

## The modified Becker–Döring system with aggregation-dominated rate coefficients

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys. A: Math. Theor. 42 045002

(<http://iopscience.iop.org/1751-8121/42/4/045002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.155

The article was downloaded on 03/06/2010 at 08:11

Please note that [terms and conditions apply](#).

# The modified Becker–Döring system with aggregation-dominated rate coefficients

**Jonathan A D Wattis**

Theoretical Mechanics, School of Mathematical Sciences, University of Nottingham,  
University Park, Nottingham NG7 2RD, UK

E-mail: [Jonathan.Wattis@nottingham.ac.uk](mailto:Jonathan.Wattis@nottingham.ac.uk)

Received 29 August 2008, in final form 11 November 2008

Published 17 December 2008

Online at [stacks.iop.org/JPhysA/42/045002](http://stacks.iop.org/JPhysA/42/045002)

## Abstract

We consider a system of Becker–Döring equations modified in the manner of Dreyer & Duderstadt (2006 *J. Stat. Phys.* **123** 55). We analyse the case of size-independent rate coefficients in the case of weak fragmentation (aggregation-dominated). We use matched asymptotic expansions to construct approximations to the cluster size-distribution as it evolves from purely monomeric initial data to the equilibrium solution in which the typical cluster size is extremely large. We compare the results with earlier calculations of a similar limit in the standard Becker–Döring system, and find a similar sequence of timescales with similar profile shapes; however, there are notable differences in the kinetic behaviour within timescales due to the modified system having a fragmentation rate which depends on the total number of clusters present in the system.

PACS numbers: 64.60.–Q, 6490.+b, 05.90.+m

## 1. Introduction

In 1935, Becker and Döring [3] constructed a mathematical description of the nucleation process which enabled the calculation of the rate of creation of cluster nuclei in steady-state which occurs due to the simultaneous processes of condensation and evaporation of a single monomer unit at a time. The original formulation of this model considered a box into which monomers were continually added so that the monomer concentration remained constant. This can be interpreted as a phase transition in which a supersaturated gas is condensing to form liquid droplets at constant pressure.

The constant mass formulation proposed by Penrose and Lebowitz [19] considers a fixed amount of matter in a box of fixed volume. This leads to the ‘constant mass’ or, equivalently termed ‘constant density’ formulation. As the transition proceeds from the pure monomer state to a developing population of clusters, the concentration of monomers

decreases. However, from a thermodynamic point of view, the Lyapunov function for the system originally proposed has an unusual form. Dreyer and Duderstadt find that by modifying the aggregation or fragmentation rates slightly, a modified Becker–Döring system is obtained which has a Lyapunov function consistent with the free energy that one would expect from thermodynamic principles. This modified system has been analysed by Hermann *et al* [12].

Part of the success of the Becker–Döring equations is their versatility, and ease of modification to apply to more general scenarios, for example, multicomponent nucleation [23, 24], the presence of inhibitors and multiple morphologies of crystal [5, 21], the presence of dimer-cluster interactions in addition to those between clusters and monomers. However, their complexity leads to considerable difficulty in solving the resulting systems of equations [9, 13, 22], and so any analytic methods which provide accurate approximations are especially welcome.

The most familiar of these is the relationship between the Becker–Döring equations and the Lifshitz–Slyozov–Wagner (LSW) theory of late-stage droplet formation, as discussed, for example by Penrose [18], Niethammer [15], and Niethammer and Pego [16, 17]. Farjoun and Neu use this LSW theory [11] in analysing a model of the end of an isothermal nucleation process in a closed system. Their asymptotic calculations rely on a small supersaturation. More recently, Fajoun [10] has used asymptotic techniques to analyse the nucleation due to a thermal quench in which clusters grow according to Becker–Döring kinetics. Further asymptotic analyses of nucleation over a barrier are described by Neu *et al* [14] and Bonilla *et al* [6].

### 1.1. The standard Becker–Döring system with constant monomer concentration

The original Becker–Döring equations for nucleation were proposed in 1935 [3]; in this formulation only cluster-monomer reactions are permitted (that is,  $C_r + C_1 \rightleftharpoons C_{r+1}$ , where  $C_r$  represents a cluster of size  $r$ ). We write

$$\frac{dc_r}{dt} = J_{r-1} - J_r, \quad (r \geq 2), \quad J_r = a_r c_r c_1 - b_{r+1} c_{r+1}, \quad (r \geq 1), \quad (1.1)$$

where  $c_r(t)$  is the concentration of clusters of size  $r$  at time  $t$  (that is,  $[C_r]$ ),  $a_r$  is the rate of the forward (aggregation) process and  $b_{r+1}$  is the rate of the reverse (fragmentation) process. In [3] a constant monomer concentration ( $c_1$ ) was assumed. The steady nucleation rate ( $J_{\text{nuc}}$ ) can then easily be computed as

$$\frac{1}{J_{\text{nuc}}} = \sum_{r=1}^{\infty} \frac{1}{a_r Q_r c_1^{r+1}}. \quad (1.2)$$

Here  $Q_r$  is the partition function, which satisfies  $Q_1 = 1$  and  $a_r Q_r = b_{r+1} Q_{r+1}$ .

### 1.2. The standard Becker–Döring system with constant total mass

A more difficult problem was posed by Penrose and Lebowitz [19] who proposed that as clusters nucleate, the monomer concentration should decrease and, so they formulated the constant total mass system in which (1.1) is augmented by

$$\frac{dc_1}{dt} = -J_1 - \sum_{r=1}^{\infty} J_r. \quad (1.3)$$

With this condition, the total mass in the system  $\varrho = M_1 = \sum_{r=1}^{\infty} r c_r$  is time-independent.

Both formulations support a unique equilibrium solution of the form  $c_r^{\text{eq}} = Q_r c_1^r$ . Furthermore, each formulation also possesses a Lyapunov function (free energy) which monotonically decreases in time

$$V_{\text{BD}} = \sum_{r=1}^{\infty} c_r \left( \log \left( \frac{c_r}{Q_r c_1^r} \right) - 1 \right), \quad V_{\text{PL}} = \sum_{r=1}^{\infty} c_r \left( \log \left( \frac{c_r}{Q_r} \right) - 1 \right). \quad (1.4)$$

The former ( $V_{\text{BD}}$ ) is for the original system (1.1) with  $c_1$  fixed; and the latter ( $V_{\text{PL}}$ ) applies to the constant total mass system (1.1) with (1.3). A more detailed introduction to the Becker–Döring equations can be found in [20].

### 1.3. The modified Becker–Döring system with constant mass

The problem we study in this paper is a constant mass Becker–Döring system in which the fragmentation term has been modified in line with the reformulation proposed by Dreyer and Duderstadt [8], that is,

$$\frac{dc_1}{dt} = -J_1 - \sum_{r=1}^{\infty} J_r \quad (1.5)$$

$$\frac{dc_r}{dt} = J_{r-1} - J_r \quad (1.6)$$

$$J_r = a_r c_1 c_r - b_{r+1} N(t) c_{r+1}. \quad (1.7)$$

Here we define the general  $k$ th moments by

$$M_k(t) = \sum_{r=1}^{\infty} r^k c_r, \quad (1.8)$$

so that the zeroth moment, which is the total number of clusters in the system, is given by

$$N(t) = M_0(t) = \sum_{r=1}^{\infty} c_r. \quad (1.9)$$

The inclusion of this in the quantity in the fragmentation term in (1.7) is what makes (1.5)–(1.7) distinct from the standard Becker–Döring equations [19]. The number  $N$  evolves according to

$$\frac{dN}{dt} = - \sum_{r=1}^{\infty} J_r. \quad (1.10)$$

The system (1.5)–(1.7) has several useful properties which are important in applications. First, the first moment of the distribution,  $M_1$  (1.8) is conserved. This quantity is referred to as the ‘mass’ or ‘density’ of the system. Second, the quantity

$$V(\{c_r\}) = \sum_{r=1}^{\infty} c_r \log \left( \frac{c_r}{Q_r N} \right), \quad (1.11)$$

is a Lyapunov function for the system; here  $Q_r$ , defined by

$$a_r Q_r = b_{r+1} Q_{r+1}, \quad Q_1 = 1, \quad (1.12)$$

is the partition function. Equation (1.11) implies

$$\frac{dV}{dt} = - \sum_{r=1}^{\infty} J_r \log \left( \frac{a_r c_r c_1}{b_{r+1} c_{r+1} N} \right), \quad (1.13)$$

which is negative at all non-equilibrium points since  $(x - y)(\log x - \log y) \geq 0$ .

There is a family of solutions of the form

$$c_r^{\text{eq}} = N Q_r \left( \frac{c_1}{N} \right)^r, \quad (1.14)$$

which automatically satisfies  $J_r = 0$  and  $c_1 = c_1$ . The quantities  $N$  and  $c_1$  then need to be found to satisfy the mass condition  $\varrho = \sum_{r=1}^{\infty} r c_r^{\text{eq}}$  and the self-consistency condition  $N = \sum_{r=1}^{\infty} c_r^{\text{eq}}$ . This pair of constraints can be rewritten as

$$\varrho = \sum_{r=1}^{\infty} r N Q_r \left( \frac{c_1}{N} \right)^r, \quad 1 = \sum_{r=1}^{\infty} Q_r \left( \frac{c_1}{N} \right)^r, \quad (1.15)$$

or, by introducing  $z = c_1/N$ , can be expressed as a sequence of single-variable problems, for  $z$ ,  $N$ , and then  $c_1$ , via

$$\sum_{r=1}^{\infty} Q_r z^r = 1, \quad N = \frac{\varrho}{\sum_{r=1}^{\infty} r Q_r z^r}, \quad c_1 = N z. \quad (1.16)$$

As noted by Ball, Carr and Penrose [2], it is possible that such a system does not have a solution. For example, if the aggregation and fragmentation rates  $(a_r, b_r)$  are such that the left-hand side of (1.16) is the power series expansion of  $\frac{1}{2}(1 - \sqrt{1-z})$ , then no real value of  $z$  (in  $0 \leq z \leq 1$ ) can satisfy the equation. There is then a maximum (or critical) mass which the system can support at equilibrium. This lack of an equilibrium solution is known as ‘metastability’. If, at  $t = 0$ , there is a mass in excess of this critical value, then the excess is converted into clusters of ever increasing size. However, the problem considered here, where the rate constants are size-independent, does not suffer from these metastability problems.

In the following section we analyse this system of equations in the asymptotic limit of small fragmentation with initial data of the form  $c_1(0) = \varrho$ ,  $c_r(0) = 0$  for all  $r \geq 2$ . This corresponds to a phase transition, since the system is initiated from the pure monomer state, and the rate coefficients are heavily biased to the formation of clusters with large size, since the aggregation rates are much larger than the fragmentation rates. Using matched asymptotic expansions it is possible to construct a solution and follow the behaviour of the system over several timescales and determine the evolution of the cluster size distribution as it evolves towards the equilibrium solution.

#### 1.4. The modified system with constant monomer concentration

The above system is a constant mass formulation; as with the standard Becker–Döring equations, it is also possible to pose a constant monomer concentration form of the problem. In this case we have

$$\frac{dc_r}{dt} = J_{r-1} - J_r, \quad J_r = a_r c_r c_1 - b_{r+1} N c_{r+1}, \quad (1.17)$$

where the fluxes  $J_r$  are defined for all  $r \geq 1$  and the concentrations given by (1.17) only for  $r \geq 2$  and  $c_1$  is a given parameter. Although this form of the problem is potentially less relevant in physical applications, it provides an instructive mathematical problem as a precursor to the analysis of the more demanding constant mass problem (1.5)–(1.7).

In the formulation (1.17) both the number of clusters and the total mass in the system vary. The quantities  $N = M_0 = \sum_{r=1}^{\infty} c_r$  and  $\varrho = M_1 = \sum_{r=1}^{\infty} r c_r$  satisfy

$$\frac{dN}{dt} = J_1, \quad \frac{d\varrho}{dt} = J_1 + \sum_{r=1}^{\infty} J_r. \quad (1.18)$$

In the standard Becker–Döring system, the constant monomer concentration had a one-parameter family of steady-state solutions, in addition to the equilibrium solution. However,

due to the inclusion of  $N(t)$  in this modified formulation (1.17), the only time-independent solution is the equilibrium solution. The time-dependence of  $N$  also hinders the finding of Lyapunov function (free energy) for the system. The candidate function

$$V_{\text{trial}} = \sum_{r=1}^{\infty} c_r \log \left( \frac{c_r N^r}{Q_r c_1^r} \right) + f(N), \quad (1.19)$$

does not qualify since

$$\frac{dV_{\text{trial}}}{dt} = \frac{J_1}{N} (N + \varrho + N \log N + f'(N)) + \sum_{r=1}^{\infty} J_r \log \left( \frac{b_{r+1} N(t) c_{r+1}}{a_r c_1 c_r} \right). \quad (1.20)$$

Whilst the sum in (1.20) is negative-definite, the remaining term (involving  $J_1$ ) cannot be made so, since both  $N$  and  $\varrho$  are time-dependent. Introducing  $\varrho$ -dependence into  $f(\cdot)$  would also introduce  $\sum_r J_r$  into  $dV_{\text{trial}}/dt$ .

### 1.5. The modified Becker–Döring system with size-independent rate coefficients

Here we analyse the case  $a_r = a, b_r = b$  and, for simplicity, we formulate the problem using a timescale in which  $a = 1$ , and  $b = \varepsilon$ . The partition function is given by  $Q_r = (a/b)^{r-1} = \varepsilon^{1-r}$ . Later we consider the kinetics of aggregation in the case  $\varepsilon \ll 1$  and where  $\varrho = \mathcal{O}(1)$ .

In section 2 we study the constant monomer formulation of the problem (1.17) in which  $c_1$  is given. We thus aim to solve

$$\frac{dN}{dt} = c_1^2 - \varepsilon N c_2, \quad \frac{dc_r}{dt} = c_1 c_{r-1} - c_1 c_r - \varepsilon N c_r + \varepsilon N c_{r+1}. \quad (1.21)$$

In the original formulation, there is a one-parameter family of steady-state solutions for this case given by  $J_r(t) = J_{\text{sss}}$  for any value of  $J_{\text{sss}}$ . Since the modified kinetic equations (1.17) include  $N(t)$ , there can only be a steady-state if  $N(t)$  itself asymptotes to a constant. However,  $dN/dt = J_1$ , so this can only be steady if  $J_r = 0$  for all  $r$ , which is the equilibrium solution. Hence there are no steady-states other than the equilibrium solution.

We then proceed, in section 3, to analyse the kinetics of the constant mass formulation of the modified Becker–Döring system (1.5)–(1.7); that is,

$$\frac{dc_r}{dt} = c_1 c_{r-1} - c_1 c_r - \varepsilon N c_r + \varepsilon N c_{r+1}, \quad (1.22)$$

$$\frac{dc_1}{dt} = N(\varepsilon N - c_1 - \varepsilon c_1) - c_1^2 + \varepsilon N c_2, \quad \frac{dN}{dt} = N(\varepsilon N - c_1 - \varepsilon c_1). \quad (1.23)$$

The Lyapunov function for the constant mass case is then

$$V = \sum_{r=1}^{\infty} c_r \log \left( \frac{c_r}{Q_r N} \right) = \sum_{r=1}^{\infty} c_r \log c_r - N \log N + (\varrho - N) \log \varepsilon. \quad (1.24)$$

However, for the remainder of this section, we make no assumption on the size of  $\varepsilon$  and calculate the equilibrium solution. In both cases, the equilibrium solution has the form

$$N = \frac{\varepsilon \varrho}{(1 + \varepsilon)}, \quad c_r^{\text{eq}} = \frac{\varepsilon^2 \varrho}{(1 + \varepsilon)^{r+1}}, \quad V_{\text{eq}} = \varrho \log \frac{\varepsilon}{1 + \varepsilon}, \quad (1.25)$$

hence the average cluster size is  $\varrho/N = \varepsilon^{-1} + 1$ .

1.6. The original constant mass system with size-independent rate coefficients

For the aggregation-dominated form of the standard constant-mass formulation (1.1)–(1.3), an asymptotic solution of the evolution of the cluster-size distribution has been constructed in section 4 of [22]. We now summarize the relevant results of that paper. To ease the comparison of the original system with the modified system considered in section 3, we transform the results quoted in [22] using  $a_r = 1, b_r = \varepsilon^2 \ll 1$  for all  $r$  (rather than  $b_r = \varepsilon \ll 1$  which is used in [22]). We impose initial data in which all material is in monomeric form ( $c_1(0) = \varrho > 0, c_r(0) = 0 \forall r > 1$ ), the solution passes through four timescales.

During the first timescale ( $T_1$ ),  $t = \mathcal{O}(1)$  and nearly all the monomer is exhausted as clusters are created (with distribution  $c_r = (\varrho(r-1)/e^r!)$ ). The second ( $T_2$ ) is also an  $\mathcal{O}(1)$  timescale but shifted by a time of  $(2e/\varrho) \log(1/\varepsilon)$  over which the monomer concentration saturates to an  $\mathcal{O}(\varepsilon^2)$  level. During the third timescale ( $T_3$ ),  $t = \mathcal{O}(1/\varepsilon^2)$ , the size distribution changes so that larger clusters are formed at the expense of the dissolution of smaller clusters. Towards the end of this timescale, the size-distribution evolves according to the similarity solution  $c_r(t) \sim \varrho r e^{-r^2/4t_3}/2\sqrt{\pi}t_3^{3/2}$  where  $t_3 = \varepsilon^2 t$ . Finally ( $T_4$ ), when  $t = \mathcal{O}(1/\varepsilon^4)$ , the system approaches its equilibrium configuration in which

$$c_1^{\text{eq}} = \varepsilon^2 \left( 1 + \frac{\varepsilon^2}{2\varrho} - \frac{\varepsilon}{\varrho} \sqrt{4\varrho + \varepsilon^2} \right) \sim \varepsilon^2 \left( 1 - \frac{1}{\sqrt{\varrho}} \right), \quad (1.26)$$

$$c_r^{\text{eq}} = \varepsilon^{2-2r} c_1^r \sim \varepsilon^2 e^{-r\varepsilon/\sqrt{\varrho}}, \quad N^{\text{eq}} \sim \varepsilon\sqrt{\varrho}. \quad (1.27)$$

The number of clusters is defined by  $N = \sum_{r=1}^{\infty} c_r$ , and satisfies

$$\frac{dN}{dt} = c_1 N - \varepsilon^2 (N - c_1). \quad (1.28)$$

In the first three timescales,  $N = \mathcal{O}(1)$  and it falls to  $\mathcal{O}(\varepsilon)$  in the last.

For size-independent rate coefficients, the free energy  $V = V_{PL}$  (1.4) has the form

$$V = \sum_{r=1}^{\infty} c_r \log c_r - N + 2(\varrho - N) \log \varepsilon. \quad (1.29)$$

Taken together with the equilibrium solution

$$c_r = \varepsilon^{2(1-r)} c_1^r, \quad \text{with} \quad c_1 = \frac{2\varrho\varepsilon^2}{2\varrho + \varepsilon^2 + \varepsilon\sqrt{4\varrho + \varepsilon^2}} \sim 1 - \frac{\varepsilon}{\sqrt{\varrho}}, \quad (1.30)$$

equation (1.29) implies that

$$V_{\text{eq}} \sim -2\varrho \log \frac{1}{\varepsilon} - 2\varepsilon\sqrt{\varrho}. \quad (1.31)$$

We use the notation  $V_{T_n}$  to denote the free energy in the timescale  $T_n$ . Over the four timescales, this implies that the free energy difference  $V_{T_n} - V_{\text{eq}}$  evolves such that

$$V_{T=0} - V_{\text{eq}} \sim 2\varrho \log \frac{1}{\varepsilon} + \varrho(\log \varrho - 1), \quad (1.32)$$

$$V_{T_2} - V_{\text{eq}} \sim \frac{2\varrho}{e} \log \frac{1}{\varepsilon}, \quad (1.33)$$

$$V_{T_3\text{end}} - V_{\text{eq}} \sim \frac{\varrho}{\sqrt{\pi}t_3} \left( 2 \log \frac{1}{\varepsilon} + \log \frac{\varrho}{t_3\sqrt{\pi}} - 2 - \frac{1}{2}\gamma \right), \quad (1.34)$$

where  $t_3 = \varepsilon^2 t$  is the scaled time variable in the third timescale, and  $\gamma$  is Euler's constant ( $\gamma \approx 0.5772$ ) [1]. We observe a rapid and considerable drop in  $V$  over the first timescale, to  $1/e$  of its initial value. There is almost no decrease over the second as only the monomer concentration changes there. Near the end of the third timescale the leading order free energy difference loses its  $\mathcal{O}(\log(1/\varepsilon))$  magnitude, the difference reducing to  $\mathcal{O}(1)$  in the fourth timescale. However, considerable changes in the shape of the distribution function still have to occur before equilibrium is achieved.

## 2. Asymptotic analysis—the constant monomer system

In this section we consider the constant monomer concentration system, that is, where  $c_1$  is a prescribed constant. We analyse the case where both the aggregation and fragmentation rates are size-independent, specifically,  $a_r = 1$  for all  $r$ , and  $b_r = \varepsilon \ll 1$ , so that fragmentation is weak. The initial conditions we assume are  $c_r(0) = 0$  for all  $r \geq 2$ .

### 2.1. Timescale T1: $t = \mathcal{O}(1)$

In this timescale, fragmentation is negligible at leading order, hence we aim to solve

$$\frac{dN}{dt} = c_1^2, \quad \frac{dc_r}{dt} = c_1(c_{r-1} - c_r). \quad (2.1)$$

This has the solution  $N = c_1 + c_1^2 t$ . At large times, the concentrations asymptote to

$$c_r \sim \frac{1}{2} c_1 \operatorname{erfc}\left(\frac{r - c_1 t}{\sqrt{2c_1 t}}\right). \quad (2.2)$$

This is because for  $r = \mathcal{O}(1)$  the distribution becomes uniform  $c_r = c_1$ , and at large cluster sizes, the distribution is slowly-varying in  $r$ , so can be approximated by the partial differential equation

$$\frac{\partial c}{\partial t} = c_1 \left( -\frac{\partial c}{\partial r} + \frac{1}{2} \frac{\partial^2 c}{\partial r^2} \right), \quad (2.3)$$

whose solution is (2.2).

This timescale ends due to the growth in  $N$  causing the fragmentation terms  $\varepsilon N c_r$  to become significant. This occurs when  $t = \mathcal{O}(1/\varepsilon)$ , hence this is the next timescale we investigate.

### 2.2. Timescale T2: $t = \mathcal{O}(1/\varepsilon)$

For the second timescale we define

$$t_2 = \varepsilon t, \quad r_2 = \varepsilon r, \quad N = \varepsilon^{-1} N_2, \quad c_r(t) = c(r_2, t_2) = \mathcal{O}(1), \quad (2.4)$$

since at the end of T1, the front has reached cluster sizes of magnitude  $r = \mathcal{O}(1/\varepsilon)$ , and the total number of clusters ( $N$ ) has also reached  $\mathcal{O}(1/\varepsilon)$ , hence the introduction of the  $\mathcal{O}(1)$  quantity  $N_2 = \varepsilon N$ .

For  $r = \mathcal{O}(1)$  we have

$$\varepsilon \frac{dc_r}{dt_2} = c_1(c_{r-1} - c_r) + N_2(c_{r+1} - c_r). \quad (2.5)$$

This is a recurrence relation with the solution  $c_r = A + B(c_1/N_2)^r$ . In order to match with the solution at the end of T1, we impose  $B = 0$  and  $A = c_1$ . Hence at leading order, the concentrations  $c_r$  are simply given by  $c_r = c_1$ .



The equation for the rescaled number of clusters  $N_2$  is

$$\frac{dN_2}{dt_2} = c_1^2 - N_2 c_2, \quad (2.6)$$

which is solved by  $N_2 = c_1(1 - e^{-c_1 t_2})$ . The concentrations of larger clusters ( $r = \mathcal{O}(1/\varepsilon)$  or  $r_2 = \mathcal{O}(1)$ ) are determined by

$$\frac{\partial c}{\partial t_2} = (N_2 - c_1) \frac{\partial c}{\partial r_2} + \frac{1}{2} \varepsilon (N_2 + c_1) \frac{\partial^2 c}{\partial r_2^2}. \quad (2.7)$$

The solution to the leading order problem is

$$c(r_2, t_2) = f(r_2 - (1 - e^{-c_1 t_2})), \quad (2.8)$$

for some shape function  $f(\cdot)$ . Writing  $z = r_2 - (1 - e^{-c_1 t_2})$  and including the first-correction term, (2.7) becomes

$$\frac{\partial c}{\partial t_2} = \varepsilon c_1 \frac{\partial^2 c}{\partial z^2} \left(1 - \frac{1}{2} e^{-c_1 t_2}\right), \quad (2.9)$$

which has the solution

$$c_r(t) = c(r_2, t_2) = \frac{1}{2} \operatorname{erfc} \left( \frac{r_2 - (1 - e^{-c_1 t_2})}{\sqrt{2\varepsilon[2c_1 t_2 - (1 - e^{-c_1 t_2})]}} \right). \quad (2.10)$$

This describes a front which separates two regimes,  $c_r = c_1$  for  $r < s(t)$  and  $c_r \approx 0$  for  $r > s(t)$ . The front, which propagated to larger sizes at a rate  $r = c_1 t$  in T1, in T2 slows and reaches a halt as  $r \rightarrow 1/\varepsilon$ .

### 2.3. Timescale T3: $t = \mathcal{O}(1/\varepsilon^2)$

At the end of T2, the transition region slows as  $r_2 \rightarrow 1^-$  becoming stationary in this limit. The width of the region scales with  $\sqrt{t_2}$ , hence a new timescale is required when  $t_2 = \mathcal{O}(\varepsilon^{-1})$ , which is equivalent to  $t = \mathcal{O}(\varepsilon^{-2})$ . Hence for the third timescale, T3, we define

$$r_3 = \varepsilon r, \quad t_3 = \varepsilon^2 t, \quad N = \varepsilon^{-1} N_3, \quad c_r(t) = c(r_3, t_3) = \mathcal{O}(1). \quad (2.11)$$

The governing equations are

$$\varepsilon \frac{dN_3}{dt_3} = c_1^2 - c_2 N_3, \quad (2.12)$$

which implies  $N_3 = c_1^2/c_2$  and, for  $r = \mathcal{O}(1)$ ,

$$\varepsilon^2 \frac{dc_r}{dt_3} = c_1(c_{r-1} - c_r) + \frac{c_1^2}{c_2}(c_{r+1} - c_r), \quad (2.13)$$

hence

$$c_r = c_1 [1 - \varepsilon(r - 1)\beta(t_3)], \quad (2.14)$$

for some function  $\beta(t_3)$ . This implies  $N_3 \sim c_1(1 + \varepsilon\beta(t_3))$ .

For  $r = \mathcal{O}(\varepsilon^{-1})$  we have

$$\frac{1}{c_1} \frac{\partial c}{\partial t_3} = \frac{\partial^2 c}{\partial r_3^2} + \beta(t_3) \frac{\partial c}{\partial r_3}. \quad (2.15)$$

Over this timescale, the system approaches equilibrium, which is given by  $c = c_1 e^{-\beta(t_3)r_3}$ . This implies that  $N_3 = \int_0^\infty c dr_3$ , and so  $\beta(t_3) \rightarrow 1$  as  $t_3 \rightarrow \infty$ .

### 3. Asymptotic analysis—the constant density system

We initiate the system from the configuration in which all mass is present in monomeric form, that is

$$c_r(0) = 0 \quad \text{for all } r > 1, \quad c_1(0) = \varrho. \quad (3.1)$$

#### 3.1. Timescale T1: $t = \mathcal{O}(1)$

We assume that all quantities are  $\mathcal{O}(1)$ , and hence at leading order obtain

$$\frac{1}{c_1} \frac{dc_r}{dt} = c_{r-1} - c_r, \quad \frac{1}{c_1} \frac{dN}{dt} = -N, \quad \frac{1}{c_1} \frac{dc_1}{dt} = -c_1 - N. \quad (3.2)$$

We transform by introducing a new timescale  $t_1$  defined such that  $(1/c_1)\partial_t = \partial_{t_1}$ , hence  $t = \int_0^{t_1} (1/c_1(t'_1)) dt'_1$ , or

$$t = -\frac{e}{\varrho} (E_1(1) - E_1(1 - t_1)), \quad (3.3)$$

where  $E_1(\cdot)$  is the exponential integral (for details see Abramowitz & Stegun [1], equation (5.1.1)). Then  $N = \varrho e^{-t_1}$ ,  $c_1 = \varrho(1 - t_1) e^{-t_1}$  and

$$c_r = \left( \frac{t_1^{r-1}}{(r-1)!} - \frac{t_1^r}{r!} \right) e^{-t_1}. \quad (3.4)$$

This timescale ends due to  $c_1$  becoming small, which occurs as  $t_1 \rightarrow 1$ , corresponding to  $t \rightarrow \infty$ .

Since  $E_1(z) \sim \log(z) + \gamma + z + \dots$  as  $z \rightarrow 0$ , the asymptotic expansion of (3.3) is  $t = -(e/\varrho) \log(1 - t_1) + \mathcal{O}(1)$  so that as  $t_1 \rightarrow 1$ , we have  $t \rightarrow +\infty$ . In particular,  $c_1 = \mathcal{O}(\varepsilon)$  when  $t = \mathcal{O}(-(e/\varrho) \log \varepsilon)$ . Hence at the end of T1,

$$N \rightarrow \frac{\varrho}{e}, \quad c_r \rightarrow \frac{\varrho(r-1)}{er!}, \quad (3.5)$$

and a new timescale is required for  $t = -(e/\varrho) \log \varepsilon + \mathcal{O}(1)$ .

#### 3.2. Timescale T2: $t = \frac{e}{\varrho} \log\left(\frac{1}{\varepsilon}\right) + \mathcal{O}(1)$

In this timescale, we find that the monomer concentration does not vanish, but rather saturates at a small ( $\mathcal{O}(\varepsilon)$ ) value. We assume  $c_1 = \varepsilon m_2$ ,  $m_2 = \mathcal{O}(1)$  and find

$$\frac{dc_r}{dt} = \varepsilon (m_2 c_{r-1} - m_2 c_r - N c_r + N c_{r+1}), \quad (3.6)$$

$$\frac{dN}{dt} = \varepsilon (N^2 - \varepsilon N m_2 - m_2 N), \quad (3.7)$$

$$\frac{dm_2}{dt} = (N^2 + N c_2 - m_2 N) - \varepsilon m_2 (1 + N). \quad (3.8)$$

Although  $t$  is large,  $m_2$  evolves at the same rate as  $c_1$  in T1; hence, this timescale is given by  $t_2 = t + (e/\varrho) \log \varepsilon$ . All  $c_r(t)$  for  $r \geq 2$  are fixed at the values they take at the end of T1; only the monomer concentration evolves significantly on this timescale. In the limit of large  $t_2$ , the rescaled monomer concentration  $m_2$  approaches the value  $N + c_2$ , according to

$$m_2 = N + c_2 + A \exp(-N t_2) = \frac{3\varrho}{2e} + A e^{-\varrho t_2/e}, \quad (3.9)$$

for some constant  $A$ .

In summary, at the end of T2, we have

$$c_1 \rightarrow \frac{3\varepsilon\rho}{2e}, \quad c_r = \frac{\rho(r-1)}{er!}, \quad N = \frac{\rho}{e}, \quad (3.10)$$

and since all concentrations have reached pseudo-steady-states (but not the equilibrium solution), the next timescale must be a longer timescale over which evolution occurs more slowly.

### 3.3. Timescale T3: $t = \mathcal{O}(1/\varepsilon)$

Since all concentrations are saturated at the end of T2, the new timescale T3 describes much slower kinetic behaviour. In the above calculation (3.6)–(3.7), we observe that all concentrations (except  $c_1$ ) are  $\mathcal{O}(1)$  and evolving over a timescale of  $\mathcal{O}(1/\varepsilon)$  hence we introduce

$$t_3 = \varepsilon t, \quad c_1(t) = \varepsilon m_3(t_3), \quad t_3, m_3 = \mathcal{O}(1). \quad (3.11)$$

We require that  $c_1$  continues to be scaled with  $\varepsilon$  and is given by  $c_1 = \varepsilon m_3 = \varepsilon(N + c_2)$ . Since the equation for the monomer concentration can be written

$$\varepsilon \frac{dm_3}{dt_3} = N(N + c_2 - m_3) - \varepsilon N m_3 - \varepsilon m_3^2, \quad (3.12)$$

we impose  $m_3 = N + c_2$ , that is, the monomer concentration  $m_3$  is slaved to  $N$  and  $c_2$ . Although this gives a similar result to that at the end of the previous timescale, there  $N$  and  $c_2$  were both constants (3.9); note that in the timescale T3, both  $N$  and  $c_2$  vary with the new, slow, time variable  $t_3$ .

The other quantities evolve according to

$$\frac{dN}{dt_3} = N(N - m_3 - \varepsilon m_3 N) \sim -Nc_2, \quad (3.13)$$

$$\frac{dc_r}{dt_3} = N(c_{r+1} - 2c_r + c_{r-1}) + c_2(c_{r-1} - c_r), \quad (3.14)$$

$$\frac{dc_2}{dt_3} = N(c_3 - 2c_2) - c_2^2. \quad (3.15)$$

At the start of this timescale, most of the mass in the system is in clusters of size  $r = \mathcal{O}(1)$ . It is not possible to describe fully the dynamics throughout this region, but we are able to determine the behaviour at the end of the timescale, where all the concentrations become small and, through aggregation, the mass in the system spreads to clusters of large size.

Whilst the equation (3.14) is valid for  $r = \mathcal{O}(1)$ , for larger aggregation numbers, a simpler form is available. We treat the aggregation number as a continuous variable, and replace (3.13)–(3.14) by

$$\frac{\partial c}{\partial t_3} = \left( N(t_3) + \frac{1}{2} c_2(t_3) \right) \frac{\partial^2 c}{\partial r^2} - c_2(t_3) \frac{\partial c}{\partial r}, \quad \frac{dN}{dt_3} = -Nc_2. \quad (3.16)$$

We should now determine which term on the right-hand side of the first equation is dominant. We assume that  $N$  dominates  $c_2$ , and return later to verify this; the concentration profile will be assumed to have the form

$$c_r(t) = g(t_3) f(\eta), \quad \text{where} \quad \eta = \frac{r}{s(t_3)} = \mathcal{O}(1). \quad (3.17)$$

This relationship specifies the rescaled cluster size. We assume that  $s(t_3) \sim \varrho/N(t_3)$  since this is the typical cluster size in the system. This condition yields the relation  $g \sim 1/s^2$ , which is equivalent to the condition that  $\varrho = M_1$  is  $\mathcal{O}(1)$  and time-invariant.

Using dots to denote derivatives with respect to  $t_3$ , the governing equation for the size-distribution implies

$$\frac{t_3 \dot{g}}{g} f - \frac{t_3 \dot{s}}{s} \eta f'(\eta) = \frac{t_3 g}{s} \Phi_0 f'' - \frac{1}{s} f'(\eta), \quad (3.18)$$

where  $\Phi_0 = \int_{\eta=0}^{\infty} f(\eta) d\eta$ . At large times, both terms on the lhs ( $t_3 \dot{g}/g$  and  $t_3 \dot{s}/s$ ) asymptote to  $\mathcal{O}(1)$  constants; on the rhs, the dominant balance will be with the first term whilst the second term vanishes in the large time limit. Imposing  $t_3 g \sim s$  with  $g \sim 1/s^2$  implies

$$s = t_3^{1/3} (1 + o(1)), \quad \text{and} \quad g = t_3^{-2/3} (1 + o(1)) \quad \text{as} \quad t_3 \rightarrow \infty. \quad (3.19)$$

This leaves the equation

$$3\Phi_0 \frac{d^2 f}{d\eta^2} + \eta \frac{df}{d\eta} + 2f = 0, \quad (3.20)$$

for the size-distribution function, which has the solution

$$f(\eta) = C \eta \exp\left(-\frac{\eta^2}{6\Phi_0}\right). \quad (3.21)$$

The constant  $C$  is determined by the consistency condition  $\Phi_0 = \int_0^\infty f(\eta) d\eta$  which implies  $C = 1/3$ . The quantity  $\Phi_0$  is determined by mass conservation

$$\varrho = \sum_{r=1}^{\infty} r c_r = g s^2 \int_0^\infty \eta f(\eta) d\eta = \frac{1}{2} \sqrt{6\pi} \Phi_0^{3/2}, \quad (3.22)$$

hence  $\Phi_0 = (2\varrho^2/3\pi)^{1/3}$  and so

$$f(\eta) = \frac{1}{3} \eta \exp\left(-\frac{\pi^{1/3} \eta^2}{(12\varrho)^{2/3}}\right). \quad (3.23)$$

To summarize, towards the end of T3 ( $t_3 \rightarrow \infty$ ), the solution behaves according to

$$\begin{aligned} c_r &\sim t_3^{-2/3} f(r/t_3^{1/3}), & \text{for } r = \mathcal{O}(t_3^{1/3}), \\ c_r &\sim \frac{1}{3}(r-1)t_3^{-1}, & \text{for } r = \mathcal{O}(1), \\ c_1 &\sim \varepsilon \Phi_0 t_3^{-1/3}, & N \sim \Phi_0 t_3^{-1/3}. \end{aligned} \quad (3.24)$$

The relation for  $c_r$ ,  $r = \mathcal{O}(1)$  is due to  $f(0) = 0$  and  $f'(0) = \frac{1}{3}$ . For  $r = \mathcal{O}(1)$ , since  $c_r = \mathcal{O}(1/t_3)$  and  $N = \mathcal{O}(t_3^{-1/3})$ , the leading order terms in (3.14) are  $c_{r+1} - 2c_r + c_{r-1} = 0$ , which implies  $c_r = (A + Br)/t$ . Equation (3.15) implies  $c_3 = 2c_2$  hence  $A = -B$ , and we find  $B = 1/3$  by matching to the outer solution.

We recall that throughout T3, we have  $m = N + c_2$ , so that  $c_1 = \varepsilon(N + c_2)$ . Whilst at the start of T3,  $N$  and  $c_2$  are of similar magnitudes, at the end,  $N$ , being  $\mathcal{O}(t_3^{-1/3})$ , dominates  $c_2$ , since  $c_2(t_3) = -(1/N) dN/dt_3 = \mathcal{O}(t_3^{-1})$  is a small correction term in comparison with  $N(t_3)$ . This confirms the assumption on which the solution was derived.

### 3.4. Timescale T4: $t = \mathcal{O}(1/\varepsilon^{5/2})$

The kinetics over this timescale is a simple extension of that observed towards the end of T3; however, deducing the form of behaviour is not trivial. As well as assuming the form of  $N$  and  $c_1$ , we consider two parts of the size-distribution,  $c_r(t)$ . To determine the correct scalings for

the new timescale we assume  $t_3^{-1/3} = \varepsilon^p$ , that is  $t_3 = \varepsilon^{-3p}$ , then, balancing terms in the next region, T4, we expect  $p = \frac{1}{2}$ . Hence we introduce

$$\begin{aligned} c_1 &= \varepsilon^{3/2} m_4, & N &= \varepsilon^{1/2} N_4, & t_4 &= \varepsilon^{5/2} t, \\ c_r &= \varepsilon^{3/2} n_r(t_4), & \text{for } r &= \mathcal{O}(1) \\ c_r &= \varepsilon n(r_4, t_4) & \text{for } r &= \varepsilon^{-1/2} r_4, \text{ with } r_4 = \mathcal{O}(1). \end{aligned} \tag{3.25}$$

This scaling implies that  $N_4 = \int_0^\infty n(r_4, t_4) dr_4$ .

An expansion of equations (1.23) for  $N$ , and the difference  $N - c_1$  leads to

$$\varepsilon \frac{dN_4}{dt_4} = N_4(N_4 - m_4 - \varepsilon m_4), \tag{3.26}$$

$$\frac{dN_4}{dt_4} = m_4^2 - N_4 n_2, \tag{3.27}$$

hence  $m_4(t_4) = N_4(t_4)$  and these quantities vary with  $t_4$ . After making use of  $m_4 = N_4$ , equation (1.22) for  $r = \mathcal{O}(1)$  implies

$$\varepsilon \frac{dn_r}{dt_4} = N_4 (n_{r-1} - 2n_r + n_{r+1}) + \mathcal{O}(\varepsilon), \tag{3.28}$$

together with  $m_4 = n_1 = N_4$ . Hence, at leading order, we have

$$n_r(t_4) = m_4(t_4) + (r - 1)B(t_4), \tag{3.29}$$

for some function  $B(t_4)$  to be determined later (see equation (3.34)).

After making use of  $m_4 = N_4$  once again, equation (1.22) for  $r = \mathcal{O}(\varepsilon^{-1/2})$  implies

$$\frac{\partial n}{\partial t_4} = N_4(t_4) \frac{\partial^2 n}{\partial r_4^2}, \tag{3.30}$$

which determines the shape and evolution of the size-distribution. The different scales chosen for  $c_r$  for  $r = \mathcal{O}(1)$  and  $r = \mathcal{O}(\varepsilon^{-1/2})$  mean that the boundary condition for  $n(r_4, t_4)$  in the limit  $r_4 \rightarrow 0$  is, to leading order,  $n(0, t_4) = 0$ . We also assume that  $n(r_4, t_4) \rightarrow 0$  as  $r_4 \rightarrow \infty$ .

Whilst equation (3.30) appears to be a conventional diffusion equation, the time-dependence of  $N_4$  means that the distribution evolves in a nonstandard fashion. However, we still expect to find similarity solutions of separable form. If we assume that  $n(r_4, t_4) = g(t_4)f(\eta)$  with  $\eta = r_4/h(t_4)$  then we find  $N_4 = g(t_4)h(t_4)\Phi_0$  where  $\Phi_0 = \int_0^\infty f(\eta) d\eta$ ; so for (3.30) to yield a separable solution for  $f(\eta)$  requires  $h(t_4) = t_4 g(t_4)$ . Conservation of density

$$\varrho = \int_0^\infty r_4 n(r_4, t_4) dr_4, \tag{3.31}$$

implies  $g(t_4)h(t_4)^2 = 1$ , hence  $h(t_4) = t_4^{1/3}$ ,  $g(t_4) = t_4^{-2/3}$  and  $m_4 = N_4 = \Phi_0 t_4^{-1/3}$ . The equation for  $f(\eta)$  where  $\eta = r_4/t_4^{1/3}$  is then

$$0 = 3\Phi_0 \frac{d^2 f}{d\eta^2} + \eta \frac{df}{d\eta} + 2f. \tag{3.32}$$

The solution of (3.32) is  $f = C\eta \exp(-\eta^2/6\Phi_0)$ ; imposing the definition of  $\Phi_0$  leads to  $C = 1/3$ . The quantity  $\Phi_0$  is determined by requiring that the total mass (or density)  $M_1$  is identical to that of the initial data ( $\varrho$ ). Applying (3.31) yields  $\varrho = \Phi_0^{3/2} \sqrt{3\pi}/2$ . Hence  $\Phi_0 = (2\varrho^2/3\pi)^{1/3}$ , and we obtain the similarity solution

$$n(r_4, t_4) = \frac{1}{3} t_4^{-2/3} \eta \exp\left(-\frac{\eta^2 \pi^{1/3}}{(12\varrho)^{2/3}}\right). \tag{3.33}$$

Equation (3.27), together with  $m_4 = N_4$  and (3.29) implies

$$\frac{dm_4}{dt_4} = m_4(m_4 - (m_4 + B)) = -m_4 B. \quad (3.34)$$

Since  $m_4 = \Phi_0 t_4^{-1/3}$ , we have  $B = 1/3t_4$ . Let us return to the size-distribution for smaller clusters ( $r = \mathcal{O}(1)$ ) as given by (3.29). Whilst both terms on the rhs are of the same magnitude in  $\varepsilon$ , at small times (small  $t_4$ ) the concentrations increase linearly with cluster size ( $r$ ); however, in the large-time limit, the first term on the rhs of (3.29) dominates the latter; and so over this timescale, the size distribution changes from one in which  $n_r$  increases with  $r$  to one which is uniform in  $r$ .

As a final confirmation of the scalings (3.25) we consider how this solution matches back into the previous timescale. Towards the end of T3, we have  $N \sim t_3^{-1/3} \sim \varepsilon^{-1/3} t^{-1/3}$  as  $t_3 \rightarrow \infty$ . The above solution implies (for all  $t_4$ , but this includes the limit  $t_4 \rightarrow 0$ ) that  $N \sim \varepsilon^{1/2} t_4^{-1/3} = \varepsilon^{1/2} (\varepsilon^{5/2} t)^{-1/3} = \varepsilon^{1/2-5/6} t^{-1/3} = \varepsilon^{-1/3} t^{-1/3}$ .

In summary, the solution in T4, where  $t = \varepsilon^{-5/2} t_4$ , is

$$\begin{aligned} c_r(t) &= \frac{\varepsilon^{3/2} \Phi_0}{t_4} + \frac{\varepsilon^{3/2} (r-1)}{3t_4}, & \text{for } r = \mathcal{O}(1), \\ c_r(t) &= \frac{\varepsilon^{3/2} r}{3t_4} \exp\left(-\frac{\varepsilon r^2 \pi^{1/3}}{(12\varrho t_4)^{2/3}}\right), & \text{for } r = \mathcal{O}(\varepsilon^{-1/2}), \\ N(t) &= \varepsilon^{1/2} \left(\frac{2\varrho^2}{3\pi t_4}\right)^{1/3}. \end{aligned} \quad (3.35)$$

The first two match smoothly with each other, the large- $r$  limit of the first being  $\varepsilon^{3/2} r / 3t_4$  which is identical to the limit of small  $\varepsilon^{1/2} r$  of the second. The distribution is single-humped, with a maximum at cluster size  $r = r_m := \varepsilon^{-1/2} (12\varrho t_4)^{1/3} / 2^{1/2} \pi^{1/6}$ . The expressions (3.35) will also help us match forward into the next timescale, T5, and to determine the appropriate scalings therein. The above cannot explain the full convergence to equilibrium, since at equilibrium all concentrations have magnitudes  $c_r = \mathcal{O}(\varepsilon^2)$ , and the above solution (3.35) does not asymptote to the equilibrium solution (1.25).

### 3.5. Timescale t5: $t = \mathcal{O}(\varepsilon^{-4})$

The final timescale is given by

$$\begin{aligned} N &= \varepsilon N_5 + \varepsilon^2 \tilde{N}, & t_5 &= \varepsilon^4 t, & c_r &= \varepsilon^2 C_r(t_5) + \varepsilon^3 \tilde{C}_r, \\ c_1 &= \varepsilon^2 m_5 + \varepsilon^3 \tilde{m}, & r_5 &= \varepsilon r, & c_r &= \varepsilon^2 C(r_5, t_5), \end{aligned} \quad (3.36)$$

the last definition on the two lines being for  $r = \mathcal{O}(1)$  and  $r = \mathcal{O}(1/\varepsilon)$  respectively. The equation for the number of clusters is thus

$$\varepsilon^2 \frac{dN_5}{dt_5} = N_5(N_5 - m_5) + \varepsilon \tilde{N}(N_5 - m_5) + \varepsilon N_5(\tilde{N} - \tilde{m} - m_5), \quad (3.37)$$

and that for the monomer concentration is

$$\varepsilon^3 \frac{dm_5}{dt_5} = N_5(N_5 - m_5) + \varepsilon \tilde{N}(N_5 - m_5) + \varepsilon N_5(\tilde{N} - \tilde{m} - m_5) - \varepsilon m_5^2 + \varepsilon N_5 C_2. \quad (3.38)$$

These give the same leading-order equation, namely  $N_5 = m_5$ , that is, the number of clusters scales with the monomer concentration. Their first correction terms yield

$$\tilde{N} - \tilde{m} = m_5, \quad C_2 \sim \frac{m_5^2}{N_5} = m_5. \quad (3.39)$$

For  $r = \mathcal{O}(1)$ , the governing equation is  $C_{r-1} - 2C_r + C_{r+1} = 0$ , which implies  $C_r(t_5) = m_5(t_5) + (r - 1)\beta(t_5)$ . Matching the solution for  $C_2(t_5)$  derived above implies  $\beta(t_5) = 0$ ; hence  $C_r \equiv m_5$  for  $r = \mathcal{O}(1)$ .

Now considering the first correction term distribution of cluster sizes for  $r = \mathcal{O}(1)$ , we obtain  $\tilde{C}_{r-1} - 2\tilde{C}_r + \tilde{C}_{r+1} = 0$ , which implies  $\tilde{C}_r = \tilde{m} + (r - 1)\tilde{\beta}(t_5)$ . Matching to the behaviour of  $c_r(t_5)$  in the previous timescale (3.35), we note that  $\tilde{\beta}(t_5) \sim 1/3t_5$  as  $t_5 \rightarrow 0$ . Matching forward to the equilibrium solution (1.25), which is approached at the end of T5, we find  $\tilde{\beta}(t_5) \rightarrow -\varrho$  as  $t_5 \rightarrow \infty$ .

Putting the ansatz (3.36) into  $(d/dt)(N - c_1)$ , at leading order, we obtain  $m_5^2 = N_5 C_2$  which is already known. The first correction term yields

$$\frac{dm_5}{dt_5} = m_5(-\tilde{\beta} - m_5). \tag{3.40}$$

Hence  $m_5$  converges to  $\varrho$  as  $t_5 \rightarrow \infty$ .

The distribution of clusters at large aggregation numbers ( $r = r_5/\varepsilon, r_5 = \mathcal{O}(1)$ ) is governed by the kinetic equation

$$\frac{1}{m_5} \frac{\partial C}{\partial t_5} = \frac{\partial^2 C}{\partial r_5^2} + \frac{\partial C}{\partial r_5}. \tag{3.41}$$

Following the definitions (3.36) we have

$$N_5 = \int_0^\infty C(r_5, t_5) dr_5, \quad \varrho = \int_0^\infty r_5 C(r_5, t_5) dr_5. \tag{3.42}$$

Density conservation ( $d\varrho/dt = 0$ ) again confirms the leading-order equation  $N_5 = m_5$ . Matching to the inner solution  $r = \mathcal{O}(1)$ , equivalent to  $r_5 = \mathcal{O}(\varepsilon)$  implies that  $\tilde{\beta}(t_5) = \partial C / \partial r_5|_{r_5=0}$ .

Solving for the equilibrium solution of (3.41) we obtain  $C = A + B e^{-r_5}$ , for suitable constants  $A, B$ . For finite mass, we require  $A = 0$ , and imposing the initial mass on the system, we obtain  $B = \varrho$ . This time-independent solution,  $c_r \sim \varepsilon^2 \varrho e^{-r/\varepsilon}$ , corresponds to the equilibrium solution of the original system (1.25). At equilibrium the majority of mass is in clusters of extremely large sizes (typical size  $\langle r \rangle \sim (\varrho/N) \sim (1/\varepsilon)$ ) thus the equilibrium solution can be simplified to

$$c_r^{\text{eq}} = \varepsilon^2 \varrho e^{-\varepsilon r} \quad \text{for } r = \mathcal{O}(1/\varepsilon), \quad N^{\text{eq}} \sim \varrho \varepsilon - \varrho \varepsilon^2. \tag{3.43}$$

Note that the typical cluster size,  $1/\varepsilon$ , is not dependent on the total mass in the system ( $\varrho$ ), unlike the equilibrium solution of the original Becker–Döring system in which  $\varrho/N = \sqrt{\varrho}/\varepsilon$  (1.27).

### 3.6. Summary

As a means of summarizing the behaviour through the timescales outlined above, let us calculate the free energy at various stages of the evolution. The form of the free energy (1.24) is more natural than the standard expression (1.29); this is one motivation for preferring the modified system (1.5)–(1.7) over the original formulation (1.1). At equilibrium the free energy takes the value

$$V_{\text{eq}} = \varrho \log \frac{\varepsilon}{1 + \varepsilon}, \tag{3.44}$$

which is negative and asymptotically large. In what follows, to see how quickly the free energy reduces, we consider  $V - V_{\text{eq}}$ .

At  $t = 0$ , the initial data (3.1) together with (1.11) imply that  $V_0 = 0$  and so

$$V_0 - V_{\text{eq}} = -\varrho \log \frac{\varepsilon}{1 + \varepsilon} \sim -\varrho \log \varepsilon + \varrho \varepsilon + \mathcal{O}(\varepsilon^2). \quad (3.45)$$

Thus there is a large free energy difference available.

At the end of T2 (at which point the size-distribution is almost identical to that at the end of T1), we have, from (3.10),

$$V_2 - V_{\text{eq}} = \frac{\varrho}{e} \left( \sum_{r=1}^{\infty} \frac{(r-1)}{r!} \log \frac{(r-1)}{r!} - \log \varepsilon + e \log(1 + \varepsilon) \right) \sim -\frac{\varrho}{e} \log \varepsilon, \quad (3.46)$$

so over the first timescale, the free energy difference drops to a factor of  $1/e$  of its initial value but retains a similar order of magnitude.

During T3 most of the remainder of the free energy difference is used up, and there is only an extremely small amount of free energy remaining to be lost between the configuration at the end of T3 (3.24) and the equilibrium solution (1.25). The form of the solution towards the end of T3 (3.24) is similar to that in the whole of timescale T4. In T4, we have  $V_4 \sim \varrho \log \varepsilon$  hence  $V_4 \sim V_{\text{eq}}$  and the difference in free energy between T4 and equilibrium is small and decreasing algebraically in time

$$V_4 - V_{\text{eq}} \sim \varepsilon^{1/2} \left( \frac{2\varrho^2}{3\pi t_4} \right)^{1/3} \left[ \frac{3}{2} \log \frac{1}{\varepsilon} + \log (2t_4(12\pi\varrho)^{1/3}) - \frac{3}{2}\gamma \right] + \mathcal{O}(\varepsilon), \quad (3.47)$$

where  $\gamma$  is Euler's constant ( $\gamma \approx 0.5772\dots$ ) [1].

In T5, we have  $V_5 \sim \varrho \log \varepsilon$ , with correction terms which yield

$$V_5 - V_{\text{eq}} \sim (\varrho - m_5(t_5))\varepsilon \log \varepsilon + \varepsilon \left( \varrho + \int_{r_5=0}^{\infty} C(r_5, t_5) \log C(r_5, t_5) dr_5 - m_5 \log m_5 \right) \quad (3.48)$$

hence, over this timescale, the dominant change in free energy is due to a reduction in the monomer concentration ( $\varepsilon^2 m_5$ ) to the equilibrium value ( $\varepsilon^2 \varrho$ ) and this is driven by a free energy gradient of size  $V_5 - V_{\text{eq}} = \mathcal{O}(\varepsilon \log \varepsilon)$ .

#### 4. Conclusions

The aim of this paper was to construct an asymptotic solution to a simple example of the modified Becker–Döring system proposed by Dreyer and Duderstadt [8]. We have analysed two cases of size-independent aggregation and fragmentation rates, first, the simpler constant monomer concentration case, and then the constant total mass case which is more complex due to the monomer concentration being unknown; this makes the problem both nonlinear and nonlocal in aggregation number. The structure of the asymptotic solution in these two examples is similar. However the presence of the number of clusters in the fragmentation term (1.7) introduces a number of differences between the modified system analysed here and the original formulation considered in [22].

Firstly the constant monomer concentration appears not to have a Lyapunov function (1.20) due to the fragmentation rate being time-dependent. Secondly, the constant monomer concentration has a unique steady-state solution, which is the equilibrium solution; this is in contrast with the original Becker–Döring system which has a one-parameter family of steady-state solutions (which includes the equilibrium solution as a special case).

Importantly, the more physically-relevant and realistic constant mass formulation of the problem passes through a greater range of timescales than the standard system. Whilst the shape of the solution is similar in the penultimate timescale, during which the size-distribution evolves according to a self-similar profile, the kinetics are less orthodox, the typical cluster size



scales with  $t^{1/3}$  as opposed to  $t^{1/2}$  which is found in the asymptotic analysis of the standard Becker–Döring formulation. The evolution of the free energy through the five timescales (3.45)–(3.48) follows a similar progression to the original system (1.32)–(1.34). We should expect to find even more exotic range of timescales and behaviours if size-dependent rate coefficients ( $a_r, b_r$ ) were used.

In [13] the Becker–Döring equations with rate coefficients which depend on size in an algebraic fashion are analysed. The constant monomer formulation is analysed using a variety of asymptotic techniques. Using WKB methods, five cases have been identified and the large-time behaviour of 23 subcases described. Similar techniques are applicable to the modified Becker–Döring model of Dreyer and Duderstadt considered here; however, the constant mass case is slightly more complex. With rates which depend in an algebraic fashion on cluster size, it should be possible to identify the sequence of relevant timescales and derive simplifying descriptions. However, it may not be possible to quote explicit solutions as have been given here. It is hoped that these issues will be the subject of future work.

### Acknowledgments

I would like to thank the Weierstrass Institute (WIAS), Berlin for their hospitality during May 2007, and am particularly grateful to Wolfgang Dreyer and Michael Herrmann for useful discussions. Part of this work was carried out whilst I was supported by an EPSRC-funded Springboard fellowship (Grant Ref EP/E032362/1). My thanks also go to the referee who pointed out several issues which required a broader commentary.

### References

- [1] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)
- [2] Ball J, Carr J and Penrose O 1986 The Becker–Döring cluster equations: basic properties and asymptotic behaviour of solutions *Commun. Math. Phys.* **104** 657–92
- [3] Becker R and Döring W 1935 Kinetische behandlung der keimbildung in übersättigten dämpfen *Ann. Phys.* **24** 719–52
- [4] Bolton C D and Wattis J A D 2002 General Becker–Döring equations: effect of dimer interactions *J. Phys. A: Math. Gen.* **35** 3183–202
- [5] Bolton C D and Wattis J A D 2004 The Becker–Döring equations with input, competition and inhibition *J. Phys. A: Math. Gen.* **37** 1971–86
- [6] Bonilla L L, Carpio A, Farjoun Y and Neu J C 2006 Asymptotic and numerical studies of the Becker–Döring model for transient homogeneous nucleation *Markov processes and related fields* **12** 341–65
- [7] da Costa F P 1998 Asymptotic behaviour of low density solutions to the generalized Becker–Döring equations *Nonlinear Differ. Equ. Appl.* **5** 23–37
- [8] Dreyer W and Duderstadt F 2006 On the Becker–Döring theory of nucleation of liquid droplets in solids *J. Stat. Phys.* **123** 55–87
- [9] Duncan D B and Soheili A R 2001 Approximating the Becker–Döring cluster equations *Appl. Numer. Math.* **37** 1–29
- [10] Farjoun Y 2008 Creation of clusters via a thermal quench [arXiv.org/cond-mat.mtrl-sci/0810.3249v1](http://arXiv.org/cond-mat.mtrl-sci/0810.3249v1)
- [11] Farjoun Y and Neu J C 2007 Exhaustion of nucleation in a closed system [arxiv.org/abs/cond-mat/0702372](http://arxiv.org/abs/cond-mat/0702372)
- [12] Herrmann M, Naldzhieva M and Niethammer B 2006 On a thermodynamically consistent modification of the Becker–Döring equations *Physica D* **222** 116–30
- [13] King J R and Wattis J A D 2002 Asymptotic solutions of the Becker–Döring equations with size-dependent rate constants *J. Phys. A: Math. Gen.* **35** 1357–80
- [14] Neu J C, Bonilla L L and Carpio A 2005 Igniting homogeneous nucleation *Phys. Rev. E* **71** 021601
- [15] Niethammer B 2003 On the evolution of large clusters in the Becker–Döring model *J. Nonlinear Sci.* **13** 115–55
- [16] Niethammer B and Pego R L 1999 Non-self-similar behaviour in the LSW theory of Ostwald ripening *J. Stat. Phys.* **95** 867–902

- [17] Niethammer B and Pego R L 2001 The LSW model for domain coarsening: asymptotic behaviour for conserved total mass *J. Stat. Phys.* **104** 1113–44
- [18] Penrose O 1997 The Becker–Döring equations at large times and their connection with the LSW theory of coarsening *J. Stat. Phys.* **89** 305–20
- [19] Penrose O and Lebowitz J L 1976 *Studies in Statistical Mechanics VII: Fluctuation Phenomena* ed E Montroll and J L Lebowitz (Amsterdam: North-Holland) pp 322–75
- [20] Wattis J A D 2006 An introduction to mathematical models of coagulation–fragmentation processes: a discrete deterministic mean-field approach *Physica D* **222** 1–20
- [21] Wattis J A D and Coveney P V 1997 Generalized nucleation theory with inhibition for chemically reacting systems *J. Chem. Phys.* **106** 9122–40
- [22] Wattis J A D and King J R 1998 Asymptotic solutions of the Becker–Döring equations *J. Phys. A: Math. Gen.* **31** 7169–89
- [23] Wall S and Elvingson C 1985 Equilibrium and kinetic properties of mixed micelles *J. Phys. Chem.* **89** 2695–705
- [24] Wu D T 1993 General approach to barrier crossing in multi-component nucleation *J. Chem. Phys.* **99** 1990–2000