)/z_1(t)$  is bounded uniformly for all  $t \in [0, \infty[$ . We proved the existence of solutions by using the standard methods discussed by Ball et al [4]. For the singular fluxes in general, uniqueness of solutions for  $z_0 = 0$  was only possible if the coefficients  $a_i$  are size independent. By making a stronger restriction on the initial data, we were able to prove uniqueness locally for the whole class of  $a_i$  given by (4.8), see Remark 4.3.5. It is important to note that the commonly used initial conditions, where all the mass is put in free molecules, do not satisfy the additional restriction. Therefore this extra result is essential for the mathematical completeness of the theory but not commonly used in practice. Maybe such initial conditions are essential in processes which involve a change from a more dense phase to a less dense one, since in this case we may have a few free molecules initially. For example vaporization or melting processes.

We note that only for  $z_0 = 0$  and non singular fluxes did Hermann et al. [24] prove the existence and uniqueness for the whole class of  $a_i$  discussed in this thesis. As pointed out in the introduction of Chapter 4, the solutions to their model solve the singular flux model for all  $t \geq 0$  if  $z_1(t)$  does not go to zero faster than  $1/t$  or if it has a lower bound other than zero. Interestingly the same conditions lead to the difficulty in proving the uniqueness of solutions to the singular problem for the whole class  $a_i = i^\alpha$ , with  $\alpha \in ]0, 1[$ .

For  $z_0 > 0$ , equilibrium solutions exist under more general cases than those for which  $z_0 = 0$ . In some cases there exists an upper bound on the mass contained in an equilibrium solution, see (4.76). This is similar to the behavior of solutions for the standard mass conserving Becker-Döring model which was discussed by Ball et al. [4].

### Metastability

We showed in our study that metastability for the modified model applies only to the case where  $R < 1$ , see (4.9) for the definition of  $R$ . This means that there is no metastability in the Gallium Arsenide example which was introduced by Dreyer and Duderstadt [16]. In addition, the existence of a metastable solution depends on the initial value of the quantity  $\tilde{\mu}$  defined in (5.4). In particular, we can construct metastable solutions only for  $\tilde{\mu}(0) \geq \mu_s = 1$ . This is in contrast to the standard mass-conserving model where metastability depends on the initial free molecule concentration. Importantly, the kinetic coefficients  $a_i = 1$  and  $b_{i+1} = \exp(\tilde{a}\{i^{2/3} - (i-1)^{2/3}\})$  with  $\tilde{a} = 1$ , which were used by Carr et al. [9] for the standard model, do not qualify for metastability in the modified model. In particular the parameter  $\tilde{a}$  must satisfy the condition  $\tilde{a} > 1.2$ .

### Numerical results

We described an efficient numerical method for solving the truncated modified mass-conserving model. The maximum system size  $n$  was assumed to be greater than the critical cluster predicted by the Thomson formula (2.16). According to Penrose and Lebowitz [48] a system can be



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restricted in its metastable phase if one prevents the growth of the mass of super-critical clusters in a given local region. The zero particle number truncation must therefore lead to steady-state solutions which represent the metastable states of the zero flux truncation. This was evident from our numerical results. It was difficult to simulate results for values of  $\tilde{\mu}(0)$  very close to  $\mu_s$ . This was because of the need to use very large systems and also the prolonged duration of the corresponding metastable states. In other words, after a very long time, the numerical errors accumulate and therefore render the results inaccurate. These difficulties were also reported by Carr et al. [9] for the classical mass conserving model. Therefore we did not validate the time bounds for metastability breakdown which were given in Chapter 5.

In the following we mention some of the future work and open problems in relation to our work.

- It would be interesting to compare the nucleation rates derived here with experimental data for crystallization in solutions. We did comparisons only for melt crystallization.
- For  $z_0 = 0$  the uniqueness result for the singular problem is open if  $a_i = i^\alpha$ , with  $\alpha \in ]0, 1[$ . We proved uniqueness only for size independent coefficients.
- From a physical point of view we believe that in the presence of an inert substance, if one initially has a supersaturated system of mass  $\rho$ , the asymptotic solution must have two phases. In particular, as  $t \rightarrow \infty$ , the solution must converge in some weak sense to an equilibrium with mass  $\rho_s$ , the difference  $\rho - \rho_s$  going to larger and larger clusters. This result was proved by Ball et al. [4] for the standard mass-conserving model. It is still an open problem for the modified model with  $z_0 > 0$ . Herrmann et al. [24] proved a similar result for  $z_0 = 0$ .
- A probable future work would be to show how the modified Becker-Döring model is related to continuous models such as the Lifshitz-Slyozov-Wagner model or the Fokker-Planck equation.

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# Appendix A

## Basic definitions and theorems

**Definition A.0.1** (Lipschitz continuity). [23, p. 3]

A function  $f(y)$  defined on a  $y$ -set  $E \subset \mathbb{R}^d$  is said to be **uniformly Lipschitz continuous** on  $E$  with respect to  $y$  if there exists a constant  $K$  satisfying

$$|f(y_1) - f(y_2)| \leq K|y_1 - y_2| \quad \text{for } y_1, y_2 \in E. \quad (\text{A.1})$$

**Definition A.0.2** (Uniform boundedness). [25, p. 9]

A family  $\mathcal{F}$  of functions  $f(y)$  defined on some  $y$ -set  $E \subset \mathbb{R}^d$  is said to be **uniformly bounded** if, for all  $y \in E$  and all  $f \in \mathcal{F}$  there exists a non-negative number  $M$  such that  $|f(y)| \leq M$ .

**Definition A.0.3** (Equicontinuity). [23, p. 3]

A family  $\mathcal{F}$  of functions  $f(y)$  defined on some  $y$ -set  $E \subset \mathbb{R}^d$  is said to be **equicontinuous** if, for every  $\epsilon > 0$ , there exists a  $\delta = \delta_\epsilon > 0$  such that  $|f(y_1) - f(y_2)| \leq \epsilon$  whenever  $y_1, y_2 \in E$ ,  $|y_1 - y_2| \leq \delta$  and all  $f \in \mathcal{F}$ .

**Definition A.0.4** (Uniform convergence). [49, p. 49]

A family  $f_n$  of functions defined on some  $y$ -set  $E$  is said to **converge uniformly** to a function  $f$  on  $E$  if given  $\epsilon > 0$ , there is an  $N$  such that for all  $y \in E$  and all  $n \geq N$ , we have  $|f(y) - f_n(y)| < \epsilon$ .

**Theorem A.0.5** (Arzéla-Ascoli). [23, p. 4]

On a compact  $y$ -set  $E \subset \mathbb{R}^d$ , let  $f_1(y), f_2(y), \dots$  be a sequence of functions which is uniformly bounded and equicontinuous. Then there exists a sub-sequence  $f_{n(1)}(y), f_{n(2)}(y), \dots$  which is uniformly convergent on  $E$ .

**Theorem A.0.6** (Gronwall's Inequality). [23, p. 24]

Let  $u(t)$  and  $v(t)$  be non-negative, continuous functions on  $[a, b]$ . For a constant  $C \geq 0$  suppose that

$$v(t) \leq C + \int_a^t v(s)u(s) ds \quad \text{for } a \leq t \leq b.$$

Then

$$v(t) \leq C \exp\left(\int_a^t u(s) ds\right).$$

In particular, if  $C = 0$ , then  $v(t) \equiv 0$ .

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**Theorem A.0.7** (Picard-Lindelöf). [23, p. 8]

Let  $y, f \in \mathbb{R}^d$ ;  $f(t, y)$  continuous on a parallelepiped  $R : t_0 \leq t \leq t_0 + a, |y_0 - y| \leq b$  and uniformly Lipschitz continuous with respect to  $y$ . Let  $|f(t, y)| \leq M$  on  $R$ . Define  $\alpha := \min(a, b/M)$ . Then

$$\dot{y} = f(t, y), \quad y(t_0) = y_0$$

has a unique solution  $y = y(t)$  on  $[t_0, t_0 + \alpha]$ .

**Theorem A.0.8** (Bounded convergence). [49, p. 84]

Let  $f_n$  be a sequence of measurable functions defined on a  $y$ -set  $E$  of finite measure. Suppose that there is a real number  $M$  such that  $|f_n(x)| \leq M$  for all  $n$  and all  $y \in E$ . If  $f(y) = \lim_{n \rightarrow \infty} f_n(y)$  for each  $y \in E$ , then

$$\int_E f \, dy = \lim_{n \rightarrow \infty} \int_E f_n \, dy.$$

**Theorem A.0.9** (Hölder's Inequality). [61, p. 135]

For all non-negative real numbers  $a_k, b_k, k = 1, 2, \dots$ , one has the bound

$$\sum_k a_k b_k \leq \left( \sum_k a_k^p \right)^{1/p} \left( \sum_k b_k^q \right)^{1/q},$$

provided that the powers  $p > 1$  and  $q > 1$  satisfy the relation

$$\frac{1}{p} + \frac{1}{q} = 1.$$

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## Appendix B

# Derivation of the steady-state formulae

### B.1 The constant free molecule model

To derive the equations (3.24) - (3.26) we note that the definition of fluxes in (3.2) shows that

$$\begin{aligned} z_1^{s,F} &= \frac{1}{a_1} \left( J^F + b_2 R (q^{in})^2 \bar{\lambda} z_2^{s,F} \right) = \mu, & \bar{\lambda} &= \frac{z_1^{s,F}}{N_D(\mathbf{z}^{s,F})}, \\ z_i^{s,F} &= \frac{1}{a_i} \left( J^F + b_{i+1} R q^{in} z_{i+1}^{s,F} \right), & 2 \leq i \leq n-1, \\ z_n^{s,F} &= \frac{1}{a_n} J^F. \end{aligned} \tag{B.1}$$

For  $i = n$  the common flux  $J^F$  is such that

$$J^F = a_n z_n^{s,F}.$$

Now working backwards, for  $i = n-1$  we note that

$$z_{n-1}^{s,F} = \frac{J^F}{a_{n-1}} \left( 1 + \frac{b_n}{a_n} R q^{in} \right) = \frac{J^F}{a_{n-1}} \left( 1 + \frac{b_n}{a_{n-1}} \frac{a_{n-1}}{a_n} R q^{in} \right).$$

Next we use the first equation in (1.29) for  $i = n-1$  to obtain

$$z_{n-1}^{s,F} = \frac{J^F}{a_{n-1}} \left( 1 + \frac{a_{n-1} Q_{n-1}}{a_n Q_n} R q^{in} \right).$$

Setting  $i = n-2$  in (B.1) and making use of the above formula for  $z_{n-1}^{s,F}$  as well as (1.29) give

$$z_{n-2}^{s,F} = \frac{J^F}{a_{n-2}} \left( 1 + \frac{a_{n-2} Q_{n-2}}{a_{n-1} Q_{n-1}} R q^{in} + \frac{a_{n-2} Q_{n-2}}{a_n Q_n} (R q^{in})^2 \right),$$

while  $i = n-3$  leads to

$$z_{n-3}^{s,F} = \frac{J^F}{a_{n-3}} \left( 1 + \frac{a_{n-3} Q_{n-3}}{a_{n-2} Q_{n-2}} R q^{in} + \frac{a_{n-3} Q_{n-3}}{a_{n-1} Q_{n-1}} (R q^{in})^2 + \frac{a_{n-3} Q_{n-3}}{a_n Q_n} (R q^{in})^3 \right).$$

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## B.2. THE MODIFIED MASS-CONSERVING MODEL

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Continuing this procedure up to  $i = 2$ , it can easily be verified that the equations (3.24) hold, that is

$$z_1^{s,F} = \mu, \quad z_i^{s,F} = J^F Q_i (1/Rq^{in})^i \sum_{r=i}^n \frac{1}{a_r Q_r (1/Rq^{in})^r}, \quad 2 \leq i \leq n. \quad (\text{B.2})$$

The common flux  $J^F$  is obtained from the first equation in (B.1) by substituting for  $z_2^{s,F}$ . This gives

$$J^F = z_1^{s,F} \left( \frac{1}{a_1} + \frac{\bar{\lambda}}{R} \sum_{i=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} \right)^{-1}, \quad \bar{\lambda} = \frac{z_1^{s,F}}{N_D(\mathbf{z}^{s,F})}. \quad (\text{B.3})$$

By using (B.2) we note that

$$N_D^{s,F}(\mathbf{z}^{s,F}) = \sum_{i=1}^n z_i^{s,F} = z_1^{s,F} + J^F \sum_{i=2}^n Q_i (1/Rq^{in})^i \sum_{r=i}^n \frac{1}{a_r Q_r (1/Rq^{in})^r}.$$

Substituting for  $J^F$  from (B.3) and dividing the resulting equation by  $N_D^{s,F}(\mathbf{z}^{s,F})$  we get

$$\left( \frac{1}{a_1} + \frac{\bar{\lambda}}{R} \sum_{i=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} \right) = \bar{\lambda} \left( \frac{1}{a_1} + \frac{\bar{\lambda}}{R} \sum_{i=2}^n \frac{1}{a_r Q_r (1/Rq^{in})^r} \right) + \bar{\lambda} \sum_{i=2}^n \sum_{r=i}^n \frac{Q_i (1/Rq^{in})^i}{a_r Q_r (1/Rq^{in})^r}.$$

The desired expression (3.26) is obtained by changing the order of summation in the last term on the right-hand side and simplifying the result.

## B.2 The modified mass-conserving model

To derive equation (3.53) we note that the fluxes in (3.31) imply that

$$z_i^{s,M} = \frac{1}{a_i} \left( J^M + \frac{b_2 R}{\lambda} z_{i+1}^{s,M} \right), \quad 1 \leq i \leq n, \quad \text{with} \quad \lambda = \frac{z_1^{s,M}}{N_D(\mathbf{z}^{s,M})} \quad \text{and} \quad z_{n+1} = 0. \quad (\text{B.4})$$

Starting with  $i = n$  we have  $z_n^{s,M} = J^M/a_n$ . We then continue backwards for  $i = n - 1$ , while using the first equation in (1.29) to get

$$z_{n-1}^{s,M} = \frac{J^M}{a_{n-1}} \left( 1 + \frac{Q_{n-1} a_{n-1}}{Q_n a_n (\lambda/R)} \right).$$

Setting  $i = n - 2$  in (B.4) and substituting for  $z_{n-1}^{s,M}$  give

$$z_{n-2}^{s,M} = \frac{J^M}{a_{n-2}} \left[ 1 + \frac{b_{n-1}}{a_{n-1} (\lambda/R)} \left( \frac{Q_{n-1} a_{n-1}}{Q_n a_n (\lambda/R)} \right) \right].$$

Next we use the first equation in (1.29) and simply the result to

$$z_{n-2}^{s,M} = \frac{J^M}{a_{n-2}} \left[ 1 + \frac{Q_{n-2} a_{n-2}}{Q_{n-1} a_{n-1} (\lambda/R)} + \frac{Q_{n-2} a_{n-2}}{Q_n a_n (\lambda/R)^2} \right].$$

Continuing this procedure for  $i = n - 3, n - 4, \dots, 1$  we obtain the general formula

$$z_i^{s,M} = J^M Q_i (\lambda/R)^i \sum_{r=i}^n \frac{1}{a_r Q_r (\lambda/R)^r},$$

which confirms the result in (3.53).

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## Appendix C

# Proofs for some theorems

### C.1 Functional spaces

#### Proof of Theorem 4.1.1.

In the proof we aim at constructing an isomorphic and bijective map between  $\mathbf{X}$  and the dual space  $\mathbf{Y}^*$  of  $\mathbf{Y}$ . First we consider  $\mathbf{z} \in \mathbf{X}$  and show that for  $\mathbf{y} \in \mathbf{Y}$  the functional

$$F_{\mathbf{z}}(\mathbf{y}) := \sum_{i=1}^{\infty} z_i y_i \quad (\text{C.1})$$

is well defined, linear and bounded. We note that

$$\begin{aligned} |F_{\mathbf{z}}(\mathbf{y})| &\leq |z_1| |y_1| + \sum_{i=2}^{\infty} (i-1) |z_i| \frac{|y_i|}{i-1} \\ &\leq \max_{i \geq 2} \left\{ |y_1|, \frac{|y_i|}{i-1} \right\} \left( |z_1| + \sum_{i=2}^{\infty} (i-1) |z_i| \right) = \|\mathbf{y}\|_{\mathbf{Y}} \|\mathbf{z}\|_{\mathbf{X}}. \end{aligned}$$

Thus  $F_{\mathbf{z}}(\mathbf{y})$  is well defined. The linearity of  $F_{\mathbf{z}}(\mathbf{y})$  is obvious from its definition. For boundedness and hence continuity, see Kreyszig [31, Theorem 2.8-3], we have

$$\begin{aligned} \|F_{\mathbf{z}}(\mathbf{y})\|_{\mathbf{Y}^*} &:= \sup_{\mathbf{y} \in \mathbf{Y}} \frac{|F_{\mathbf{z}}(\mathbf{y})|}{\|\mathbf{y}\|_{\mathbf{Y}}} \\ &\leq \|\mathbf{z}\|_{\mathbf{X}}. \end{aligned} \quad (\text{C.2})$$

For a fixed  $\mathbf{z} \in \mathbf{X}$  and  $n \geq 1$  we define  $\mathbf{y}^{(n)}$  by

$$y_i^{(n)} = \begin{cases} (i-1) \cdot \text{sign}(z_i); & \text{for } 2 \leq i \leq n \\ \text{sign}(z_i) & \text{otherwise.} \end{cases} \quad (\text{C.3})$$

Clearly  $\mathbf{y}^{(n)} \in \mathbf{Y}$  with  $\|\mathbf{y}^{(n)}\|_{\mathbf{Y}} = 1$  and

$$\begin{aligned} \|F_{\mathbf{z}}(\mathbf{y}^{(n)})\|_{\mathbf{Y}^*} &\geq |F_{\mathbf{z}}(\mathbf{y}^{(n)})| = |z_1| + \sum_{i=2}^n (i-1) |z_i| + \sum_{i=n+1}^{\infty} |z_i|, \\ &= \|\mathbf{z}\|_{\mathbf{X}} + \sum_{i=n+1}^{\infty} |z_i| - \sum_{i=n+1}^{\infty} (i-1) |z_i|, \\ &= \|\mathbf{z}\|_{\mathbf{X}} - \varepsilon, \quad \text{for } n \text{ large enough.} \end{aligned}$$

Since  $\varepsilon$  can be arbitrarily small, we must have

$$\|F_{\mathbf{z}}(\mathbf{y}^{(n)})\|_{\mathbf{Y}^*} \geq \|\mathbf{z}\|_{\mathbf{X}}. \quad (\text{C.4})$$

Combining (C.2) and (C.4) we obtain

$$\|F_{\mathbf{z}}(\mathbf{y}^{(n)})\|_{\mathbf{Y}^*} = \|\mathbf{z}\|_{\mathbf{X}}. \quad (\text{C.5})$$

Up to now we have shown that for each  $\mathbf{z} \in \mathbf{X}$  we can construct a bounded linear functional  $F_{\mathbf{z}}(\mathbf{y}) \in \mathbf{Y}^*$  and that the map  $I : \mathbf{X} \rightarrow \mathbf{Y}^*$  is isomorphic and hence injective. To prove that  $I$  is a bijection, we have to show that each element of  $\mathbf{Y}^*$  has a preimage in  $\mathbf{X}$ , that is,  $I$  is surjective. A Schauder basis for  $\mathbf{Y}$  is  $\mathbf{e}_i$ , where  $\mathbf{e}_i = (\delta_{ij})$  has 1 in the  $i^{\text{th}}$  position and zeros otherwise. Then every  $\mathbf{y} \in \mathbf{Y}$  can be uniquely represented as

$$\mathbf{y} = \sum_{i=1}^{\infty} y_i \mathbf{e}_i.$$

Let  $F \in \mathbf{Y}^*$ , then for every  $\mathbf{y} \in \mathbf{Y}$  we have

$$F(\mathbf{y}) = \sum_{i=1}^{\infty} y_i F(\mathbf{e}_i).$$

Define  $z_i := F(\mathbf{e}_i)$ , then the proof is finished once we establish that  $\mathbf{z} = (z_i)_{i \geq 1} \in \mathbf{X}$ . Choose  $\tilde{\mathbf{y}} := (\text{sign}(z_i))_{i \geq 1}$ . Then  $\|\tilde{\mathbf{y}}\|_{\mathbf{Y}} = 1$  and

$$\sum_{i=1}^{\infty} |z_i| := \sum_{i=1}^{\infty} z_i \text{sign}(z_i) = F(\tilde{\mathbf{y}}) < \infty.$$

As before we choose  $\mathbf{y}^{(n)}$  defined by (C.3) so that

$$\begin{aligned} \|F\|_{\mathbf{Y}^*} &\geq |F(\mathbf{y}^{(n)})| = |z_1| + \sum_{i=2}^n (i-1)|z_i| + \sum_{i=n+1}^{\infty} |z_i|, \\ &= |z_1| + \sum_{i=2}^n (i-1)|z_i| + \varepsilon \quad \text{for } n \text{ large enough.} \end{aligned}$$

Therefore for  $n$  large enough we have

$$\|F\|_{\mathbf{Y}^*} + 1 \geq |z_1| + \sum_{i=2}^n (i-1)|z_i|.$$

Taking the limit as  $n \rightarrow \infty$  we obtain the result that  $\mathbf{z} \in \mathbf{X}$  and this ends the proof.  $\square$

**Proof of Lemma 4.1.2.**

For bounded linear functionals a sequence  $F^{(n)}$  converges weak\* if there is an  $F \in \mathbf{Y}^*$  such that  $F^{(n)} \rightarrow F$  as  $n \rightarrow \infty$ . Therefore in the proof we show that weak\* convergence as defined above is exactly weak\* convergence in  $\mathbf{Y}^*$ .

## APPENDIX C. PROOFS FOR SOME THEOREMS

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“ $\Rightarrow$ “: As in the proof of Theorem 4.1.1 we use the Schauder basis for  $\mathbf{Y}$  and define a sequence  $\mathbf{z}^{(n)}$  by  $z_i^{(n)} := F_{z_i^{(n)}}(\mathbf{e}_i)$ . Then convergence in  $\mathbf{Y}^*$  leads to

$$z_i^{(n)} := F_{z_i^{(n)}}(\mathbf{e}_i) \xrightarrow{n \rightarrow \infty} F_{z_i}(\mathbf{e}_i) = z_i.$$

For part (ii) we note that weak\* convergent sequences are bounded, see Kreyszig [31, Corollary 4.9-7].

“ $\Leftarrow$ “: If (i) and (ii) hold, then we prove that  $F_{\mathbf{z}^{(n)}}(\mathbf{y}) \xrightarrow{n \rightarrow \infty} F_{\mathbf{z}}(\mathbf{y})$  for  $\mathbf{y} \in \mathbf{Y}$ . By using definition (C.1) we observe that

$$\begin{aligned} |(F_{\mathbf{z}^{(n)}} - F_{\mathbf{z}})(\mathbf{y})| &= \left| \sum_{i=1}^{\infty} (z_i^n - z_i) y_i \right|, \\ &\leq |z_1^n - z_1| |y_1| + \sum_{i=2}^m (i-1) |z_i^n - z_i| \frac{|y_i|}{i-1} + \sum_{i=m+1}^{\infty} (i-1) |z_i^n - z_i| \frac{|y_i|}{i-1}, \\ &\leq \|\mathbf{y}\|_{\mathbf{Y}} \left( |z_1^n - z_1| + \sum_{i=2}^m (i-1) |z_i^n - z_i| \right) + \max_{i>m} \frac{|y_i|}{i-1} \sum_{i=m+1}^{\infty} (i-1) |z_i^n - z_i|. \end{aligned}$$

We first take the limit  $m \rightarrow \infty$  so that the second term on the right of the last inequality is less than  $\varepsilon/2$  for some  $\varepsilon > 0$ . This is possible since  $\lim_{i \rightarrow \infty} y_i/(i-1) = 0$ . Secondly to end the proof we take the limit  $n \rightarrow \infty$  so as to make the first term less than  $\varepsilon/2$  due to (i) in Lemma 4.1.2.  $\square$

## C.2 Additional results on metastability

### Proof of Lemma 5.1.2

The proof is mostly taken from Penrose [46].

*Proof.* We first construct the solution  $f_i(\mu)$  to the difference equation (5.1). This equation implies that the quantity  $J(\mu)$  defined by

$$J(\mu) := a_i \mu f_i(\mu) - b_{i+1} f_{i+1}(\mu) \tag{C.6}$$

is independent of  $i$ . By applying McDonalds's trick [37] we divide both sides of the above formula by  $Q_i \mu^{i+1}$  to obtain

$$\frac{J(\mu)}{Q_i \mu^{i+1}} = \frac{a_i \mu f_i(\mu)}{Q_i \mu^{i+1}} - \frac{b_{i+1} f_{i+1}(\mu)}{Q_i \mu^{i+1}}.$$

We use the first equation in (1.29) and rearrange the result to get

$$\frac{J(\mu)}{a_i Q_i \mu^{i+1}} = \frac{f_i(\mu)}{Q_i \mu^i} - \frac{f_{i+1}(\mu)}{Q_{i+1} \mu^{i+1}}. \tag{C.7}$$

The ratio of successive terms of the series  $\sum_{i=1}^{\infty} Q_i \mu^i$  in the limit of large  $i$  is  $\mu/\mu_s$ . To see this we note that

$$\frac{Q_{i+1} \mu^{i+1}}{Q_i \mu^i} = \frac{a_i \mu}{b_{i+1}} = \frac{a_i}{b_i} \cdot \frac{b_i}{b_{i+1}} \mu.$$



## C.2. ADDITIONAL RESULTS ON METASTABILITY

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We then take the limit  $i \rightarrow \infty$  and use Assumptions 5.1.1 (ii) and (iii) to get the desired result. Since we require that  $\mu > \mu_s$ , the denominators on the right-hand side of (C.7) grow without bound as  $i \rightarrow \infty$ . Hence by the requirement of boundedness of  $f_i(\mu)$  for large  $i$ , both terms on the right of (C.7) tend to zero as  $i \rightarrow \infty$ . Summing both sides of this equation from  $i = 1$  to infinity and simplifying the result give (5.2). The series is a convergent sum of positive terms so that we can be sure that  $J(\mu) > 0$ . To obtain  $f_i(\mu)$  we sum both sides of (C.7) from  $i$  to infinity. After a simplification of the resulting equation we obtain (5.3). It is clear by substitution that  $f_i$  given by (5.3) is a solution of (5.1). To prove uniqueness suppose that the sequences  $g_i$  and  $f_i$  are two solutions to (5.1). Define  $\bar{h}_i := f_i - g_i$  for  $i \in \mathbb{N}$ . Then  $\bar{h}_i$  must satisfy

$$a_{i-1}\bar{h}_{i-1} - (b_i + \mu a_i)\bar{h}_i + b_{i+1}\bar{h}_{i+1} = 0,$$

and

$$\bar{h}_1 = 0.$$

By following the same procedure used in the derivation of (5.2) from (C.7), we observe that

$$J(\mu) = a_i \mu \bar{h}_i - b_{i+1} \bar{h}_{i+1} = 0,$$

or equivalently that

$$a_i \mu \bar{h}_i = b_{i+1} \bar{h}_{i+1} \quad \text{for all } i.$$

Solving this recurrence relation by starting with  $\bar{h}_1 = 0$  we obtain  $\bar{h}_i = 0$  for all  $i$ . Hence  $f_i$  given by (5.3) is the unique solution of (5.1).

To prove part (i) of Lemma 5.1.2 we note from (5.3) that

$$\begin{aligned} \mu a_i f_i(z) &= J(\mu) \left[ 1 + \sum_{r=i+1}^{\infty} \frac{a_r Q_r}{a_r Q_r} \mu^{i-r} \right] \\ &= J(\mu) [1 + h_{i+1} \mu^{-1} + h_{i+1} h_{i+2} \mu^{-2} + \dots], \end{aligned}$$

where now for  $i \in \mathbb{N}$

$$h_{i+1} := \frac{a_i Q_i}{a_{i+1} Q_{i+1}} = \frac{b_{i+1}}{a_{i+1}}.$$

By Assumption 5.1.1 (iii),  $h_i$  is a decreasing function of  $i$  and hence every term in the series for  $a_i f_i(\mu)$  is a decreasing function of  $i$ . To end the proof of this part we repeat the same expansion for  $a_{i+1} f_{i+1}$  and compare the resulting powers of  $\mu$ . We note that this result, together with Assumption 5.1.1 (i), implies that

$$f_{i+1} \leq \frac{a_1 f_1(\mu)}{a_{i+1}} < \frac{a_1 f_1(\mu)}{A'} = \text{const.}$$

This shows that  $f_i$  is indeed bounded for all  $i$ . In addition, if the coefficients  $a_i$  increase without bound then we have  $\lim_{i \rightarrow \infty} f_i = 0$ .

Next we prove part (ii) by defining two new sequences for  $\mu, \mu' > \mu_s$  as

$$\tilde{f}_i(\mu', \mu) := \mu' f_i(\mu) - \mu f_i(\mu') \quad i \geq 1 \tag{C.8}$$

## APPENDIX C. PROOFS FOR SOME THEOREMS

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and

$$\tilde{J}_i(\mu', \mu) := a_i \mu' \tilde{f}_i(\mu', \mu) - b_{i+1} \tilde{f}_{i+1}(\mu', \mu) \quad i \geq 1. \quad (\text{C.9})$$

Using these definitions we obtain for  $i \geq 2$

$$\begin{aligned} \tilde{J}_{i-1}(\mu', \mu) - \tilde{J}_i(\mu', \mu) &= a_{i-1} \mu' \tilde{f}_{i-1}(\mu', \mu) - b_i \tilde{f}_i(\mu', \mu) - a_i \mu' \tilde{f}_i(\mu', \mu) + b_{i+1} \tilde{f}_{i+1}(\mu', \mu), \\ &= a_{i-1} \mu' [\mu' f_{i-1}(\mu) - \mu f_{i-1}(\mu')] - (a_i \mu' + b_i) [\mu' f_i(\mu) - \mu f_i(\mu')] \\ &\quad + b_{i+1} [\mu' f_{i+1}(\mu) - \mu f_{i+1}(\mu)], \\ &= \mu' [a_{i-1} \mu' f_{i-1}(\mu) - (a_i \mu' + b_i) f_i(\mu) + b_{i+1} f_{i+1}(\mu)] \\ &\quad - \mu [a_{i-1} \mu' f_{i-1}(\mu') - (a_i \mu' + b_i) f_i(\mu') + b_{i+1} f_{i+1}(\mu')]. \end{aligned}$$

By using the difference equation (5.1) for  $f_i(\mu')$  we see that the second bracketed term on the right-hand side is zero. Next we eliminate the term  $b_{i+1} f_{i+1}(\mu)$  from the remaining expression with the help of (5.1) for  $f_i(\mu)$ . This gives

$$\begin{aligned} \tilde{J}_{i-1}(\mu', \mu) - \tilde{J}_i(\mu', \mu) &= \mu' [a_{i-1} \mu' f_{i-1}(\mu) - (a_i \mu' + b_i) f_i(\mu) - a_{i-1} \mu f_{i-1}(\mu) + (a_i \mu + b_i) f_i(\mu)] \\ &= \mu' (\mu' - \mu) [a_{i-1} f_{i-1}(\mu) - a_i f_i(\mu)] \\ &\geq 0 \end{aligned}$$

since  $\mu' \geq \mu$  and part (i) of the lemma hold. Thus the sequence  $\tilde{J}_1, \tilde{J}_2, \dots$  is monotonically decreasing and can therefore change sign at most once. Let  $\tilde{i}$  be the unique value of  $i$  at which this happens so that

$$\tilde{J}_i \begin{cases} \geq 0, & \text{if } i < \tilde{i}; \\ < 0, & \text{if } i \geq \tilde{i}, \end{cases} \quad (\text{C.10})$$

where we take  $\tilde{i} = 0$  if all terms are negative and  $\tilde{i} = \infty$  if all are nonnegative. By the same manipulations as in the derivation of (5.3) from (C.6) we can solve (C.9) for  $\tilde{f}_i$  to obtain

$$\tilde{f}_i = Q_i \mu'^i \sum_{r=i}^{\infty} \frac{J_r(\mu', \mu)}{a_r Q_r \mu'^{r+1}}. \quad (\text{C.11})$$

Setting  $i = 1$  and noting that  $\tilde{f}_1(\mu', \mu) = 0$  we obtain

$$Q_1 \mu'^1 \sum_{r=1}^{\tilde{i}-1} \frac{J_r(\mu', \mu)}{a_r Q_r \mu'^{r+1}} + Q_1 \mu'^1 \sum_{r=\tilde{i}}^{\infty} \frac{J_r(\mu', \mu)}{a_r Q_r \mu'^{r+1}} = 0. \quad (\text{C.12})$$

By (C.10) the first term consists entirely of nonnegative terms and the second term consists of negative terms. The proof is completed by showing that  $\tilde{f}_i(z', z)$  is non positive. If  $i > \tilde{i}$  then by (C.10) all terms of the sum in (C.11) are negative and so  $\tilde{f}_i(z', z)$  is negative. If  $i < \tilde{i}$  then there may be some positive terms as well, but by (C.12) these terms can at most cancel the contribution of the negative terms. Thus in either case we have

$$\tilde{f}_i(\mu', \mu) \leq 0. \quad (\text{C.13})$$

Using the definition (C.8) of  $\tilde{f}_i(z', z)$  in (C.13) and  $\mu' \geq \mu$  we get the desired result  $f_i(\mu)/\mu \leq \tilde{f}_i(\mu')/\mu'$ .

## C.2. ADDITIONAL RESULTS ON METASTABILITY

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The first inequality in part (iii) of the lemma follows directly by substituting (5.2) for  $J(\mu)$  in (5.3) and using the positivity of all terms in the series. To prove the second inequality we note that for any two integers  $m$  and  $n$  satisfying  $1 \leq m < n$ , we have

$$\begin{aligned} \frac{Q_n}{Q_m} &= \left(\frac{a_m}{a_n}\right) \prod_{r=m+1}^n \left(\frac{a_r}{b_r}\right) \quad \text{by (1.8),} \\ &\leq \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ - \sum_{r=m+1}^n Gr^{-\gamma} \right], \end{aligned}$$

by using the first inequality in Assumption 5.1.1 (iv). Then we bound the sum by an integral to have

$$\begin{aligned} \frac{Q_n}{Q_m} &\leq \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ - \int_{m+1}^n Gr^{-\gamma} dr \right] \\ &= \left(\frac{a_m}{a_n}\right) \mu_s^{m-n} \exp \left[ -G \left( \frac{n^{1-\gamma} - (m+1)^{1-\gamma}}{1-\gamma} \right) \right]. \end{aligned}$$

To end the proof of part (iii) we set  $m = 1$ ,  $n = i$  and use  $Q_1 = 1$  to obtain

$$Q_i \mu^i \leq \frac{a_1}{a_i} \mu_s \left(\frac{\mu}{\mu_s}\right)^i \exp \left[ -G \left( \frac{i^{1-\gamma} - 2^{1-\gamma}}{1-\gamma} \right) \right]. \quad (\text{C.14})$$

For part (iv) we take the limit  $\mu \rightarrow \mu_s$  in (C.6) and show that

$$\lim_{\mu \rightarrow \mu_s} J(\mu) = 0. \quad (\text{C.15})$$

To do this we use (1.8) to substitute for  $Q_i$  in (5.2). This gives

$$J(\mu)^{-1} = \frac{1}{a_1} \sum_{i=1}^{\infty} \frac{1}{\mu^{i+1}} \prod_{k=2}^i \frac{b_k}{a_k}.$$

We then use Assumption 5.1.1 (iii) to get

$$J(\mu)^{-1} \geq \frac{1}{a_1} \sum_{i=1}^{\infty} \frac{1}{\mu \mu_s} \left(\frac{\mu_s}{\mu}\right)^i.$$

The right-hand side of this inequality is a geometric series with a common ratio  $z_s/z < 1$ . This gives

$$J(\mu)^{-1} \geq \frac{1}{a_1 \mu (\mu - \mu_s)}.$$

In the limit  $\mu \rightarrow \mu_s$  the right-hand side goes to infinity, thereby proving (C.15) and thus ending the proof of Lemma 5.1.2.  $\square$

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