Renormalisation-theoretic analysis of non-equilibrium phase transitions: II. The effect of perturbations on rate coefficients in the Becker-Döring equations

2001 J. Phys. A: Math. Gen. 34 8697

(http://iopscience.iop.org/0305-4470/34/41/321)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **34** (2001) 8697–8726 PII: S0305-4470(01)28546-1

Renormalisation-theoretic analysis of non-equilibrium phase transitions: II. The effect of perturbations on rate coefficients in the Becker–Döring equations

Jonathan A D Wattis[1] **and Peter V Coveney**[2]

[1] Division of Theoretical Mechanics, School of Mathematical Sciences, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[2] Centre for Computational Science, Department of Chemistry, Queen Mary, University of London, Mile End Road, London, E1 4NS, UK

E-mail: Jonathan.Wattis@nottingham.ac.uk and p.v.coveney@qmul.ac.uk

Received 20 October 2000, in final form 14 August 2001
Published 5 October 2001
Online at stacks.iop.org/JPhysA/34/8697

Abstract

We study in detail the application of renormalization theory to models of cluster aggregation and fragmentation of relevance to nucleation and growth processes. In particular, we investigate the Becker–Döring equations, originally formulated to describe and analyse non-equilibrium phase transitions, but more recently generalized to describe a wide range of physicochemical problems. We consider here rate coefficients which depend on the cluster size in a power law fashion, but now perturbed by small-amplitude random noise. Power law rate coefficients arise naturally in the theory of surface-controlled nucleation and growth processes. The noisy perturbations on these rates reflect the effect of microscopic variations in such mean-field coefficients, thermal fluctuations and/or experimental uncertainties. In this paper we generalize our earlier work that identified the nine classes into which all dynamical behaviour must fall (Wattis J A D and Coveney P V 2001 *J. Phys. A: Math. Gen.* **34** 8679–95) by investigating how random perturbations of the rate coefficients influence the steady-state and kinetic behaviour of the coarse-grained, renormalized system. We are hence able to confirm the existence of a set of up to nine universality classes for such Becker–Döring systems.

PACS numbers: 64.60.-I, 64.60.Ht, 82.20.-w

1. Introduction

The purpose of this paper is to demonstrate the robust nature of renormalization methods in the theoretical description of nucleation and growth processes. We show that even in the presence of random perturbations the methods presented in our previous papers [11, 19]

provide correct asymptotic solutions. This paper thus extends and completes our earlier published work [11, 19], wherein we derived a renormalization procedure for the Becker–Döring equations and applied it to the case where the aggregation and fragmentation rate coefficients are of power law form, given respectively by $a_r = ar^p$, $b_{r+1} = br^p$, r being the aggregation number of a cluster (that is, the number of monomer particles within it). As previously described [11, 19], these coefficients describe the rate at which a cluster of size r adsorbs monomer to grow to size $r + 1$, and the rate at which a cluster of size $r + 1$ sheds a monomer; this choice is well known to be appropriate for the description of surface-limited nucleation and growth processes [11, 19]. The Becker–Döring cluster equations are then

$$\dot{c}_r = J_{r-1} - J_r \qquad J_r = a_r c_r c_1 - b_{r+1} c_{r+1} \tag{1.1}$$

where $c_r(t)$ denotes the concentration of clusters of size r. Here we generalize our earlier work to consider rates given by the formulae

$$a_r = ar^p + \delta_r \qquad b_{r+1} = br^p + \varepsilon_{r+1} \tag{1.2}$$

in which the extra terms represent random perturbations to the deterministic rates, and which will be further quantified later on. While other authors have considered the effect of noise in such systems, the main thrust of such analyses has been to elucidate the temporal evolution of perturbations on cluster size distribution: see, for example, the work of van Dongen and Ernst [12, 13].

Renormalization theory has been widely applied in the analysis of equilibrium phase transitions in statistical physics [5]. In statistical mechanics, the basic idea underlying renormalization theory is the transition from a microscopic to a macroscopic description of some phenomenon by the systematic filtering out of unwanted degrees of freedom. In equilibrium phase transitions, near a critical point the system looks the same on all length scales and this physical insight can be translated into a set of transformations which leave the essential physical properties of the system unchanged—a procedure known as renormalization. The widely used term 'the renormalization group' (RG) is technically inappropriate since the transformation loses information, and so is at most a *semi*-group, while the procedure comprises many different ideas and distinct methods, rather than being a formal monolithic edifice as the definite article would imply. Of more recent interest is the application of renormalization ideas to non-equilibrium phenomena. While the physical motivation behind the RG programme of coarse-graining microscopic models still seems appropriate to obtain the macroscopic properties, the complexity of far-from-equilibrium dynamics is such that in practice each specific system must be shown to be suitably scale invariant.

Of central interest in this paper is the late-time asymptotic macroscopic behaviour of complex dynamical systems. Bricmont and Kupiainen have taken ideas from renormalization theory together with asymptotic methods for the analysis of diffusive processes including nonlinear parabolic equations [1–3] while Woodruff has recast multiple-timescale problems using renormalization ideas in [22–25]. Woodrfuff's method allows the separation of equations for larger-scale phenomena and small-scale dynamics from a more general theory. Velazquez has recently used a renormalization technique in an attempt to draw together the theories of Lifshitz–Slyozov coarsening and nucleation as modelled by the Becker–Döring equations [16].

We apply underlying concepts from renormalization theory to study the Becker–Döring equations, which were originally formulated to study the kinetics of first-order phase transitions. They describe the stepwise growth and fragmentation of clusters in terms of the rates of the individual processes wherein monomer particles join or leave each cluster. The Becker–Döring equations have recently been subjected to more conventional analysis using matched asymptotic expansions [14, 21]. Rather than use the coarse-graining approximation,

which emphasizes the discrete nature of the equations, that analysis concentrates on the large-time limit where continuum approximations become valid [21]. We have recently applied generalizations of these equations to a wide range of physicochemical processes, ranging from those involving surfactant self-assembly [9, 10] through RNA polymer formation [7, 8, 18] to cement setting [8, 17]. In these studies coarse-graining procedures reduce large systems of equations down to lower-dimensional—'mesoscopic'—dynamical systems capable of theoretical analysis using standard techniques from the theory of differential equations. The coarse-graining contraction procedure summarized below is analogous to other renormalization methods used in statistical physics.

There is some similarity between our methods and Woodruff's approach: we write the microscopic aggregation number r of a cluster as $r = (\lambda - 1)n + 1 + k$ where n is of mesoscopic size and k is a microscopic correction; we then aim to determine the problem on the mesoscale in a form which does not require us to simultaneously solve the microscopic problem. Thus microscopic detail is filtered out, but we are able to construct a simpler model which remains valid on larger scales.

Preliminary results of this work were reported in an earlier publication [11]. In the present paper, the particular and physically relevant example of simple power law rate coefficients is generalized by the addition of small random perturbations. These perturbations influence the system's steady states and large-time kinetics and their effects are studied here in detail. Following a brief recapitulation of the model and the coarse-graining scheme underpinning our renormalization procedure in the remainder of this section, the perturbations are introduced in section 2. The central part of the paper is concerned with an analysis of the effects which these perturbations have on our renormalization procedure, and how such noise influences the contracted description of the model (sections 3). The main issue at stake is the stability of the models under such minor perturbations of rate coefficients: our analysis leads directly to the identification of a set of nine generic classes of behaviour and true *universality classes* whose asymptotic behaviour is independent of all microscopic details (sections 3 and 4). We suggest physicochemical scenarios that may correspond to the generic classes identified by our renormalization analysis; future work, especially of an experimental nature, will be helpful in relating real-world nucleation and growth processes to these distinct universality classes.

1.1. The Becker–Döring cluster equations

In this section we give a basic outline of the Becker–Döring system of equations and their properties (consult [11, 19] for more details). Let us start with a system in which a precursor chemical, P, spontaneously decays to form the monomer C_1, at some rate $k_f(p)$ where $p = p(t) = [P]$ is the concentration of P. Further, we assume that this mechanism is reversible, with backward rate $k_b(c_1)$. The monomer is allowed to aggregate, with clusters growing and fragmenting according to the usual Becker–Döring cluster equations. Clusters are formed by two processes: either by the next smallest cluster size coalescing with a monomer, or by the next largest size losing a monomer. Only such monomer–cluster interactions are permitted in the Becker–Döring model of nucleation; cluster–cluster interactions are ignored. The system is thus governed by

$$\dot{p} = k_b(p, c_1)c_1 - k_f(p, c_1)p \tag{1.1}$$

$$\dot{c}_1 = k_f(p, c_1)p - k_b(p, c_1)c_1 - J_1 - \sum_{r=1}^{\infty} J_r \tag{1.2}$$

$$\dot{c}_r = J_{r-1} - J_r \quad (r \geqslant 2) \qquad J_r = a_r c_r c_1 - b_{r+1} c_{r+1} \tag{1.3}$$

where $c_r(t)$ represents the concentration of clusters containing r monomers, and the constants a_r, b_r are aggregation and fragmentation rates respectively.

In this paper we consider the case for which the monomer concentration (c_1) is held constant; thus the Becker–Döring equations we are concerned with are

$$\dot{c}_r = J_{r-1} - J_r \quad (r \geqslant 2) \qquad J_r = a_r c_r c_1 - b_{r+1} c_{r+1} \tag{1.4}$$

with c_1 a given constant; we leave the more general formulation (1.1)–(1.3) for a future paper. The assumption of a constant monomer concentration corresponds to the case where the precursor chemical supplies monomer at a rate given by $\dot{p} = -J_1 - \sum_{r=1}^{\infty} J_r$, so that $\dot{c}_1 = 0$. This assumption is made in situations where the so-called 'pool chemical approximation' is valid, namely where there is a large source of monomer species entering into the system at a rate which maintains the monomer concentration essentially fixed and independent of time.

Given the rate coefficients a_r, b_r the partition function Q_r is defined by $Q_1 = 1$ and $a_r Q_r = b_{r+1} Q_{r+1}$. This generates the equilibrium solution $c_r = Q_r c_1^r$, which is an equilibrium solution of the constant monomer model (1.4), and also an equilibrium solution of the generalized system (1.1)–(1.3) for the particular concentration of precursor chemical given by $p = k_b c_1 / k_f$. In both cases the equilibrium solution corresponds to zero flux, that is $J_r = 0$ for all r, and the flux from precursor to monomer is also zero ($k_f p - k_b c_1 = 0$). For certain choices of rate coefficients a_r, b_r and certain monomer concentrations c_1, the equilibrium solution will not decay to zero in the limit $r \to \infty$. In these cases, an alternative steady-state solution will be approached in the large-time limit. This solution is given by a constant nonzero flux through the system, that is $J_r = J$ independent of r. This condition yields the family of solutions

$$c_r = Q_r c_1^r \left(1 - J \sum_{k=1}^{r-1} \frac{1}{a_k Q_k c_1^{k+1}} \right) \tag{1.5}$$

which contains the equilibrium solution as the special case $J = 0$. The steady-state flux J is determined by requiring the concentrations c_r to decay to zero in the large-r limit, giving

$$J = 1 \Big/ \sum_{r=1}^{\infty} \frac{1}{a_r Q_r c_1^{r+1}}. \tag{1.6}$$

1.2. The Becker–Döring system with power law coefficients

We now proceed to consider the renormalization of Becker–Döring models in which the cluster rate coefficients are of power law form, a dependence which is of immediate relevance to the description of surface-limited aggregation processes. We assume the rate coefficients for aggregation and fragmentation are respectively

$$a_r = a r^p \qquad b_{r+1} = b r^p \tag{1.7}$$

so that the parameter $\theta = a c_1 / b$ is useful for classifying dynamical behaviour. The parameter p determines the variability of rate with cluster size, with $p > 0$ implying that large cluster sizes have larger aggregation and fragmentation rates, and $p < 0$ giving rates which decrease with increasing cluster size. The latter case is the less physically relevant, but is nevertheless also studied here for the sake of completeness. Typical values for p are $p = 0, \frac{1}{2}, \frac{1}{3}, \frac{2}{3}, 1$ for the examples of linear chain polymerization, coagulation kinetics in two space dimensions, diffusion-limited coagulation in three dimensions, surface-limited coagulation in three dimensions, and branched chain polymerization, respectively. Since a cluster's volume scales with aggregation number r, if we assume that clusters are spherical

then their surface area scales with $r^{2/3}$ and their diameter with $r^{1/3}$, accounting for the presence of these exponents. More general exponents can be manifest in other situations [6].

The partition function Q_r is defined by $Q_r = (a/b)^{r-1}$ as in the $p = 0$ case considered earlier [21]. For $\theta \leqslant 1$ the system approaches the equilibrium solution given by solving $J_r = 0$, that is $c_r = \theta^{r-1}c_1$. Note that this solution is independent of p, although the way in which the equilibrium solution is approached depends on p. For $\theta > 1$ the equilibrium solution diverges at large r. Instead, for $\theta > 1$ the system approaches one of a family of time-independent solutions in which all fluxes are equal; $J_r = J$ for all r implies

$$c_r = \theta^{r-1}c_1\left(1 - J\sum_{k=1}^{r-1}\frac{1}{bc_1k^p\theta^k}\right). \tag{1.8}$$

Since, for $\theta > 1$ the sum is convergent in the limit $r \to \infty$, the flux which gives the least singular behaviour in this limit is

$$J = bc_1\Big/\sum_{k=1}^{\infty}k^{-p}\theta^{-k}. \tag{1.9}$$

1.3. Coarse-graining procedure

Following the general coarse-grained contraction with constant mesh size λ in aggregation number (so that we only retain the aggregation numbers $r = \Lambda_n = (n-1)\lambda + 1$), the kinetic equations reduce to

$$\dot{x}_n = L_{n-1} - L_n \quad (r \geqslant 2) \qquad L_n = \alpha_n x_n x_1^{\lambda} - \beta_{n+1}x_{n+1} \tag{1.10}$$

$$\alpha_n = Ta_{\Lambda_n}a_{\Lambda_n+1}\ldots a_{\Lambda_{n+1}-1} \qquad \beta_{n+1} = Tb_{\Lambda_n+1}b_{\Lambda_n+2}\ldots b_{\Lambda_{n+1}} \tag{1.11}$$

where the retained coarse-grained cluster concentrations are relabelled as $x_n := c_r$ with $x_1 := c_1$ the monomer concentration; c_1 is not involved in the coarse-graining since it has a special role in the Becker–Döring theory [9, 11]. The parameters α_n, β_n are the coarse-grained aggregation and fragmentation rates, now representing the addition or removal of λ monomers to or from a cluster (rather than just a single monomer which occurs in the full Becker–Döring system). This flux of matter is denoted by L_n. The concentration $x_n(t)$ is representative of the concentrations c_r for cluster sizes $(\Lambda_{n-1} + 1) \leqslant r \leqslant \Lambda_n$. The factor T represents a change of timescale which ensures that the large-time asymptotic behaviour of the reduced system coincides exactly with the original fine-grained system in the case of size-independent aggregation and fragmentation rates ($a_r = a, b_r = b$). Technically speaking, the need to redefine the timescale makes this procedure a *dynamical* renormalization.

1.4. Coarse-graining of power law coefficients

If the rate coefficients in the original formulation in equations (1.4) are determined by simple power laws, namely $a_r = ar^p$ and $b_{r+1} = br^p$, then the coefficients in the reduced model are

$$\alpha_n = a^{\lambda}\{[(r-1)\lambda + 1][(n-1)\lambda + 2]\cdots[n\lambda]\}^p. \tag{1.12}$$

Thus

$$\begin{aligned}\log\alpha_n &= \lambda\log a + p\sum_{j=1}^{\lambda}\log(n\lambda - \lambda + j)\\ &\approx \lambda\log a + p\int_0^{\lambda}\log(n\lambda - \lambda + x)\,\mathrm{d}x\\ &= \lambda\log a + p\lambda\left[\log(n\lambda) - 1 + (1-n)\log\left(1 - \frac{1}{n}\right)\right].\end{aligned} \tag{1.13}$$

For large n this asymptotes to $\log \alpha_n \sim \lambda \log a + p\lambda \log(\lambda n)$, so for simplicity we shall take $\alpha_n = (a\lambda^p n^p)^\lambda$, which differs slightly at small values of n. The backward rate coefficient is then $\beta_{n+1} = (b\lambda^p n^p)^\lambda$.

The new system has its own θ parameter determining the balance between aggregation and fragmentation rates in the system which, for the moment, we shall call $\tilde{\theta} = \alpha_r x_1^\lambda / \beta_{r+1} = \theta^\lambda$, so contraction of the system maps θ to θ^λ. The parameter θ thus plays an important role in the renormalization procedure, the fixed points of this mapping corresponding to $\theta = 0, 1, \infty$; hence such systems are of special interest to us. Also, the contraction maps coefficients with exponent p to those with exponent $p\lambda$. Thus, following a contraction, there are only three limits to consider: small p (namely $p = 0$) and large p (positive and negative).

The effect of coarse-graining a Becker–Döring system is to modify the rate coefficients, by the map $(\theta, p) \mapsto (\theta^\lambda, \lambda p)$. If λ is allowed to take on large values, there are only nine combinations of (θ, p) which merit attention, namely all possible combinations of $\theta = \{0, 1, \infty\}$ and $p = 0, p > 0, p < 0$. These nine cases and their associated fixed points will be the basis of the analysis presented in section 3 of this paper, which follows on from section 2 where we develop the general theory for perturbed rates for the coarse-grained Becker–Döring system with arbitrary λ.

2. General analysis of the role of noise in coarse-grained Becker–Döring systems

2.1. Form of rate perturbations

Whilst a simple power law description of rate coefficients might give the correct general behaviour over a large range of aggregation numbers, in any given physical system there will be some minor deviations from such a regular description which may be due to a number of separate effects. For instance, the presence of microscopic fluctuations and/or experimental uncertainties suggest that one should be concerned about the stability of such theoretical models to minor modifications in the assumed rate coefficients. Indeed, figure 2.3 of Lewis's contribution in the monograph [15] shows that the dependence of free energy on cluster size can in reality be much more complicated than the simple smooth curves obtained from simple derivations (for example by considering surface and bulk energies and assuming all clusters are spheres, discs or needles; or by working back from simple laws for aggregation and fragmentation rates). In mathematical terms, therefore, we wish to know whether small random perturbations to the rates alter the results we have derived previously using renormalization methods. The hope is that they will not have a major effect, so that the renormalization scheme is stable with respect to such perturbations and points to the existence of true universality classes. To analyse the effect of such perturbations, we perturb the rates from a simple power law form by small random amounts, in such a way that all rates remain positive. Thus we assume that the rate coefficients have the form

$$a_r = ar^p + \delta_r \qquad b_{r+1} = br^p + \varepsilon_{r+1} \tag{2.1}$$

where δ_r, ε_r are independent random variables, with small mean and small variance, so we can assume that $\delta_r \sim \varepsilon_r \sim \nu \ll 1$ for all r. Many of the approximations used in the ensuing analysis rely on the noise being small ($\nu \ll 1$). Even with such a restrictive assumption, by calculating the first higher-order term in the asymptotic expansion, many important and interesting results are obtained. Later, we shall discuss cases in which $\nu \gg 1$ and $\nu = \mathcal{O}(1)$. In the nine special cases analysed below, the constants a, b in equations (2.1) are taken to be either zero or unity. When $\lim_{r\to\infty} a_r$ or $\lim_{r\to\infty} b_r$ is zero, the corresponding perturbation (δ_r, ε_r respectively) is assumed to be strictly positive and have mean ν. Specifically, we assume

that they are distributed according to some continuous probability distribution functions $f_\delta(x)$, $f_\varepsilon(x)$ respectively, with $f(\cdot) = 0$ whenever δ, ε lies more than $\mathcal{O}(\nu)$ away from zero. The expectation operator $\mathbb{E}[\cdot]$ is defined by

$$\mathbb{E}[g(\delta)] = \int g(x) f_\delta(x)\,\mathrm{d}x \qquad \text{and} \qquad \mathbb{E}[g(\varepsilon)] = \int g(x) f_\varepsilon(x)\,\mathrm{d}x \quad (2.2)$$

the integrals being over all real x. The variance operator $\mathbb{V}[\cdot]$ is defined by

$$\mathbb{V}[g] = \mathbb{E}[g^2] - \mathbb{E}[g]^2. \quad (2.3)$$

The conditions on the mean reduces to $\mathbb{E}[\delta_r] = \nu$ and/or $\mathbb{E}[\varepsilon_r] = \nu$ for all r; in cases where $\lim_{r\to\infty} a_r$ and/or $\lim_{r\to\infty} b_r$ are unity or larger δ_r, ε_r are allowed to take negative values as well as positive and we assume that they have zero mean and their variance is $\mathcal{O}(\nu^2)$ (e.g. $\mathbb{E}[\delta_r] = 0$ with $\mathbb{E}[\delta_r^2] = \mathcal{O}(\nu^2)$). In all cases the perturbations are assumed to be small enough that the total rate constants in equation (2.1) are all positive.

2.2. *Effect of noise on cluster partition functions*

We first derive and analyse the modified equilibrium and steady states which are approached in the large-time limit. The kinetics by which these states are achieved is described in detail later (section 2.3). First we aim to find the effect which the perturbations to the rate coefficients $(\delta_r, \varepsilon_r)$ have on the cluster partition function Q_r in each of the nine special cases described above. Since the partition function is defined in terms of the rate constants, the presence of nonzero perturbations δ_r, ε_r will affect Q_r. Due to the definition $c_1 = 1$, the partition function is identical to the equilibrium configuration. However, in cases III, VI, IX and V (if $p > 1$) it is not the equilibrium solution which is approached in the large-time limit; instead the system evolves to a steady-state solution. Perturbations to the rate coefficients $(\delta_r, \varepsilon_r)$ thus modify the steady-state and equilibrium solutions through the partition function, and such modifications will be found here. In general the partition function is given by

$$Q_r = \prod_{k=1}^{r-1} \frac{a_k}{b_{k+1}} \quad (2.4)$$

whilst steady-state solutions are determined by the constant flux condition $J = J_r = a_r c_r - b_{r+1} c_{r+1}$, for all values of r. We shall pay particular attention to the large aggregation number (r) behaviour, since this determines the observed behaviour of the system on the mesoscopic scale, and is the region we shall probe later with the coarse-grained contraction of this perturbed Becker–Döring system.

2.3. *Effect of noise on cluster growth kinetics*

The equations we study in this section are the kinetic equations with noisy coefficients, namely

$$\dot{c}_r = (a(r-1)^p + \delta_{r-1})c_{r-1} - (ar^p + \delta_r)c_r - (b(r-1)^p + \varepsilon_r)c_r + (br^p + \varepsilon_{r+1})c_{r+1} \quad (r \geqslant 2). \quad (2.5)$$

Having found the states which are approached in the large-time limit, we now find time-dependent solutions by using large-time asymptotics. We write the solution as $c_r(t) = Q_r \psi(r,t)$ or $c_r(t) = c_r^{\mathrm{sss}} \psi(r,t)$ in order to investigate the manner in which $\psi(r,t) \to 1$ as $t \to +\infty$. In general, this leads to

$$\dot{\psi}_r = a_r(\psi_{r+1} - \psi_r) - b_r(\psi_r - \psi_{r-1}) - \frac{J}{c_r^{\mathrm{sss}}}(\psi_{r+1} - \psi_{r-1}) \quad (2.6)$$

where J represents the steady-state flux into the system; convergence to equilibrium corresponds to $J = 0$.

2.4. Effect of perturbations on rate coefficients in the contracted system

The rate coefficients following contraction are given by

$$\alpha_n = T \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} a_r \qquad \beta_{n+1} = T \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} b_{r+1} \tag{2.7}$$

where we shall use $T = \lambda^{-p\lambda}$ so that the 'clean' coefficients $a_r = ar^p$, $b_{r+1} = br^p$ are mapped to $\alpha_n = \alpha n^{p\lambda}$, $\beta_{n+1} = \beta n^{p\lambda}$ with $\alpha = a^\lambda$ and $\beta = b^\lambda$ (see section 1.4 and [19]). Since the nine special cases which will be studied in detail later correspond to a, b equal to zero or unity, following the coarse-graining contraction we are concerned with establishing like-for-like correspondence in which α, β equal zero or unity. Here T is chosen to simplify the algebra; an alternative expression could be used, with a consequent increase in the complexity of the ensuing equations. Alternative choices for T merely influence the units of time, and have no effect on the equilibrium or steady-state solutions or the effect of the rate perturbations; the large-time asymptotics will only be affected by a linear transformation to the time variable, t. The problems we are concerned with here involve properties of the noise following contraction: for example, whether its amplitude is dependent on aggregation number, and its order of magnitude as a function of ν. We now reduce the randomly perturbed coefficients from (2.1) in the microscopic description of cluster formation to the mesoscopic description in which $\alpha_n = \alpha n^{p\lambda} + \Delta_n$, $\beta_{n+1} = \beta n^{p\lambda} + E_{n+1}$ with the aim of finding how the perturbations Δ_n, E_n in the contracted model depend on the perturbations δ_r, ε_r in the full description of the model. In some cases this is trivial, since $a = 0$ or $b = 0$, and in these cases Δ_n, E_{n+1} is the product of a set of δ_r, ε_r, but in other cases the relationship is more complex, and in such cases we give the leading-order expression for Δ_n, E_{n+1} in the asymptotic limit $\nu \to 0$. We have

$$\alpha_n = T\left(\prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} ar^p\right)\left(\prod_{r=\Lambda_n}^{\Lambda_{n+1}-1}\left[1+\frac{\delta_r}{ar^p}\right]\right) \sim T\left(\prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} ar^p\right)\left(1+\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1}\frac{\delta_r}{ar^p}\right) \tag{2.8}$$

since $\delta_r = \mathcal{O}(\nu) \ll ar^p = \mathcal{O}(1)$; correction terms to the above approximation are thus $\mathcal{O}(\nu^2)$. Using (1.12), (1.13), the leading-order term is approximated by $\alpha n^{p\lambda}$ where $\alpha = Ta^\lambda \lambda^{p\lambda}$ and the first correction term due to the rate perturbations is defined by

$$\Delta_n = \alpha n^{p\lambda} \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \frac{\delta_r}{ar^p}. \tag{2.9}$$

Similarly, for the fragmentation rates we have $\beta_{n+1} = \beta n^{p\lambda} + E_{n+1}$ with $\beta = Tb^\lambda \lambda^{p\lambda}$ and

$$E_{n+1} = \beta n^{p\lambda} \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \frac{\varepsilon_{r+1}}{br^p}. \tag{2.10}$$

2.5. Consistency and accuracy analysis

Having derived coarse-grained rate coefficients which include the leading-order corrections due to random perturbations from a power law, we now use these rate coefficients to construct a partition function Υ_n for the coarse-grained model from the macroscopic rates α_n, β_n. This is determined by

$$\Upsilon_1 = 1 \qquad \alpha_n \Upsilon_n = \beta_{n+1}\Upsilon_{n+1} \quad (n \geqslant 1) \tag{2.11}$$

which implies

$$\Upsilon_N = \prod_{n=1}^{N-1} \frac{\alpha_n}{\beta_{n+1}} \qquad \text{and} \qquad \log \Upsilon_N = \sum_{n=1}^{N-1} (\log \alpha_n - \log \beta_{n+1}). \tag{2.12}$$

We can then compare this result with the full partition function as a check on the coarse-graining procedures, with the hope of finding $\Upsilon_N = Q_R$ when $R = \Lambda_N$ to leading order in ν. For cases in which a steady-state solution is approached as $t \to \infty$, we compare the steady-state solution x_n^{sss} calculated from the noisy contracted rates, α_n, β_{n+1}, with the steady-state solution of the full model, c_r^{sss}. If, moreover, $c_r = x_n$ when $r = \Lambda_n$ then we will have demonstrated that no crucial information has been lost in the coarse-graining reduction. This test thus amounts to a consistency check which we shall carry out not just at leading order, but also to first order in ν (that is in Δ_r, E_{r+1}) for the purposes of accuracy assessment. These checks will enable us to demonstrate if and when we have successfully bridged the scales from microscopic to mesoscopic for certain choices of the coarse-graining parameter λ.

2.6. Effect of noise on the late-time kinetics of the contracted system

Having checked that the equilibrium and steady-state solutions of the microscopic description of the system have been faithfully reproduced in the coarse-grained system, we perform one final calculation to check that the late-time asymptotic form of the kinetics is also correctly replicated. In general the contracted system of equations can be written using (1.10) and (2.8)–(2.10) as

$$\dot{x}_n = \left[\alpha(n-1)^{p\lambda} + \Delta_{n-1}\right] x_{n-1} - \left[\beta(n-1)^{p\lambda} + E_n\right] x_n - \left[\alpha n^{p\lambda} + \Delta_n\right] x_n + \left[\beta n^{p\lambda} + E_{n+1}\right] x_{n+1}. \tag{2.13}$$

In the following section we examine the equilibrium and steady-state solutions of this model, as well as the manner in which the time-dependent solutions convergence to these solutions. We then compare this behaviour with the properties of the microscopic system prior to coarse-graining. We now analyse in greater detail the nine cases summarized at the end of section 1.4; that is those corresponding to $p = 0$, $p > 0$ and $p < 0$ in the three cases $\theta = 0, 1, \infty$. The conditions $\theta = 0, 1, \infty$ correspond to (α, β) equalling $(0, 1)$, $(1, 1)$, $(1, 0)$ respectively. The fourth case $(\alpha, \beta) = (0, 0)$ yields a special limiting system which will be described in section 3.10.

3. The nine generic classes of asymptotic behaviour

Nine distinct generic classes of asymptotic behaviour were picked out by the RG analysis in section 1.4 (see also [11, 19]). For each class or case we shall perform the five calculations described above. We start with the effect of the perturbations on the partition function, and hence the equilibrium solution. In cases where a steady state is approached rather than the equilibrium we also calculate the modified form of the steady-state solution. We then calculate the effect on the kinetics of approach to steady state or equilibrium. Following these two calculations we turn to the contracted description of the system. The latter three calculations combine the problems of dealing with the noise and the coarse-grained system. We analyse the contracted Becker–Döring system derived from the full microscopic model with rate coefficients given by a combination of a power law with random perturbations, and investigate whether coarse-graining averages noise out of the system or exaggerates its effect. In so doing, we discover how perturbations to the microscopic rates manifest themselves in the rates of the contracted system. We then establish consistency by showing that the partition function calculated from the coarse-grained rates is the same, to leading order, as the partition function from the microscopic system sampled over the coarse mesh. Finally, we analyse the effect of the perturbations in the mesoscopic model on the large-time kinetics of the coarse-grained system.

3.1. Case I

This case corresponds to a fragmentation-dominated system where the fragmentation rate is independent of cluster size, that is the rate at which large clusters shed monomers is the same as that for small clusters. Such situations may arise in certain types of polymer degradation, if the breakdown of chains takes place through end-monomer fission processes.

In the non-perturbed version of this case, $a_r = 0$ for all r, so the partition function is identically zero. Introducing noise to the aggregation coefficient makes the partition function nonzero

$$Q_r = \prod_{k=1}^{r-1} \frac{\delta_k}{1+\varepsilon_{k+1}} \sim \left(\prod_{k=1}^{r-1} \delta_k\right)\left(1 - \sum_{k=1}^{r-1} \varepsilon_{k+1} + \mathcal{O}(\nu^2)\right). \tag{3.1}$$

Thus the partition function Q_r depends primarily on the perturbations δ_r; the perturbations ε_r only enter at higher order. Since $\mathbb{E}[\delta_r] = \nu \ll 1$, Q_r decays rapidly to zero with increasing r, according to $Q_r = \mathcal{O}(\nu^{r-1})$, thus $Q_{r+1} \ll Q_r$ for all r. Case I may hence correspond to a situation in which finite-length polymers or oligomers break down via stepwise fission processes.

In the noisy case, there is a nonzero partition function Q_r to which the system converges. To determine the manner of this convergence we transform from $c_r(t)$ to new coordinates, $c_r = Q_r \psi_r(t)$ so that at equilibrium $\psi_r \equiv 1$. Then $\psi_r(t)$ satisfies

$$\dot{\psi}_r = \psi_{r-1} - \psi_r + \delta_r(\psi_{r+1} - \psi_r) - \varepsilon_r(\psi_r - \psi_{r-1}) \tag{3.2}$$

for large aggregation numbers (r) and at large times (t), the continuum limit is valid and this equation goes over into the following partial differential equation:

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}\frac{\partial^2 \psi}{\partial r^2}(1 + \delta_r + \varepsilon_r) - \frac{\partial \psi}{\partial r}(1 + \varepsilon_r - \delta_r). \tag{3.3}$$

The solutions of this type of equation typically approach equilibrium via a diffusive wave, whose position we denote by $r = s(t)$. We transform from r to the new position variable $z = r - s(t)$ relative to the wavefront. The leading-order terms are then those involving $\frac{\partial \psi}{\partial z}$, formally yielding the equation $\dot{s} = 1 + \varepsilon_s - \delta_s$ for the position of the wave. The expected value of the first perturbation (due to δ_r) is zero, since $\mathbb{E}[\varepsilon_r] = 0$ for all r, but that of the second (due to ε_r) is positive, that is $\mathbb{E}[\delta_r] = \nu$ for all r. Thus we have $\mathbb{E}[\dot{s}] = 1 - \nu$, and the presence of perturbations slows the wave. This is not, however, a leading-order effect since small noise makes only a small difference to the system's approach to equilibrium. Higher-order terms from equation (3.3) lead to a description of the shape of the wavefront. If we start the system from a state of compact support (that is $c_r(0) = 0$ for $r \geqslant R$ for some $R < \infty$), then the large-time and large aggregation number asymptotic solution is given by

$$c_r(t) = \frac{1}{2} Q_r \operatorname{erfc}\left(\frac{r - (1-\nu)t}{\sqrt{2(1+\nu)t}}\right) \tag{3.4}$$

where Q_r is the partition function defined by equation (3.1). Thus, as well as travelling slightly more slowly than in the noiseless case, the wave is widened slightly, being spread out over a larger number of cluster sizes. These effects would be hard to measure experimentally since the typical concentration of large cluster sizes would be extremely small. Both these effects are due to the differing expected values of the perturbations to the forward and backward rate constants (namely that $\mathbb{E}[\varepsilon_r] = 0$ whilst $\mathbb{E}[\delta_r] = \nu$).

Moving now to the coarse-grained, mesoscopic description of the problem, we find $a_r = 0$, $b_r = 1$ implies $\alpha_n = \Delta_n$ and $\beta_{n+1} = 1 + E_{n+1}$ where

$$\Delta_n = \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} \delta_r \qquad E_{n+1} = \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \varepsilon_{r+1} + \mathcal{O}(\nu^2). \tag{3.5}$$

Thus, following an application of the coarse-graining contraction procedure, to $\mathcal{O}(1)$ the rates are $\alpha_n = 0$ and $\beta_{n+1} = 1$ with small perturbations to the rates, $\Delta_r = \mathcal{O}(\nu^\lambda)$ and $E_{r+1} = \mathcal{O}(\nu)$. Thus the perturbations to the aggregation rates are much smaller than those to the fragmentation rates, making the system *appear* more fragmentation dominated than the uncontracted version. However, this effect is due to the contracted model only representing some cluster sizes: growth from x_r to x_{r+1} requires the addition of λ monomers and hence happens at a rate of $\mathcal{O}(\nu^\lambda)$ rather than the $\mathcal{O}(\nu)$ rate for growth from c_r to c_{r+1} in the full model. Thus the contracted description is dominated by fragmentation to the correct extent. Since the perturbations in the full model are independent, and distributed with $\mathbb{E}[\delta_r] = \nu$, $\mathbb{E}[\varepsilon_r] = 0$, $\mathbb{V}[\delta_r] = \mathcal{O}(\nu^2)$, $\mathbb{V}[\varepsilon_r] = \mathcal{O}(\nu^2)$, in the contracted description we have $\mathbb{E}[\Delta_n] = \nu^\lambda$, $\mathbb{E}[E_n] = 0$, $\mathbb{V}[\Delta_n] = \mathcal{O}(\nu^{2\lambda})$, and $\mathbb{V}[E_n] = \mathcal{O}(\nu^2)$.

We now use the contracted rates given by $\alpha_n = \Delta_n$ and $\beta_{n+1} = 1 + E_{n+1}$ to calculate a partition function for the coarse-grained system. Using (2.12) and (3.5), we find

$$\Upsilon_N = \left(\prod_{n=1}^{N-1} \Delta_n\right)\left(1 - \sum_{n=1}^{N-1} E_{n+1} + \mathcal{O}(\nu^2)\right) = \left(\prod_{r=1}^{\Lambda_N - 1} \delta_r\right)\left(1 - \sum_{r=1}^{\Lambda_N - 1} \varepsilon_{r+1} + \mathcal{O}(\nu^2)\right). \tag{3.6}$$

Thus the first two terms of the equilibrium solution of the reduced model agree exactly with that of Q_R with $R = \Lambda_N$ in the full model (3.1).

In this case we know that the system will tend to the equilibrium solution given by $x_n = \Upsilon_n$ as in (3.6), which closely approximates Q_r (3.6) with $r = \Lambda_n$. To find the way in which the solution is approached, we use a similar method to that successfully applied to the microscopic description above, namely that of transforming to new dependent variables $\psi_n(t)$ given by $x_n(t) = \Upsilon_n \psi_n(t)$. Then to first order in ν we have

$$\dot{\psi}_n = \psi_{n-1} - \psi_n - E_n(\psi_n - \psi_{n-1}) \tag{3.7}$$

since in this case $\Delta_n = \mathcal{O}(\nu^\lambda)$ and $E_n = \mathcal{O}(\nu)$. For large times and large n-values the continuum approximation

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}(1 + E_n)\frac{\partial^2 \psi}{\partial n^2} - (1 + E_n)\frac{\partial \psi}{\partial n} \tag{3.8}$$

is formally valid. Since $\mathbb{E}[E_n] = 0$, the diffusive wave travels at unit expected speed and suffers no $\mathcal{O}(\nu)$ correction term. Thus if the system is initiated from $x_n(0) = 0$ for $n \geqslant 2$, the equilibrium is reached is via a diffusive wave moving from $n = 1$ to large n leaving the new equilibrium solution behind it as described by $x_n(t) \sim \frac{1}{2}\Upsilon_n \mathrm{erfc}((n-t)/\sqrt{2t})$. The noise thus has no effect at leading order, or at $\mathcal{O}(\nu)$, although higher-order terms will influence the evolution of the system. Thus, in this case, coarse-graining has *reduced* the effect of the noise, since in the non-coarse-grained case, the kinetics *are* affected by $\mathcal{O}(\nu)$ terms, decelerating and widening the wavefront as described by equation (3.4).

3.2. Case II

In this case the aggregation and fragmentation rates are both relevant and both size independent. This situation can be expected to arise in a wide variety of nucleation and growth problems: for example, it is likely to pertain for cluster formation at saturation or low supersaturation levels during crystal growth.

In this case introducing perturbations δ_r, ε_r to the rates $a_r = ar^p$, $b_{r+1} = br^p$ as in (2.1) modifies the partition function from $Q_r = 1$ for all r to

$$Q_r \sim 1 + \sum_{k=1}^{r-1}(\delta_k - \varepsilon_{k+1}) + \mathcal{O}(\nu^2). \tag{3.9}$$

Small-amplitude noise in the coefficients thus does not affect the leading-order behaviour of the system, at small values of r. To examine the large-r behaviour, we use the central limit theorem. For simplicity we assume that each of the random variables δ_k, ε_k is distributed uniformly on the interval $[-\nu, \nu]$, thus each has an expected value of zero and variance of $\sigma^2 = \frac{1}{3}\nu^2$. The difference $\delta_k - \varepsilon_{k+1}$ thus has mean of zero and variance of $\frac{2}{3}\nu^2$; and the above sum (equivalent to $Q_r - 1$) has mean zero and variance $\frac{2}{3}(r-1)\nu^2$. At large values of r, the central limit theorem implies the sum can be approximated by a normally distributed random variable with zero mean and variance $\sigma^2 = \frac{2}{3}r\nu^2$. Thus perturbations have a cumulative effect and may become significant when $r = \mathcal{O}(\nu^{-2})$; at this order of magnitude, the approximation in equation (3.9) ceases to be valid, since neglected higher-order terms then become significant.

For case II the kinetic equations are

$$\dot{c}_r = (1+\delta_{r-1})c_{r-1} - (1+\varepsilon_r)c_r - (1+\delta_r)c_r + (1+\varepsilon_{r+1})c_{r+1} \tag{3.10}$$

where δ_r, ε_r can be positive or negative, and are $\mathcal{O}(\nu)$ with $\mathbb{E}[\delta_r] = \mathbb{E}[\varepsilon_r] = 0$. Formally, for large times and large aggregation numbers, this leads to the continuum equation

$$\frac{\partial \psi}{\partial t} = \left(1 + \frac{1}{2}(\delta_r + \varepsilon_r)\right)\frac{\partial^2 \psi}{\partial r^2} + (\delta_r - \varepsilon_r)\frac{\partial \psi}{\partial r} \tag{3.11}$$

for $\psi(r,t) = c_r(t)/Q_r$. Since $\mathbb{E}[\delta_r - \varepsilon_r] = 0$, and $\mathbb{E}[(\delta_r - \varepsilon_r)^2] \sim \nu^2 \ll 1$, diffusion dominates the advection terms, and there is no overall driving force on the diffusive wave. Effectively, it is pinned at $r = 1$ and equilibrium is reached by purely diffusive mechanisms. If we use compact initial conditions (that is $c_r(0) = 0$ for all $r \geqslant R$ for some $R < \infty$) then the large-time asymptotic solution is

$$c_r(t) = Q_r \operatorname{erfc}\left(\frac{r}{2\sqrt{t}}\right). \tag{3.12}$$

Note that $\mathbb{E}[\delta_r] = 0 = \mathbb{E}[\varepsilon_r]$ implies that the width scale is unchanged by the perturbations, in contrast with case I, where the wave was widened due to $\mathbb{E}[\delta_r] > 0$.

Following the coarse-graining contraction, the reaction rates are given by $\alpha_n = 1 + \Delta_n$ and $\beta_{n+1} = 1 + E_{n+1}$, where

$$\Delta_n = \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \delta_r + \mathcal{O}(\nu^2) \qquad E_{n+1} = \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \varepsilon_{r+1} + \mathcal{O}(\nu^2). \tag{3.13}$$

Thus a system in which aggregation and fragmentation are balanced is mapped to a similar system following a coarse-grained reduction. Since $\mathbb{E}[\delta_r] = 0 = \mathbb{E}[\varepsilon_r]$ and $\mathbb{V}[\delta_r], \mathbb{V}[\varepsilon_r] = \mathcal{O}(\nu^2)$ we have $\mathbb{E}[\Delta_n] = 0 = \mathbb{E}[E_n]$ and $\mathbb{V}[\Delta_n], \mathbb{V}[E_n] = \mathcal{O}(\nu)$. The central limit theorem implies that the variances of the noise will increase linearly with λ. Since both δ_k, ε_k have variance proportional to ν^2, then Δ_r, E_r have variance proportional to $\lambda\nu^2$. So in order for the noise to remain a small correction term, one has to ensure that $\lambda \ll \nu^{-2}$; for small perturbations ($\nu \ll 1$) this does not constitute a significant restriction.

Using (2.12) and (3.13), we find the partition function Υ_n for the coarse-grained system is given by

$$\Upsilon_N = 1 + \sum_{n=1}^{N-1}(\Delta_n - E_{n+1}) + \mathcal{O}(\nu^2) = 1 + \sum_{r=1}^{\Lambda_N - 1}(\delta_r - \varepsilon_{r+1}) + \mathcal{O}(\nu^2). \tag{3.14}$$

Thus the first two terms of the equilibrium solution of the reduced model agree exactly with that of Q_R with $R = \Lambda_N$ in the full model (3.9). Thus, in the presence of noise, the contracted system tends to an equilibrium solution of the same form, to first order, as the full system.

The kinetic equations determining the approach to equilibrium are

$$\dot{x}_n = (1+\Delta_{n-1})x_{n-1} - (1+E_n)x_n - (1+\Delta_n)x_n + (1+E_{n+1})x_{n+1} \tag{3.15}$$

where Δ_n, E_n are $\mathcal{O}(\nu)$ with $\mathbb{E}[\Delta_n] = \mathbb{E}[E_n] = 0$. The system tends to the equilibrium solution $x_n = \Upsilon_n$ by a purely diffusive mechanism as described formally by the continuum limit equation

$$\frac{\partial\psi}{\partial t} = \left(1 + \frac{\Delta_n + E_n}{2}\right)\frac{\partial^2\psi}{\partial n^2} + (\Delta_n - E_n)\,\frac{\partial\psi}{\partial n} \tag{3.16}$$

for $\psi(n,t) = x_n(t)/\Upsilon_n$, so that $\psi \to 1$ as $t \to \infty$. Since the expected values of perturbations Δ_n and E_n are both zero, there are no $\mathcal{O}(\nu)$ correction terms to $\psi(n,t)$ in the large-time limit, and we have the solution $x_n(t) = \Upsilon_n \mathrm{erfc}(n/2\sqrt{t})$. Thus to $\mathcal{O}(\nu)$ the large-time kinetics of the system are almost identical to the uncontracted model. Using $r = \Lambda_n$, $c_r = x_n$ and $Q_r = \Upsilon_n$, the above formula for $x_n(t)$ implies $c_r = Q_r \mathrm{erfc}(r/2\lambda\sqrt{t})$ whereas analysis of the full model gave (3.12); thus the only difference between full and contracted models is in the timescale.

3.3. Case III

This case models situations which favour the formation of clusters since the system is dominated by aggregation; however, the rate of aggregation is size independent so that nucleation and cluster growth processes are balanced. One physicochemical scenario that this case may describe arises in certain surfactant self-assembly processes, in which amphiphile monomers attach to a growing assembly (for example, wormlike micelles, vesicles, and so on).

In the pure aggregation case with no noise the partition function is not defined since all the fragmentation coefficients b_r vanish. The presence of noise makes it possible to define the partition function

$$Q_r = \left(\prod_{k=1}^{r-1}\frac{1}{\varepsilon_{k+1}}\right)\left(1 + \sum_{k=1}^{r-1}\delta_k + \mathcal{O}(\nu^2)\right). \tag{3.17}$$

This is strongly dependent on the perturbations ε_k, implying rapid growth in Q_r with r, specifically $Q_r = \mathcal{O}(\nu^{-(r-1)})$. However, the system does not approach the equilibrium state $c_r = Q_r$, rather it tends to a steady-state configuration. In the unperturbed problem this state is $c_r = 1$ for all r, which has the steady-state flux $J = 1$; when noise is added to the rate coefficients this state is modified to $J = 1 + (\delta_1 - \varepsilon_2) + \mathcal{O}(\nu^2)$ by the calculation (1.6). Since the expected values of δ_k, ε_k satisfy $\mathbb{E}[\delta_k] = 0$ and $\mathbb{E}[\varepsilon_k] = \nu > 0$, the expected value of the steady-state flux is reduced by the presence of small-amplitude noise from $J = 1$ in the noise-free system to $\mathbb{E}[J] = 1 - \nu$. The concentrations asymptote to the modified steady state

$$c_r^{\mathrm{sss}} = 1 + (\delta_1 - \varepsilon_2 + \varepsilon_{r+1} - \delta_r) + \mathcal{O}(\nu^2). \tag{3.18}$$

The presence of $\mathcal{O}(\nu)$ noise in the reaction rates alters the steady-state solution by an amount of $\mathcal{O}(\nu)$. Note that the noise in the two rate constants a_1, b_2 affects the limiting concentrations of clusters of all sizes.

The kinetics of this case are governed by the approach to the steady-state solution (not the equilibrium solution). Since the perturbations to the fragmentation rates (ε_k) are all positive and the perturbations to the coagulation rates can be positive or negative, we have $\mathbb{E}[\delta_k] = 0$ and $\mathbb{E}[\varepsilon_k] = \nu$. We replace the differential–difference system by a partial differential equation by taking the continuum limit and then seeking a diffusive wave solution of this partial differential equation. First, we transform variables by $c_r(t) = c_r^{\mathrm{sss}}\psi_r(t)$ so that $\psi_r(t) \to 1$ as $t \to \infty$ according to

$$\dot{\psi}_r = (1+\delta_r)(\psi_{r+1} - \psi_r) + \varepsilon_r(\psi_{r-1} - \psi_r) + \frac{J}{c_r^{\mathrm{sss}}}(\psi_{r-1} - \psi_{r+1}) \tag{3.19}$$

which formally goes over to the continuum limit

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}(1+\delta_r+\varepsilon_r)\frac{\partial^2 \psi}{\partial r^2} - (1+\delta_r+\varepsilon_r-2\varepsilon_{r+1})\frac{\partial \psi}{\partial r}. \tag{3.20}$$

We define $s(t)$ to be the position of the wave and transform from r to an as yet unknown coordinate which moves with the diffusive wave by $r = s(t) + z$. The wavefront is then determined by $\dot{s} = 1 - \nu$, an equation which is derived from the leading-order terms of (3.20) by taking expectation values. The speed of propagation is reduced slightly by the noisy coefficients, although this is a first-order effect, only being present in the $\mathcal{O}(\nu)$ terms. The large-time and large-size asymptotic solution is

$$c_r(t) \sim \frac{1}{2} c_r^{\text{sss}} \text{erfc}\left(\frac{r-(1-\nu)t}{\sqrt{2\,(1+\nu)\,t}}\right) \tag{3.21}$$

showing that the noise also broadens the diffusive wave in aggregation space as in case I. The erfc shape is determined by the higher-order terms of (3.20).

The domination of aggregation over fragmentation in the contracted form of case III is not altered by the presence of small-amplitude noise

$$\Delta_n = \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \delta_r + \mathcal{O}(\nu^2) \qquad E_{n+1} = \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} \varepsilon_{r+1}. \tag{3.22}$$

In this case $\alpha_n = 1+\Delta_n$ and the noise in the aggregation term, Δ_n, is $\mathcal{O}(\nu)$ whereas the noise in the fragmentation term, $\beta_{n+1} = E_{n+1}$, is much smaller, being of magnitude $\mathcal{O}(\nu^\lambda)$. Superficially this gives the impression of the contracted system being more strongly aggregation-dominated than the full system; however, this accentuated dominance is correct for similar reasons to those expounded for case I. Since $\mathbb{E}[\delta_r] = 0$ and $\mathbb{V}[\delta_r] = \mathcal{O}(\nu^2)$, we have $\mathbb{E}[\Delta_n] = 0$ and $\mathbb{V}[\Delta_n] = \mathcal{O}(\nu^2)$; also $\mathbb{E}[\varepsilon_r] = \nu$ and $\mathbb{V}[\varepsilon_r] = \mathcal{O}(\nu^2)$ implies $\mathbb{E}[E_{n+1}] = \nu^\lambda$ and $\mathbb{V}[E_{n+1}] = \mathcal{O}(\nu^{2\lambda})$. Equations (2.12) and (3.22) imply

$$\Upsilon_N \sim \left(\prod_{n=1}^{N-1}\frac{1}{E_{n+1}}\right)\left(1+\sum_{n=1}^{N-1}\Delta_n+\mathcal{O}(\nu^2)\right) = \left(\prod_{r=1}^{\Lambda_N-1}\frac{1}{\varepsilon_{r+1}}\right)\left(1+\sum_{r=1}^{\Lambda_N-1}\delta_r+\mathcal{O}(\nu^2)\right) \tag{3.23}$$

so the contraction procedure does not lose information from the first two terms of the partition function—to see this, compare Υ_N in the above with Q_R in (3.17) with $R = \Lambda_N$. However, in this case the partition function does not play such an important role as in cases I and II where it determines the large-time asymptotic solution which is approached; here, it is the steady-state solution which determines the large-time asymptotics. Since $E_r = \mathcal{O}(\nu^\lambda)$, whilst $\Delta_r = \mathcal{O}(\nu)$, perturbations to the forward coefficients influence the first correction term whereas those to the backward rates do not. The steady-state solution is thus modified to

$$x_n^{\text{sss}} \;=\; 1+\Delta_1-\Delta_r+\mathcal{O}(\nu^2) \;=\; 1+\sum_{k=1}^{\lambda}(\delta_k-\delta_{(n-1)\lambda+k})+\mathcal{O}(\nu^2) \tag{3.24}$$

which has constant flux $L = 1 + \Delta_1 + \mathcal{O}(\nu^2)$. The leading-order terms ($x_n = 1$, $L = 1$) agree with the full model and with the model without noisy coefficients; however, the first correction term is not in agreement with the full solution of the noisy model. The contracted model predicts a steady-state flux of $L \sim 1+\sum_{k=1}^{\lambda}\delta_k+\mathcal{O}(\nu^2)$, whereas the full model has flux $J \sim 1+\delta_1-\varepsilon_2+\mathcal{O}(\nu^2)$, so agreement is limited to the leading-order terms ($J = L = 1$) only, with the first-order correction terms differing, being $\mathcal{O}(\nu)$. In this case microscopic detail in the first correction is involved in determining the steady-state flux, but the information is lost in the coarse-graining contraction, so the procedure only gives the correct result to leading order in ν.

To determine the kinetics of approach to steady state in the reduced model we transform from $x_n(t)$ to $\psi_n(t)$ by $x_n(t) = x_n^{\mathrm{sss}}\psi_n(t)$ to gain

$$\dot{\psi}_n = (1+\Delta_n)(\psi_{n+1}-\psi_n) + E_n(\psi_{n-1}-\psi_n) + \frac{L}{x_n^{\mathrm{sss}}}(\psi_{n-1}-\psi_{n+1}). \tag{3.25}$$

Since $\Delta_n = \mathcal{O}(\nu)$ and $E_n = \mathcal{O}(\nu^\lambda)$, the two-term continuum expansion of (3.25) correct to $\mathcal{O}(\nu)$ is

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}(1+\Delta_n)\frac{\partial^2\psi}{\partial n^2} - (1+\Delta_n)\frac{\partial\psi}{\partial n}. \tag{3.26}$$

Thus, including the $\mathcal{O}(\nu)$ terms, the diffusive wave has an expected speed of unity since $\mathbb{E}[\Delta_n] = 0$. This differs slightly from the result for the full model presented in (3.21), where the nonzero $\mathcal{O}(\nu)$ perturbations to the fragmentation rates caused the wave to be slowed. After taking expectations, (3.26) is solved by $\psi = \frac{1}{2}\mathrm{erfc}((n-t)/\sqrt{2t})$ which yields the large-time solution

$$x_n(t) \sim \frac{1}{2}\,(1+\Delta_1-\Delta_n)\,\mathrm{erfc}\left(\frac{n-t}{\sqrt{2t}}\right). \tag{3.27}$$

Thus, coarse-graining has altered the $\mathcal{O}(\nu)$ correction terms in the kinetics of the approach to the steady state, as well as the $\mathcal{O}(\nu)$ corrections to the steady state itself. However, the leading-order behaviour is faithfully reproduced.

3.4. Case IV

This generic class of behaviour describes systems dominated by fragmentation, in which larger clusters break up at a much faster rate than smaller ones.

When noise is absent, the partition function is identically zero (for $r \geqslant 2$); however, the presence of noise alters the partition function to

$$Q_r \sim \frac{1}{[(r-1)!]^p}\left(\prod_{k=1}^{r-1}\delta_k\right)\left(1-\sum_{k=1}^{r-1}\frac{\varepsilon_{k+1}}{k^p}\right). \tag{3.28}$$

Thus, Q_r rapidly decays with increasing r since as $r \to \infty$, $Q_r = \mathcal{O}(\nu^{r-1})$ and $p > 0$. The presence of perturbations to the rate coefficients provides a nonzero equilibrium solution $c_r = Q_r$ given by equation (3.28) which is approached, as we shall now show, via a diffusive wave. Transforming to new variables $\psi_r(t) = c_r(t)/Q_r$, we find

$$\dot{\psi}_r = \delta_r(\psi_{r+1}-\psi_r) + \left[(r-1)^p + \varepsilon_r\right](\psi_{r-1}-\psi_r) \tag{3.29}$$

where $\delta_r > 0$ with $\mathbb{E}[\delta_r] = \nu$ for all r, and $\mathbb{E}[\varepsilon_r] = 0$ for all r, with ε_r taking both positive and negative values. In the large-r and large-time limit, ψ_r becomes smooth in r so it is valid to take the continuum limit which formally yields

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}\left[(r-1)^p + \delta_r + \varepsilon_r\right]\frac{\partial^2\psi}{\partial r^2} - \left[(r-1)^p + \varepsilon_r - \delta_r\right]\frac{\partial\psi}{\partial r}. \tag{3.30}$$

This type of equation has a diffusive wave solution; we denote its position by $s(t)$ and transform to a coordinate which moves with the wave, via $r = s(t) + z$. At leading order, this formally yields the equation $\dot{s} = (s-1)^p + \varepsilon_s - \delta_s$. Since $\mathbb{E}[\varepsilon_k] = 0$ and $\mathbb{E}[\delta_k] = \nu > 0$, there is an $\mathcal{O}(\nu)$ term in the equation for the expected value of $s(t)$, namely

$$\dot{s} = (s-1)^p - \nu. \tag{3.31}$$

Thus the noise has a slowing influence on the wave, but since $s \to \infty$ as $t \to \infty$, the leading-order term is $\dot{s}_0 = s_0^p$, and we have

$$s_0(t) = [(1-p)(t-t_0)]^{1/(1-p)}. \tag{3.32}$$

An $\mathcal{O}(\nu)$ correction term can be calculated by putting $s(t) = s_0(t) + \nu s_1(t)$ into equation (3.31); one finds $s_0(t)$ is determined by (3.32) and $s_1(t)$ by $\dot{s}_1 = -1 + p s_0^{p-1} s_1$, which yields

$$s_1 = \frac{-(1-p)(t-t_0)}{(1-2p)} + K(t-t_0)^{p/(1-p)} \tag{3.33}$$

for some constant K. Thus, for $p < 1$, the wave experiences a deceleration which reduces the speed by a constant amount but which is insufficient to stop the wave since the growth in equation (3.32) has the faster growth rate in the limit $t \to \infty$. A higher-order effect is that noise broadens the wave very slightly, since noise in (3.30) has the effect of increasing the diffusion coefficient. The effect of this, however, is minimal since the diffusion constant which the wave experiences grows without bound in the large-time limit. In cases where $p < \frac{1}{2}$, higher-order terms from equation (3.30) yield the shape of the front as $\psi = \frac{1}{2}\mathrm{erfc}(z/\sqrt{(2s(t)+4\nu t)})$ so that the large-time asymptotic solution (including the first correction term due to ν) is given by

$$c_r(t) \sim \frac{1}{2} Q_r \mathrm{erfc}\left(\frac{r - s(t)}{\sqrt{2s(t) + 4\nu t}}\right) \tag{3.34}$$

where $s(t) = s_0(t) + \nu s_1(t)$ is given by equations (3.32) and (3.33). As $t \to +\infty$, the effects of perturbations to the rate coefficients decrease in significance, both in the position and in the shape of the wavefront.

The rates in the contracted model are given by $\alpha_n = \Delta_n$ and $\beta_{n+1} = n^{p\lambda} + E_{n+1}$ where the perturbations are determined by

$$\Delta_n = \lambda^{-p\lambda} \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} \delta_r = \mathcal{O}(\nu^\lambda) \qquad E_{n+1} = n^{p\lambda} \sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} \frac{\varepsilon_{r+1}}{r^p} + \mathcal{O}(\nu^2) \tag{3.35}$$

where in the latter, we have again made the approximation (1.13) valid for large r. Note that, as in case I, $\alpha_r = \mathcal{O}(\nu^\lambda)$ whereas $\beta_{r+1} = r^{p\lambda} + \mathcal{O}(\nu)$, suggesting that while the contracted model equations have the same structure as the full ones, they are more heavily fragmentation dominated, due to the rate at which a cluster $x_{n+1} = c_{\Lambda_n+\lambda}$ grows from the cluster $x_n = c_{\Lambda_n}$ being much less than for c_{r+1} growing from c_r. If we assume that the perturbations are independent and randomly distributed with

$$\mathbb{E}[\delta_r] = \nu \qquad \mathbb{E}[\varepsilon_{r+1}] = 0 \qquad \mathbb{V}[\delta_r] = V_\delta \nu^2 \qquad \mathbb{V}[\varepsilon_{r+1}] = V_\varepsilon \nu^2 \tag{3.36}$$

then the perturbations to the contracted rates satisfy

$$\begin{aligned} &\mathbb{E}[\Delta_n] = \lambda^{-p\lambda}\nu^\lambda \qquad \mathbb{E}[E_{n+1}] = 0 \\ &\mathbb{V}[\Delta_n] = \lambda^{-2p\lambda}\left[(V_\delta+1)^\lambda - 1\right]\nu^{2\lambda} \qquad \mathbb{V}[E_{n+1}] \approx V_\varepsilon \lambda^{1-2p} n^{2p(\lambda-1)} \nu^2 \end{aligned} \tag{3.37}$$

where the last formula includes a simplifying approximation valid for large r and large λ (namely replacing $\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} r^z$ with $\int_{r=\Lambda_n}^{\Lambda_{n+1}-1} r^z \,\mathrm{d}r$, to yield $\lambda^{1-z} r^{-z}$). The formulae in (3.37) show that the contraction procedure makes the amplitude of the perturbations to the fragmentation rate dependent on the aggregation number, with larger sizes having a greater variance in the fragmentation rates. However, at larger sizes the standard deviation of the noise grows with $\mathcal{O}(n^{p(\lambda-1)})$, thus the noise never becomes as large as the deterministic component of the rate ($\beta_n = \mathcal{O}(n^{p\lambda})$).

We now use this knowledge of the rates in the contracted system including the leading-order perturbations to construct a partition function for the contracted system Υ_n and, for consistency, verify that $\Upsilon_n = Q_r$ when $n = \Lambda_r$. Using (2.12) and (3.35), we find

$$\begin{aligned} \log \Upsilon_N &\sim -p\lambda N(\log N - 1) + \sum_{n=1}^{N-1} \log \Delta_n - \sum_{n=1}^{N-1} \frac{E_{n+1}}{n^{p\lambda}} \\ &\sim -p\lambda N(\log(\lambda N) - 1) + \sum_{r=1}^{\Lambda_N - 1} \log \delta_r - \sum_{r=1}^{\Lambda_N - 1} \frac{\varepsilon_{r+1}}{r^p} \end{aligned} \tag{3.38}$$

where a similar approximation to that of (1.13) has been made. This result should be compared with Q_R for $R = \Lambda_N$ from (3.28), which yields

$$\log Q_R \sim -pR(\log R - 1) + \sum_{r=1}^{R-1} \log \delta_r - \sum_{r=1}^{R-1} \frac{\varepsilon_{r+1}}{r^p}. \tag{3.39}$$

Thus there are differences between Q_{Λ_N} and Υ_N, but at large N these scale with $\log N$, which is of lower order of magnitude than the first two terms of Υ_N or Q_{Λ_N}. For large N, the leading-order and first correction terms in the log of the partition function grow with $N \log N$ and N respectively, so both are reproduced correctly in the contracted description, as are the perturbations $\delta_k, \varepsilon_{k+1}$ as can be seen by comparing (3.38) with (3.39); it is only high-order correction terms which differ. An alternative comparison can be made between

$$\mathbb{E}[\Upsilon_N] = \frac{((N-1)!)^{p\lambda}}{\lambda^{-p\lambda(N-1)}\nu^{\lambda(N-1)}} \qquad \text{and} \qquad \mathbb{E}[Q_R] = \frac{((R-1)!)^p}{\nu^{R-1}} \tag{3.40}$$

again showing that for large N and $R = \Lambda_N$ the leading-order terms agree, since Stirling's formula leads to the dominant terms in both expressions being $(\lambda N)^{p\lambda N}\mathrm{e}^{-p\lambda N}/\nu^{\lambda N}$.

In the present case, the system tends to the modified equilibrium solution $x_n = \Upsilon_n$ given by (3.38). The transformation $\psi_n(t) = x_n(t)/\Upsilon_n$ enables us to find the large-time asymptotics; when applied to the equation

$$\dot{x}_n = \Delta_{n-1}x_{n-1} - \Delta_n x_n - \left[(n-1)^{p\lambda} + E_n\right]x_n + \left[n^{p\lambda} + E_{n+1}\right]x_{n+1} \tag{3.41}$$

it yields

$$\dot{\psi}_n = \Delta_n(\psi_{n+1} - \psi_n) + \left[(n-1)^{p\lambda} + E_n\right](\psi_{n-1} - \psi_n). \tag{3.42}$$

Since $\Delta_n = \mathcal{O}(\nu^\lambda)$ whilst $E_n = \mathcal{O}(\nu)$ we keep only those terms involving perturbations to the fragmentation rate (E_n); thus on formally taking the continuum limit, we find

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}\left[(n-1)^{p\lambda} + E_n\right]\frac{\partial^2 \psi}{\partial n^2} - \left[(n-1)^{p\lambda} + E_n\right]\frac{\partial \psi}{\partial n}. \tag{3.43}$$

The substitution from independent variable n to $z = n - s(t)$ yields the expression $\dot{s} = (s-1)^{p\lambda}$ since $\mathbb{E}[E_n] = 0$; hence the noise has no $\mathcal{O}(\nu)$ effect on the expected speed of the wave in the large-time limit unlike the full model (see equation (3.31)). Thus, as $s \to \infty$, we have $\dot{s} = s^{p\lambda}$ and so $s(t) = [(1-p\lambda)(t-t_0)]^{1/(1-p\lambda)}$ as in the full model with noiseless rate coefficients. As in case I, the coarse-graining process has reduced the effect of the perturbations. These solutions are only valid for $p\lambda < 1$; when $p\lambda > 1$ the system instantly gels as noted by Brilliantov and Krapivsky [4], and the large-time asymptotics differ significantly. However, this case is less relevant physically, since the aggregation rate cannot normally grow faster than the cluster size, and usually grows much more slowly, giving rise to exponents strictly less than unity (i.e. $p < 1$).

3.5. Case V

This is perhaps the most interesting of all the nine classes of generic behaviour. Both aggregation and fragmentation are present and finely balanced; both occur faster at larger aggregation numbers than smaller ones. As expected in general crystal growth and dissolution processes, there is relatively slow nucleation of critical nuclei from the free 'monomer' phase and faster growth/dissolution of supercritical clusters.

In the case with no noise, aggregation and fragmentation are perfectly balanced, implying the same value for the partition function $Q_r = 1$ for all r. The presence of perturbations to the rates alters this, to

$$Q_r = 1 + \sum_{k=1}^{r-1}\left(\frac{\delta_k - \varepsilon_{k+1}}{k^p}\right) + \mathcal{O}(\nu^2). \tag{3.44}$$

Thus for $\nu \ll 1$ the leading-order behaviour ($Q_r = 1$) is unaltered, but suffers an $\mathcal{O}(\nu)$ correction term. However, for $p < 1$ a result similar to that derived in case II holds, where the effect of the perturbations accumulates, so that at large r the noise may become a leading-order effect. For case V we assume each δ_k, ε_k has a mean of zero, a variance of ν^2 and all are independent random variables. Thus at large r, Q_r has an expected value of unity with a variance of $\nu^2 r^{1-p}/(1-p)$. Thus when $r = \mathcal{O}(\nu^{-2/(1-p)})$, the variance is $\mathcal{O}(1)$ and so the perturbations influence the leading-order term in the asymptotic expression for Q_r. Note that if $p > 1$ then the variance of Q_r approaches $\nu^2\zeta(p)$ (where $\zeta(z)$ is the Riemann zeta function which arises in the solution of the noiseless time evolution for case V; see [11, 19]), and so the accumulation does not become a leading-order effect.

In the case $p > 1$, however, the system does not evolve towards the equilibrium solution, but instead is attracted to a steady-state solution with a more rapid decay in the limit $r \to \infty$ which we now examine in more detail. Perturbing the rate coefficients modifies this state from one of constant flux with $J = 1/\zeta(p)$ to $J = 1/\zeta(p) + J_1$, where

$$J_1 = \frac{1}{\zeta(p)^2} \sum_{k=1}^{\infty} \left(\frac{\delta_k}{k^p} \sum_{n=k}^{\infty} \frac{1}{n^p} - \frac{\varepsilon_{k+1}}{k^p} \sum_{n=k+1}^{\infty} \frac{1}{n^p} \right). \tag{3.45}$$

This gives the steady-state concentrations

$$c_r = \frac{1}{\zeta(p)} \sum_{k=r}^{\infty} \frac{1}{k^p} + \sum_{k=1}^{r-1} \left(\frac{\delta_k}{\zeta(p) k^p} \sum_{i=k}^{\infty} \frac{1}{i^p} - \frac{\varepsilon_{k+1}}{\zeta(p) k^p} \sum_{i=k+1}^{\infty} \frac{1}{i^p} - \frac{J_1}{k^p} \right). \tag{3.46}$$

Unlike the steady states in cases III and VI, the perturbations δ_1, ε_2 do not play a special role in this solution; rather all perturbations influence the steady-state flux and concentrations.

Let us now analyse the approach to equilibrium for $p < 1$. The equilibrium solution is identical to the partition function Q_r since $c_1 = 1$. We transform to new independent variables $\psi_r(t) = c_r(t)/Q_r$, with Q_r modified by the presence of noise, as in (3.44); for large r, we formally obtain the continuum approximation

$$\frac{1}{r^p} \frac{\partial \psi}{\partial t} = \left(1 + \frac{\delta_r + \varepsilon_r}{2 r^p} \right) \frac{\partial^2 \psi}{\partial r^2} + \left(\frac{p}{r} + \frac{\delta_r - \varepsilon_r}{r^p} \right) \frac{\partial \psi}{\partial r}. \tag{3.47}$$

This describes physical behaviour that approaches equilibrium neither by a diffusive wave nor by a simple diffusive process as case II did; instead there is a more complicated similarity solution. Including $\mathcal{O}(\nu)$ correction terms, taking the expectation of this leads to $\psi_t = (r^p \psi_r)_r$ so the similarity solution

$$\psi(r, t) = \frac{\int_{r/t^{1/(2-p)}}^{\infty} u^{-p} \exp(-u^{2-p}/(2-p)^2)\, \mathrm{d}u}{\int_0^{\infty} u^{-p} \exp(-u^{2-p}/(2-p)^2)\, \mathrm{d}u} \tag{3.48}$$

provides the correct asymptotic approximation in the limit $\nu \ll 1$; the correction terms being much smaller than $\mathcal{O}(\nu)$ (that is $\mathrm{o}(\nu)$), in contrast with cases IV and VI where the correction terms are $\mathcal{O}(\nu)$.

When $p > 1$ a steady state with nonzero flux is approached. We convert to new variables $c_r(t) = c_r^{\mathrm{sss}} \psi_r(t)$. For $1 < p < 2$ the continuum approximation valid at large r is formally

$$\frac{1}{r^p} \frac{\partial \psi}{\partial t} = \left(1 + \frac{\delta_r + \varepsilon_r}{2 r^p} \right) \frac{\partial^2 \psi}{\partial r^2} + \left(\frac{2-p}{r} + \frac{\delta_r - \varepsilon_r}{r^p} \right) \frac{\partial \psi}{\partial r} \tag{3.49}$$

which, when we take the expected value of each term, reduces to

$$\frac{\partial \psi}{\partial t} = r^p \frac{\partial^2 \psi}{\partial r^2} + (2-p) r^{p-1} \frac{\partial \psi}{\partial r} \tag{3.50}$$

the correction terms due to δ_r and ε_r again being much smaller than $\mathcal{O}(\nu)$, that is of magnitude $o(\nu)$. This equation has the solution

$$\psi = \frac{\int_{r/t^{1/(2-p)}}^{\infty} u^{p-2}\exp(-u^{2-p}/(2-p)^2)\,\mathrm{d}u}{\int_0^{\infty} u^{p-2}\exp(-u^{2-p}/(2-p)^2)\,\mathrm{d}u}. \tag{3.51}$$

Because $p > 1$, the perturbations are uniformly small in r in both advection and diffusion terms. Thus this is a uniformly valid leading-order solution. For $p \geqslant 2$, the similarity solution of equation (3.51) is not well-defined, and so does not determine convergence to the steady state.

In the contracted system of equations, the rates are given by $\alpha_n = n^{p\lambda} + \Delta_n$ and $\beta_{n+1} = n^{p\lambda} + E_{n+1}$, where, again using (1.13), we find

$$\Delta_n = n^{p\lambda}\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1}\frac{\delta_k}{k^p} \qquad E_{n+1} = n^{p\lambda}\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1}\frac{\varepsilon_{k+1}}{k^p}. \tag{3.52}$$

In contrast to cases IV and VI, perturbations to the forward and backward rates in the contracted equations have the same order of magnitude. If the noise in the full model is assumed to be randomly distributed according to

$$\mathbb{E}[\delta_r] = 0 \qquad \mathbb{E}[\varepsilon_{r+1}] = 0 \qquad \mathbb{V}[\delta_r] = V_\delta\nu^2 \qquad \mathbb{V}[\varepsilon_{r+1}] = V_\varepsilon\nu^2 \tag{3.53}$$

then in the contracted model we have

$$\begin{aligned}&\mathbb{E}[\Delta_n] = 0 \qquad \mathbb{E}[E_{n+1}] = 0 \qquad \mathbb{V}[\Delta_n] \approx V_\delta\lambda^{1-2p}n^{2p(\lambda-1)}\nu^2\\ &\mathbb{V}[E_{n+1}] \approx V_\varepsilon\lambda^{1-2p}n^{2p(\lambda-1)}\nu^2.\end{aligned} \tag{3.54}$$

As in equation (3.37), the approximations replace $\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1} r^p$ by $\int_{r=\Lambda_n}^{\Lambda_{n+1}-1} r^p\,\mathrm{d}r$. From (3.54) we see that the amplitude of the noise is size dependent in the contracted description but, even at large aggregation numbers, it never rivals the deterministic component of the rate coefficients. The expected values and the orders of magnitude (in ν) of the variance are correctly maintained in the reduced model.

Following a similar method to that of case IV, we insert the contracted rates (3.52) into (2.12) to find the contracted partition function

$$\Upsilon_N = 1 + \sum_{n=1}^{N-1}\frac{\Delta_n - E_{n+1}}{n^{p\lambda}} + \mathcal{O}(\nu^2) = 1 + \sum_{r=1}^{\Lambda_N-1}\frac{\delta_r - \varepsilon_{r+1}}{r^p} + \mathcal{O}(\nu^2). \tag{3.55}$$

In this case the partition function constructed from the reduced rate coefficients matches the first two terms of the full (microscopic) partition function Q_R with $R = \Lambda_N$ as in (3.44). This function also provides the large-time asymptotic approximation to the equilibrium solution for $p\lambda \leqslant 1$.

In cases where $p > 1/\lambda$, a steady state is approached instead of the equilibrium. This differs from the full model, where the transition from equilibrium to steady state occurs at $p = 1$. Values of p satisfying $1/\lambda < p < 1$ will approach a steady state in the contracted description but the equilibrium solution in the full model. Thus when $0 < p < 1$, in order to capture the correct qualitative behaviour, one must ensure that $\lambda < 1/p$.

The steady-state solution for $p > 1/\lambda$ has flux $L = 1/\zeta(p\lambda) + L_1$ where

$$L_1 = \frac{1}{\zeta(p\lambda)^2}\sum_{r=1}^{\infty}\left(\frac{\Delta_r}{r^{p\lambda}}\sum_{k=r}^{\infty}\frac{1}{k^{p\lambda}} - \frac{E_{r+1}}{r^{p\lambda}}\sum_{k=r+1}^{\infty}\frac{1}{k^{p\lambda}}\right) \tag{3.56}$$

the steady state being given by

$$x_n^{\mathrm{sss}} = \frac{1}{\zeta(p\lambda)}\sum_{k=n}^{\infty}\frac{1}{k^{p\lambda}} + \frac{1}{\zeta(p\lambda)}\sum_{r=n}^{\infty}\left(\frac{L_1\zeta(p\lambda)}{r^{p\lambda}} + \frac{E_{r+1}}{r^{p\lambda}}\sum_{k=r+1}^{\infty}\frac{1}{k^{p\lambda}} - \frac{\Delta_r}{r^{p\lambda}}\sum_{k=r}^{\infty}\frac{1}{k^{p\lambda}}\right). \tag{3.57}$$

This clearly has a similar form to (3.46); however, whilst (3.57) displays the same qualitative behaviour as (3.46), there are quantitative differences. The leading-order part of (3.46) at large r decays according to $c_r \sim 1/(p-1)\zeta(p)r^{p-1}$, implying that for $r = \Lambda_n$ the quantity c_r asymptotes to $1/(p-1)\zeta(p)\lambda^{p-1}n^{p-1}$ whilst $x_n \sim 1/(p\lambda-1)\zeta(p\lambda)n^{p\lambda-1}$; while both decay algebraically, the coarse-graining procedure has altered the exponent of the decay.

Let us turn now to the kinetics of the system's approach to equilibrium or a steady state. Since both Δ_n and E_n are $\mathcal{O}(\nu)$ the kinetics of the contracted system is very similar to that of the full system. For $p < 1/\lambda$ the system approaches the equilibrium solution $x_n = \Upsilon_n$, where to $\mathcal{O}(\nu)$, Υ_n is identical to Q_r with $r = \Lambda_n$—compare equations (3.44) and (3.55). The manner of approach is remarkably similar to (3.47), namely for $\psi(n,t) = x_n(t)/\Upsilon_n$ we formally have

$$\frac{1}{n^{p\lambda}}\frac{\partial\psi}{\partial t} = \left(1 + \frac{\Delta_n + E_n}{2n^{p\lambda}}\right)\frac{\partial^2\psi}{\partial n^2} + \left(\frac{p\lambda}{n} + \frac{\Delta_n - E_n}{n^{p\lambda}}\right)\frac{\partial\psi}{\partial n} \tag{3.58}$$

which, on taking expectations, leads to the solution

$$\psi(n,t) = \frac{\int_{n/t^{1/(2-p\lambda)}}^{\infty} u^{-p\lambda}\exp(-u^{-p\lambda}/(p\lambda)^2)\,\mathrm{d}u}{\int_0^{\infty} u^{p\lambda-2}\exp(-u^{-p\lambda}/(p\lambda)^2)\,\mathrm{d}u}. \tag{3.59}$$

When $p > 1/\lambda$ the system approaches the perturbed steady-state solution x_n^{sss} given in (3.56), (3.57) according to

$$\frac{1}{n^{p\lambda}}\frac{\partial\psi}{\partial t} = \left(1 + \frac{\Delta_n + E_n}{2n^{p\lambda}}\right)\frac{\partial^2\psi}{\partial n^2} + \left(\frac{2-p\lambda}{n} + \frac{\Delta_n - E_n}{n^{p\lambda}}\right)\frac{\partial\psi}{\partial n} \tag{3.60}$$

where $\psi(n,t) = x_n(t)/x_n^{\mathrm{sss}}$. Equation (3.60) corresponds to the kinetics of the full model (3.49). As in the full model, there are also $\mathcal{O}(n^{-2})$ corrections to the advection term which are more significant than the $n^{-p\lambda}$ terms if $p > 2/\lambda$. After taking the expectation of equation (3.60), the solution

$$\psi(n,t) = \frac{\int_{n/t^{1/(2-p\lambda)}}^{\infty} u^{p\lambda-2}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u}{\int_0^{\infty} u^{p\lambda-2}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u} \tag{3.61}$$

can be found.

3.6. Case VI

In this generic case there is virtually no fragmentation; the system is dominated by aggregation which occurs more rapidly for large cluster sizes. This scenario is typical of nucleation and growth processes in heavily supersaturated solutions, in which critical nuclei form relatively slowly, but then grow in size very rapidly.

As in case III, the partition function is not defined when noise is absent since all the fragmentation rates are then zero; when the fragmentation rates are perturbed by noise the partition function Q_r can be defined but is sensitive to the amplitude of ε_k

$$Q_r \sim [(r-1)!]^p\left(\prod_{k=1}^{r-1}\frac{1}{\varepsilon_{k+1}}\right)\left(1 + \sum_{k=1}^{r-1}\frac{\delta_k}{k^p}\right) \tag{3.62}$$

thus $Q_r = \mathcal{O}(\nu^{-(r-1)})$. However, in this case the system does not tend to the equilibrium state $c_r = Q_r$; instead, it tends to a steady state given by constant flux $J = 1 + (\delta_1 - 2^{-p}\varepsilon_2) + \mathcal{O}(\nu^2)$, which implies

$$c_r^{\mathrm{sss}} = \frac{1}{r^p}\left[1 + \left(\delta_1 - 2^{-p}\varepsilon_2 + \frac{\varepsilon_{r+1}}{(r+1)^p} - \frac{\delta_r}{r^p}\right)\right]. \tag{3.63}$$

Thus, altering a_r, b_{r+1} by $\mathcal{O}(\nu)$ alters the steady state by an $\mathcal{O}(\nu)$ amount. As one might expect, the perturbations to rates at larger aggregation numbers are less significant than those to lower aggregation numbers; also as in case III, the first two perturbations δ_1, ε_2 influence all other concentrations at $\mathcal{O}(\nu)$. Whilst the presence of noise restores the existence of the partition function, equation (3.63) is the more physically relevant result, in that the partition function which increases with r will not be directly manifest in a simulation or experiment, whereas the steady-state concentrations will be. These decrease with increasing r since $p > 0$.

The manner in which the steady-state solution is approached is found by substituting $c_r(t) = c_r^{\mathrm{sss}}\psi_r(t)$ into the determining equations (2.5) which, with $b = 0$ and $a = 1$, gives

$$\dot{\psi}_r = \varepsilon_r(\psi_{r-1} - \psi_r) + (r^p + \delta_r)(\psi_{r+1} - \psi_r) + \frac{J}{c_r^{\mathrm{sss}}}(\psi_{r-1} - \psi_{r+1}) \tag{3.64}$$

where J is the steady-state flux into the system. We have two-term asymptotic expansions for J and c_r^{sss} given in, and just before, (3.63) which enable us to simplify this equation. In the large-time and large aggregation number limits, we formally take the continuum limit

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}(r^p + \delta_r + \varepsilon_r)\frac{\partial^2\psi}{\partial r^2} - \left(r^p + \delta_r + \varepsilon_r - 2\varepsilon_{r+1}\right)\frac{\partial\psi}{\partial r}. \tag{3.65}$$

As noted earlier (case IV, equation (3.29)), this equation has a solution in the form of an advective–diffusive wave; to determine the speed and shape of such a wave we transform to a frame of reference which moves with the wave by $r = s(t) + z$ where $r = s(t)$ denotes the position of the wave. The leading-order terms in (3.65) yield

$$\dot{s} = s^p + \delta_s + \varepsilon_s - 2\varepsilon_{s+1} \tag{3.66}$$

as $s \to \infty$. Since $\mathbb{E}[\delta_k] = 0$ and $\mathbb{E}[\varepsilon_k] = \nu > 0$, taking expectations leads to $\dot{s} = s^p - \nu$, so perturbations have a small slowing effect on the progress of the diffusive wave. We solve (3.66) by assuming $s(t) = s_0(t) + \nu s_1(t)$ with leading-order solution (3.32), as in case IV. As $s_0 \to \infty$, the $\mathcal{O}(\nu)$ correction term is determined by $\dot{s}_1 = -1 + ps_0^{p-1}s_1$ with solution (3.33). A higher-order effect is that noise broadens the wave very slightly, since noise in (3.65) has the effect of increasing the diffusion coefficient. The effect of this, however, is minimal since the diffusion constant which the wave experiences grows without bound in the large-time limit. When $p < \frac{1}{2}$ the shape of the wavefront can be calculated in the same way as for case IV, the solution for $\psi(r, t)$ being identical, leading to

$$c_r(t) \sim \frac{1}{2}c_r^{\mathrm{sss}}\mathrm{erfc}\left(\frac{r - s(t)}{\sqrt{2s(t) + 4\nu t}}\right) \tag{3.67}$$

where $s(t) = s_0(t) + \nu s_1(t)$ is given by equations (3.32) and (3.33).

In this case, coarse-graining maps the rates to $\alpha_n = n^{p\lambda} + \Delta_n$, $\beta_{n+1} = E_{n+1}$ where the perturbations to the reaction rates Δ_n, E_{n+1} are given by the formulae

$$\Delta_n = n^{p\lambda}\sum_{r=\Lambda_n}^{\Lambda_{n+1}-1}\frac{\delta_r}{r^p} + \mathcal{O}(\nu^2) \qquad E_{n+1} = \lambda^{-p\lambda}\prod_{r=\Lambda_n}^{\Lambda_{n+1}-1}\varepsilon_{r+1} = \mathcal{O}(\nu^\lambda). \tag{3.68}$$

Thus the domination of aggregation over fragmentation persists. We assume that the perturbations in the full microscopic model satisfy

$$\mathbb{E}[\delta_r] = 0 \qquad \mathbb{E}[\varepsilon_{r+1}] = \nu \qquad \mathbb{V}[\delta_r] = V_\delta\nu^2 \qquad \mathbb{V}[\varepsilon_{r+1}] = V_\varepsilon\nu^2 \tag{3.69}$$

whence we find the perturbations in the reduced description satisfy

$$\begin{aligned}&\mathbb{E}[\Delta_n] = 0 \qquad \mathbb{E}[E_{n+1}] = \lambda^{-p\lambda}\nu^\lambda \qquad \mathbb{V}[\Delta_n] \approx V_\delta\lambda^{1-2p}n^{2p(\lambda-1)}\nu^2\\ &\mathbb{V}[E_{n+1}] = \lambda^{-2p\lambda}[(V_\varepsilon+1)^\lambda - 1]\nu^{2\lambda}.\end{aligned} \tag{3.70}$$

These results are identical to case IV (3.37), but with aggregation and fragmentation rates reversed.

Following the method used in the earlier cases, we insert (3.68) into (2.12) and find

$$\log \Upsilon_N \sim p\lambda N(\log N - 1) - \sum_{n=1}^{N-1} \log E_{n+1} + \sum_{n=1}^{N-1} \frac{\Delta_k}{k^{p\lambda}}$$
$$\sim p\lambda N(\log(\lambda N) - 1) - \sum_{k=1}^{\Lambda_N - 1} \log \varepsilon_{k+1} + \sum_{k=1}^{\Lambda_N - 1} \frac{\delta_k}{k^p} \tag{3.71}$$

which agrees with a direct expansion of Q_R (3.62)

$$\log Q_R \sim pR(\log R - 1) - \sum_{k=1}^{R-1} \log \varepsilon_{k+1} + \sum_{k=1}^{R-1} \frac{\delta_k}{k^p}. \tag{3.72}$$

For large $R = \Lambda_N$, the differences between $\log Q_R$ and $\log \Upsilon_N$ grow with $\log R$, or $\log N$, whereas the quantities themselves grow at the much faster rates of $R \log R$ and $N \log N$. An alternative comparison can be made between

$$\mathbb{E}[\Upsilon_N] = \frac{\lambda^{-p\lambda(N-1)} \nu^{\lambda(N-1)}}{(N-1)!^{p\lambda}} \qquad \text{and} \qquad \mathbb{E}[Q_R] = \frac{\nu^{R-1}}{(R-1)!^p} \tag{3.73}$$

for $R = \Lambda_N$, where Stirling's approximation can be used to show that both expressions are dominated by $\nu^{\lambda N}(\mathrm{e}/\lambda N)^{p\lambda N}$.

However, in this case the system approaches a steady-state solution. When the leading-order effects of the perturbations are incorporated, the steady state becomes

$$x_n^{\mathrm{sss}} = \frac{1}{n^{p\lambda}} \left[1 + \left(\Delta_1 - n^{-p\lambda}\Delta_n\right)\right] \tag{3.74}$$

which has constant flux $L = 1 + \Delta_1$. This has the correct qualitative behaviour, decaying as n increases. The leading-order term for large n is $x_n \sim n^{-p\lambda}$ whilst the microscopic model predicts $c_r \sim r^{-p}$ so that for maximum accuracy we should have $c_r \sim (\lambda n)^{-p\lambda}$ when $r = \Lambda_n$ which has a qualitatively similar shape (the decay is algebraic), but differs quantitatively since the exponent differs. The steady-state flux also differs. In the full model it is given by $J = 1 + \delta_1 - \varepsilon_2$ which depends on noise in the fragmentation rate coefficient (ε_2) and has the expected value $\mathbb{E}[J] = 1 - \nu$ (since $\mathbb{E}[\delta_r] = 0$ and $\mathbb{E}[\varepsilon_r] = \nu$ for all r). In the contracted model the flux depends only on the perturbations to the aggregation rates, with $\mathbb{E}[L] = 1 + \mathrm{o}(\nu)$ since $L = 1 + \Delta_1$ and Δ_1 involves the perturbations to the aggregation rates δ_r for $r = 1, 2, \ldots, \lambda$.

To $\mathcal{O}(\nu)$, the equations which determine the kinetics of the approach to steady state are

$$\dot{x}_n = \left[(n-1)^{p\lambda} + \Delta_{n-1}\right] x_{n-1} - \left[n^{p\lambda} + \Delta_n\right] x_n \tag{3.75}$$

since $\Delta_n = \mathcal{O}(\nu)$ and $E_n = \mathcal{O}(\nu^\lambda)$. The approach can be elucidated by substituting $x_n(t) = x_n^{\mathrm{sss}} \psi_n(t)$ into (3.75), where x_n^{sss} is as given in (3.74), since then

$$\dot{\psi}_n = (n^{p\lambda} + \Delta_n)(\psi_{n+1} - \psi_n) + \frac{L}{x_n^{\mathrm{sss}}}(\psi_{n-1} - \psi_{n+1}). \tag{3.76}$$

The steady-state solution x_n^{sss} has as an asymptotic approximation (3.74) with steady flux $L = 1 + \Delta_1$. In the large-n and large-time limit, we take the continuum limit, obtaining the partial differential equation

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}(n^{p\lambda} + \Delta_n)\frac{\partial^2 \psi}{\partial n^2} - (n^{p\lambda} + \Delta_n)\frac{\partial \psi}{\partial n}. \tag{3.77}$$

Following earlier analysis, we transform to a moving coordinate frame by $n = s(t) + z$, obtaining the equation $\dot{s} = s^{p\lambda} + \Delta_s$ for the position of the wavefront. Since $\mathbb{E}[\Delta_s] = 0$, there

is no effect of the noise on the leading-order progression of the wave through the system, and we have

$$s(t) = [(1 - p\lambda)(t - t_0)]^{1/(1-p\lambda)} \tag{3.78}$$

the corrections due to noise being of order $\mathcal{O}(\nu^2)$ and above. For $p\lambda < \frac{1}{2}$ the shape of the wave is given by $\psi = \frac{1}{2}\mathrm{erfc}(z\sqrt{1-2p\lambda}/\sqrt{2s(t)})$, so that the large-time asymptotics are governed by

$$x_n(t) \sim \frac{1}{2n^{p\lambda}}\left(1 + \Delta_1 - \frac{\Delta_n}{n^{p\lambda}}\right)\mathrm{erfc}\left(\frac{(n - s(t))\sqrt{1-2p\lambda}}{\sqrt{2s(t)}}\right) \tag{3.79}$$

for $n - s(t) \sim \sqrt{s(t)}$ as $t \to \infty$. For $\frac{1}{2} < p\lambda < 1$ the shape of the wave depends on the initial data for all time. These results are consistent with cases I, III, and IV, where the coarse-graining procedure reduces the effect of perturbations to fragmentation rates.

3.7. Case VII

Here fragmentation is the dominant process, with smaller clusters shedding monomers much more readily than larger clusters.

The coagulation and fragmentation rates are given by $a_r = \delta_r$ and $b_{r+1} = br^p + \varepsilon_{r+1}$ with $p < 0$, and in all of cases VII–IX, the perturbations are taken to be positive random parameters distributed according to

$$\mathbb{E}[\delta_r] = \nu \qquad \mathbb{E}[\varepsilon_{r+1}] = \nu \qquad \mathbb{V}[\delta_r] = V_\delta \nu^2 \qquad \mathbb{V}[\varepsilon_{r+1}] = V_\varepsilon \nu^2. \tag{3.80}$$

As with cases I and IV, if there are no perturbations to the rates then the partition function is identically zero; when noise is introduced we find

$$Q_r = \prod_{k=1}^{r-1} \frac{\delta_k}{k^p + \varepsilon_{k+1}} \tag{3.81}$$

so that Q_r decreases rapidly in magnitude as r increases ($Q_r = \mathcal{O}(\nu^{r-1})$). However, since $p < 0$, this ceases to be valid when $r = \mathcal{O}(\nu^{1/p})$, because the perturbations have the same order of magnitude as the deterministic part of the coefficients. When $r\nu^{1/(1-p)} < 1$ the approximation (3.28) is valid; however, this ceases to be hold when $r = \mathcal{O}(\nu^{-1/(1-p)})$, where the variance of the sum reaches $\mathcal{O}(1)$. At this point the random perturbations affect the leading-order behaviour of the partition function.

At large times the system approaches its equilibrium solution. As in case IV, the equation determining the progression of the diffusive wave is formally $\dot{s} = (s-1)^p + \varepsilon_s - \delta_s$. On taking expectations of this equation, all ν-dependence disappears, indicating that the noise has no net effect on the progress of the wave. The equation $\dot{s} = s^p$ is valid until $s = \mathcal{O}(\nu^{1/p})$, hence $s(t)$ follows (3.32) until $t = \mathcal{O}(\nu^{-1+1/p})$. After this time, the random components of the coefficients influence the leading-order motion of the wave. Thus there are subtle differences between case IV ($p > 0$), where (3.32) holds for all time, and case VII ($p < 0$), where (3.32) holds only for times up to $\mathcal{O}(\nu^{1/p})$. At $r = \mathcal{O}(\nu^{1/p})$ the random component of the rate coefficients in the diffusive term in (3.30) becomes leading order. Since this term contains the sum of two positive perturbations, there is a net increase in the diffusivity, hence the wavefront widens as described by (3.34).

Following the coarse-graining contraction, formulae (3.35) still hold, so the noise satisfies

$$\begin{aligned} &\mathbb{E}[\Delta_n] = \lambda^{-p\lambda}\nu^\lambda \qquad \mathbb{E}[E_{n+1}] = n^{p\lambda}\nu \sum_{k=\Lambda_n}^{\Lambda_{n+1}-1} \frac{1}{k^p} \\ &\mathbb{V}[\Delta_n] \approx \lambda^{-2p\lambda}\nu^{2\lambda}(V_\delta + 1)^\lambda \qquad \mathbb{V}[E_{n+1}] \approx V_\varepsilon n^{2p\lambda}\nu^2 \sum_{k=\Lambda_n}^{\Lambda_{n+1}-1} \frac{1}{k^p}. \end{aligned} \tag{3.82}$$

Due to the decay in fragmentation rates at large r, there is an aggregation size at which the perturbations assume the same order of magnitude as the deterministic part of the rate coefficients. To find this threshold, we equate $n^{p\lambda}$ with the expectation of E_{n+1} in (3.82). This yields $n = \nu^{1/p}\lambda^{-1+1/p}$, corresponding to an aggregation number of $r = \nu^{1/p}\lambda^{1/p}$ in the full description of the model (before contraction), showing the correct order of magnitude when compared with the full model, which gives $r = \nu^{1/p}$.

Using the coarse-grained rate coefficients to construct a partition function Υ_N, we find (3.38) holds for $N = \mathcal{O}(1)$. Together with equations (3.82) and (3.28), for R, $N = \mathcal{O}(1)$, these imply

$$\mathbb{E}[\Upsilon_N] = \frac{\nu^{\lambda(N-1)}}{(N-1)!^{p\lambda}}\left(1 - \nu\sum_{n=1}^{N-1}\frac{1}{n^{p\lambda}}\right) \qquad \text{and} \qquad \mathbb{E}[Q_R] = \frac{\nu^{R-1}}{(R-1)!^{p}}\left(1 - \nu\sum_{k=1}^{R-1}\frac{1}{k^{p}}\right) \tag{3.83}$$

so that for $R = \Lambda_N$ we have both expressions growing with R (or equivalently with N), whilst their difference only grows with $\log R$. This shows nice agreement. At large R, N the formulae (3.83) fail due to the noise in the fragmentation rate becoming leading order. This occurs for $R = \mathcal{O}(\nu^{1/(p-1)})$ in the latter case and, upon using (3.82), $N = \mathcal{O}(\nu^{1/(p-1)})$ in the former, again showing good agreement between the full and contracted models.

As with case IV, the system converges to equilibrium via a diffusive wave which travels from small to large n, invading the region where the initial conditions $x_n = 0$ have not yet been modified, and leaving behind (at smaller n) the equilibrium solution $x_n = \Upsilon_n$. Thus we use the substitution $\psi_n(t) = x_n(t)/\Upsilon_n$, which satisfies (3.42). Since $\mathbb{E}[\Delta_n] = \mathcal{O}(\nu^{\lambda})$ and $\mathbb{E}[E_{n+1}] \sim \lambda^{1-p}n^{p(\lambda-1)}\nu$ from (3.82), the continuum limit of (3.42) to $\mathcal{O}(\nu)$ reduces to

$$\frac{\partial\psi}{\partial t} = \left((n-1)^p\lambda + \lambda^{1-p}n^{p(\lambda-1)}\nu\right)\left(\frac{1}{2}\frac{\partial^2\psi}{\partial n^2} - \frac{\partial\psi}{\partial n}\right). \tag{3.84}$$

At large times, the leading-order term determines the speed of the wavefront ($\dot{s}$), giving the equation $\dot{s} = s^{p\lambda} + \lambda^{1-p}s^{p(\lambda-1)}\nu$. As $\nu \to 0$, the solution of this equation can be formulated as $s(t) = s_0(t) + \nu s_1(t)$ where

$$s_0(t) = [(1-p\lambda)t]^{1/(1-p\lambda)} \qquad \text{and} \qquad s(t) \sim s_0(t)\left(1 + \frac{\nu\lambda^{1-p}s_0(t)^{1-p}}{2-p-p\lambda}\right). \tag{3.85}$$

This shows that as the wave reaches larger values of n, perturbations to the rate coefficients influence the *leading-order* motion of the wave. This occurs when $s \sim n = \mathcal{O}(\nu^{1/(p-1)})$, or when $t = \mathcal{O}(\nu^{-1-p(\lambda-1)/(p-1)})$, which is the same order of magnitude as in the uncontracted case. At this order of magnitude the perturbations to the rate coefficients also cause the shape of the wavefront to be modified.

3.8. Case VIII

Here aggregation and fragmentation are finely balanced, but occur much more rapidly at small cluster sizes than at large cluster sizes, a situation that may arise in growth processes in solution below saturation without nucleation barriers.

In the noise-free case this system converges to the equilibrium solution $c_r = 1$. When noisy coefficients are introduced, defined by $a_r = ar^p + \delta_r$, $b_{r+1} = br^p + \varepsilon_{r+1}$, with $p < 0$ and the perturbations distributed according to (3.80), then the partition function is modified to

$$Q_r = \prod_{k=1}^{r-1}\frac{1 + k^{-p}\delta_k}{1 + k^{-p}\varepsilon_{k+1}} \tag{3.86}$$

and so for $r = \mathcal{O}(1)$, the equilibrium solution can be approximated by

$$c_r = 1 + \sum_{k=1}^{r-1} k^{-p}(\delta_k - \varepsilon_{k+1}) + \mathcal{O}(\nu^2). \tag{3.87}$$

However, this approximation ceases to be valid at large r due to the perturbations becoming a leading-order effect. Given that the variance of each perturbation is $\mathcal{O}(\nu^2)$, the variance of c_r in equation (3.87) is $\mathcal{O}(\nu^2 r^{1-p})$ so that at $r = \nu^{-2/(1-p)}$, the leading-order expression for c_r is no longer unity. At this aggregation number the cumulative effect of the perturbations becomes as important as the leading-order term.

When we turn to the analysis of the kinetics of the approach to equilibrium, we note the similarities between this case (where $p < 0$), and the approach to equilibrium in case V for $0 < p < 1$. The continuum equation (3.47) is also valid here, but whereas in case V $\mathbb{E}[\delta_r + \varepsilon_r] = 0$, here $\mathbb{E}[\delta_r + \varepsilon_r] = 2\nu$, so when we take the expectation of (3.47) we obtain an equation with an increased diffusivity, namely

$$\frac{\partial \psi}{\partial t} = (r^p + \nu)\frac{\partial^2 \psi}{\partial r^2} + p r^{p-1}\frac{\partial \psi}{\partial r}. \tag{3.88}$$

Thus there is a large-r region where the perturbations influence the leading-order kinetics. This occurs for $r = \mathcal{O}(\nu^{1/p})$ and larger, where noise in the diffusion term is comparable with the deterministic part of the diffusivity. In the advection term, the noise has zero mean. Thus for $r\nu^{-1/p} < 1$, we expect the similarity solution $\psi = f(\eta)$ with $\eta = r/t^{1/(2-p)}$ to be valid and $\psi(r, t)$ determined by equation (3.48); but for $r \geqslant \mathcal{O}(\nu^{1/p})$, the leading-order kinetics are influenced by the noise.

In the coarse-grained contracted system, the forward and backward rate coefficients are given by

$$\alpha_n = \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} (r^p + \delta_r) \qquad \beta_{n+1} = \prod_{r=\Lambda_n}^{\Lambda_{n+1}-1} (r^p + \varepsilon_{r+1}) \tag{3.89}$$

and whilst (3.52) is a valid approximation for small n, it breaks down at larger n. Assuming that the noise is distributed according to (3.80) before the contraction procedure, we find

$$\begin{aligned} &\mathbb{E}[\Delta_n] = \mathbb{E}[E_{n+1}] = \nu\lambda^{1-p} n^{p(\lambda-1)} \qquad \mathbb{V}[\Delta_n] = V_\delta n^{2p\lambda}\nu^2 \sum_{k=\Lambda_n}^{\lambda_{n+1}-1} \frac{1}{k^{2p}} \\ &\mathbb{V}[E_{n+1}] = V_\varepsilon n^{2p\lambda}\nu^2 \sum_{k=\Lambda_n}^{\Lambda_{n+1}-1} \frac{1}{k^{2p}} \end{aligned} \tag{3.90}$$

following the coarse-grained renormalization. The even balance of aggregation and fragmentation is reflected in the identical expectations of Δ_n and E_{n+1} and in the same order of magnitude of their variances. When $n = \mathcal{O}(\nu^{1/p})$ the formulaic component of the rates ($\mathcal{O}(\nu^{p\lambda})$) matches the random element (providing λ is not large); this aggregation number agrees with the analysis of the fully microscopic model.

We now use the coarse-grained rates to calculate the partition function (Υ_n) for the coarse-grained system. Equation (3.55) is valid for $r = \mathcal{O}(1)$; however, since p is negative the sums are divergent at large n and large r. Although $\mathbb{E}[\Upsilon_N] = 1 = \mathbb{E}[Q_R]$ for all N and for all R, the variance of Υ_N grows with N according to

$$\mathbb{V}[\Upsilon_N] = \nu^2(V_\delta + V_\epsilon) \sum_{n=1}^{(N-1)\lambda+1} \frac{1}{n^{2p}} \tag{3.91}$$

which agrees with $\mathbb{V}[Q_R]$ for $R = \Lambda_n$. The asymptotic expression (3.55) thus ceases to be uniformly valid when the variance becomes $\mathcal{O}(1)$, namely when $n = \mathcal{O}(\nu^{-2/(1-p)})$ giving the

same order of magnitude of aggregation number ($r = \Lambda_n$) as can be derived from the full system of equations (3.44).

The kinetics of approach to equilibrium are similar to case V with $p < 1/\lambda$; that is by a perturbed similarity solution rather than a moving diffusive wavefront. Since in the present case the perturbations obey equation (3.80), when we take the expectation of equation (3.58) we obtain

$$n^{-p\lambda}\frac{\partial \psi}{\partial t} = \left(1 + 2\lambda^{1-p}n^{-p}\nu\right)\frac{\partial^2 \psi}{\partial n^2} + \frac{p\lambda}{n}\frac{\partial \psi}{\partial n}. \tag{3.92}$$

Thus when one ignores the $\mathcal{O}(\nu)$ terms, a similarity solution can be found; and for $n < \mathcal{O}(\nu^{1/p})$, we expect the similarity solution to give the leading-order behaviour. This solution has the form $\psi_n(t) = f(\eta)$ with $\eta = n/t^{1/(2-p\lambda)}$ as in (3.59). However, for $n = \mathcal{O}(\nu^{1/p})$ and larger, another more complicated solution takes effect, where the noise influences the dynamical behaviour at leading order. For n larger than $\mathcal{O}(\nu^{1/p})$ the system behaves as if all rates had been chosen at random.

3.9. Case IX

The final case corresponds to a system in which aggregation dominates fragmentation at smaller cluster sizes; at larger cluster sizes, the perturbations to both aggregation and fragmentation rate coefficients entirely swamp this effect.

Here, we have $a_r = r^p + \delta_r$, $b_{r+1} = \varepsilon_{r+1}$ with the perturbations $\delta_r, \varepsilon_{r+1}$ distributed according to (3.80). Formally the presence of noise allows the partition function to be written as

$$Q_r = \prod_{k=1}^{r-1}\frac{k^p + \delta_k}{\varepsilon_{k+1}}. \tag{3.93}$$

With noiseless rate coefficients, the system evolves to the steady state with unit flux ($J = 1$); however, using the perturbed coefficients in equation (1.5), a calculation of the steady-state flux leads to $J = 0$ since at large values of r, the term $1/a_r Q_r$ has a positive expectation value which is independent of r, making the sum divergent. Thus in this case the presence of noisy coefficients changes the large-time behaviour from an approach to steady state with unit flux to an approach to the equilibrium solution, which is given by $c_r = Q_r$ where, for $r = \mathcal{O}(1)$, Q_r is given by equation (3.62). This expression, however, ceases to be valid for values of r larger than $\mathcal{O}(\nu^{-1/(1-p)})$. At intermediate times, before mass has been transported to larger aggregation numbers, we expect the steady-state solution to be manifest. At larger times, the system undergoes a complex transition from a steady-state solution to the equilibrium solution. Evolution will then be dominated by the random perturbations to the rate coefficients, and will follow the kinetics described in the next section.

In the coarse-grained description of the system the equation for Δ_n in (3.68) is valid for small n, but ceases to be valid when $n = \mathcal{O}(\nu^{1/p})$, where the noise becomes leading order; thus there is an intermediate asymptotic regime where the system remains aggregation dominated. Using (3.80) we find the distribution of perturbations to be as follows:

$$\begin{aligned} \mathbb{E}[\Delta_n] &= n^{p\lambda}\nu\sum_{k=\Lambda_n}^{\Lambda_{n+1}-1}\frac{1}{k^p} \qquad & \mathbb{E}[E_{n+1}] &= \lambda^{-p\lambda}\nu^{\lambda} \\ \mathbb{V}[\Delta_n] &= V_\delta n^{2p\lambda}\nu^2\sum_{k=\Lambda_n}^{\Lambda_{n+1}-1}\frac{1}{k^{2p}} \qquad & \mathbb{V}[E_{n+1}] &= \lambda^{-2p\lambda}\nu^{2\lambda}\left[(V_\varepsilon+1)^{\lambda} - 1\right]. \end{aligned} \tag{3.94}$$

However, at larger aggregation numbers the system is dominated by the random perturbations.

Calculating the partition function Υ_N from the coarse-grained rates we find (3.71) holds for small and intermediate values of N. For large N, however, it fails since p is negative and the second term becomes the same order of magnitude as the first when $N = \mathcal{O}(\nu^{1/p})$. The presence of noise transforms this case from one which approaches steady-state solution (with $L \approx 1$) to one which approaches equilibrium (i.e. $L = 0$), as in the microscopic system. Thus the coarse-graining procedure has faithfully retained the structural difference that noise has made to the full system of equations.

In the large-time limit, this case shows convergence to the equilibrium solution, since at large aggregation numbers, the system appears identical to the case with all rates chosen at random described below, in section 3.10. In this case the kinetics are dominated by the random perturbations to the rates, so it is impossible to give a detailed description of the time-dependent solution.

At intermediate times, when there is little mass in large aggregation numbers, however, we expect the system to behave as in case VI, namely the approach to a steady-state solution. Since the rate coefficients at small and intermediate aggregation numbers are dominated by aggregation, we expect a diffusive wave to move into the larger-n region leaving behind the steady-state solution $x_n = n^{-p\lambda}$. Since this moves at a rate given by (3.78), when $t = \mathcal{O}(\nu^{1/p-\lambda})$ the wave reaches aggregation sizes $n = \mathcal{O}(\nu^{1/p})$, where the perturbations to the rates are of the same order of magnitude as the deterministic component of the rates. Thus after this time the system undergoes a transition from the state

$$x_n(t) \sim \begin{cases} n^{-p\lambda} & \text{for} \quad n \ll \nu^{1/p} \\ 0 & \text{for} \quad n \gg \nu^{1/p} \end{cases} \tag{3.95}$$

to the equilibrium state $x_n = \Upsilon_n$.

3.10. The system with totally random rates

The previous three sections have shown that, at large times and with the rate perturbations as defined in section 2.1, in each of the cases VII–IX the temporal evolution tends to the equilibrium solution rather than a steady-state solution; at large r the partition function Q_r is dominated by the perturbations, hence so too is the equilibrium solution in all three cases. From this perspective, these three cases can then be thought of as lying in the same universality class, namely a Becker–Döring system with 'totally random' rate coefficients. By this we mean a formulation of the Becker–Döring equations (1.4) in which all the rate coefficients a_r, b_r are chosen at random (but remain independent of time); in the notation of this paper, we have $a = b = 0$, leaving $a_r = \delta_r$, $b_r = \varepsilon_r$. Here the rates δ_r, ε_r are independent random parameters whose expectation and variance is size independent.

If we take the monomer concentration to be fixed at unity, the governing equations are

$$\dot{c}_r = \delta_{r-1}c_{r-1} - \varepsilon_r c_r - \delta_r c_r + \varepsilon_{r+1}c_{r+1} \qquad r \geqslant 2. \tag{3.96}$$

It is possible to define a partition function Q_r from the coefficients δ_r, ε_r provided none are zero. If we assume that in the large-time limit the system will tend to a steady state

$$c_r = Q_r\left(1 - J\sum_{k=1}^{r-1}\frac{1}{\delta_k Q_k}\right) \tag{3.97}$$

then imposing the fastest possible decay on the concentrations in the limit of large r, we find

$$\frac{1}{J} = \sum_{k=1}^{\infty}\frac{1}{\delta_k Q_k}. \tag{3.98}$$

Since neither $Q_k \to \infty$ nor $\delta_k \to \infty$ as $k \to \infty$ the terms in the sum do not decay, so the sum diverges. We thus have $J = 0$, and the system must tend to the equilibrium solution $c_r = Q_r$. To find the kinetics in the large-time limit we substitute $c_r = Q_r \psi_r$; then ψ_r satisfies the difference equation

$$\dot{\psi}_r = \varepsilon_r \psi_{r-1} - \delta_r \psi_r - \varepsilon_r \psi_r + \delta_r \psi_{r+1}. \tag{3.99}$$

This is a system of equations similar to that with which we started in equation (3.96); the essential difference is that $\psi \to 1$ as $t \to \infty$. We expect $\psi_r(t)$ to be slowly varying in the large-time limit, in turn enabling us to take the continuum limit which gives the following partial differential equation for ψ_r:

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}(\delta_r + \varepsilon_r)\frac{\partial^2 \psi}{\partial r^2} + (\delta_r - \varepsilon_r)\frac{\partial \psi}{\partial r}. \tag{3.100}$$

Thus the advective component of the process $(\delta_r - \varepsilon_r)\frac{\partial \psi}{\partial r}$ has zero mean (since $\mathbb{E}[\delta_r] = \mathbb{E}[\varepsilon_r] = \nu$), whilst the diffusive component is always positive, having mean ν. The expectation of the solution is thus $\psi = \frac{1}{2}\mathrm{erfc}(r/2\sqrt{\nu t})$ and so we see that the system shares several similarities with case II, notably convergence to equilibrium via the same kinetics albeit on a slower timescale.

In cases VII and IX we expect the waves to cease moving when they reach the large-r region where perturbations become dominant, namely when the wavefront reaches $r = \mathcal{O}(\nu^{1/p})$; which occurs after a time of $t = 1/(1-p)\nu^{(1-p)/p^2}$. However, in all three cases VII–IX the final approach to equilibrium is by a predominantly diffusive mechanism.

4. Discussion

A previous paper described in detail nine generic classes of behaviour into which the asymptotic dynamics of the Becker–Döring equations with power law coefficients falls [19]. The nine classes capture qualitatively different physical properties which are shared by all models within the same class. In this paper, we have concentrated on the detailed analysis of these nine cases; for each case we have considered the effect of the perturbations to the rate constants on the equilibrium or steady-state solution and on the large-time asymptotics.

In cases IV–VI, where the rate constants grow with increasing cluster size, larger perturbations could be considered, (that is the perturbations to the forward and backward rate coefficients δ_r, ε_r are each $\mathcal{O}(1)$). Because the unperturbed rates grow with r, there would then be a large-r region where the perturbations are insignificant and a smaller-r region where they should be taken into account. Since we are dealing with a discrete system, the small-r region consists of a complicated finite-dimensional system joined to a simpler large-r system whose behaviour we already know by asymptotic analysis [14]. By taking a coarse-graining contraction with λ sufficiently large, the whole of this small r regime could be mapped to a small-dimensional system with only a few concentrations needing to be retained. As in the unperturbed problem analysed previously [11, 19], coarse-graining retains the correct leading-order structure of the problem, although critical exponents of $p = 1$ where the behaviour changes are mapped to $p = 1/\lambda$.

Cases VII–IX are much more complex, since here the rate coefficients decay with increasing aggregation number. Thus in the limit $r \to \infty$, the perturbations δ_r, ε_r dominate the partition function (Q_r) and the large-time kinetics. If we assume the perturbations are small (as we have done here), there is a small-r region where regular behaviour occurs, and a larger-r region where perturbations dominate the rate coefficients, the partition function and the kinetics; in this region the system behaves as if the rate coefficients had been chosen at

random. Following an application of the coarse-graining process the positions of these regions remain invariant and, in the small-r region, the leading-order behaviour agrees with that of the full model. The only case in which the large-time solution which is approached is altered by the presence of noise is case IX, which changes from convergence to a steady-state solution in the large-time limit into a system which converges to equilibrium. The equilibrium solution to which cases VII and VIII approach in the large-time limit also suffer major modification due to the presence of noise.

In renormalization-theoretic jargon, cases I–VI can be referred to as *universality classes*, whereas this is not in general true for cases VII–IX, because the perturbations destabilize the steady-state solution, modify the equilibrium solution and alter the associated large-time dynamics of convergence to equilibrium. However, all of cases VII–IX share the same large-aggregation-number and large-time behaviour, and so fall into a seventh universality class, which we have referred to as the system with totally random rates (section 3.10). This classification occurs with the rate perturbations as described in section 2.1, namely those with size-independent mean and variance.

If an alternative form of rate-perturbations were applied to the system, then an alternative universality classification would be produced. For example, if the rate perturbations had the same size dependence as the power law component, that is $\mathbb{E}[\delta_r] = \nu r^p$ and $\mathbb{E}[\varepsilon_{r+1}] = \nu r^p$ then the large-time asymptotics of cases VII–IX suffer no leading-order modification due to the perturbations and each of these cases then corresponds to its own universality class. However, this one-to-one correspondence of our nine special cases with universality classes only holds in situations where the added noise decays faster than the specified power law for the rate coefficients as $r \to \infty$. We believe such scenarios to be somewhat artificial, thus in this paper we have concentrated our analysis on the more generic and interesting case where the behaviour of the rate perturbations at large aggregation numbers differs from that of the power law.

In future work, we plan to extend and generalize these renormalization-theoretic results to a range of other Becker–Döring systems, including ones with different forms of rate coefficients which describe quite distinct physicochemical processes [20], as well as the constant-density formulation of the Becker–Döring equations. It turns out that, for certain well motivated choices of rate coefficients, the renormalization procedure is *exact* (in the sense that the approximation made after equation (1.13) is not necessary). The constant-density Becker–Döring system has the added complication of being inherently nonlinear, and our renormalization scheme accentuates the nonlinearity, making analysis of this problem even more challenging.

Acknowledgments

We are grateful to John Cardy for several useful discussions regarding renormalization theory, and to Bob O'Malley for pointing out related work in the literature. PVC is grateful to the Department of Theoretical Physics and Wolfson College, University of Oxford, for a Wolfson–Harwell Visiting Fellowship, and for hosting our discussions. JADW thanks John King for many instructive conversations.

References

[1] Bricmont J and Kupiainen A 1991 Renormalisation group for diffusion in a random medium *Phys. Rev. Lett.* **66** 1689–92

[2] Bricmont J and Kupiainen A 1992 Renormalisation group and the Ginzburg–Landau equation *Commun. Math. Phys.* **150** 193–208
[3] Bricmont J, Kupiainen A and Lin G 1994 Renormalisation group and asymptotics of solutions of nonlinear parabolic equations *Commun. Pure Appl. Math.* **47** 893–922
[4] Brilliantov N V and Krapivsky P L 1991 Non-scaling and source-induced scaling behaviour in aggregation models of movable monomers and immovable clusters *J. Phys. A: Math. Gen.* **24** 4787–803
[5] Cardy J 1996 *Scaling and Renormalization in Statistical Physics (Cambridge Lecture Notes in Physics vol 5)* (Cambridge: Cambridge University Press)
[6] da Costa F P 1998 A finite-dimensional dynamical model for gelation in coagulation processes *J. Nonlinear Sci.* **8** 619–53
[7] Coveney P V and Highfield R R 1990 *The Arrow of Time* (London: Allen)
[8] Coveney P V and Highfield R R 1995 *Frontiers of Complexity* (London: Faber and Faber)
[9] Coveney P V and Wattis J A D 1996 Analysis of a generalised Becker–Döring model of self-reproducing micelles *Proc. R. Soc.* A **452** 2079–102
[10] Coveney P V and Wattis J A D 1998 A Becker–Döring model of self-reproducing vesicles *J. Chem. Soc. Faraday Trans.* **102** 233–46
[11] Coveney P V and Wattis J A D 1999 Cluster renormalization for the Becker–Döring equations *J. Phys. A: Math. Gen.* **32** 7145–52
[12] van Dongen P G J and Ernst 1987 Fluctuations in coagulating systems I *J. Stat. Phys.* **49** 879–926
[13] van Dongen P G J and Ernst 1987 Fluctuations in coagulating systems II *J. Stat. Phys.* **49** 927–75
[14] King J R and Wattis J A D 2000 Asymptotic solutions to the Becker–Döring equations with non-constant coefficients, in preparation
[15] Lewis B 1975 *Crystal Growth* ed B R Pamplin (Oxford: Pergamon) pp 12–39
[16] Velazquez J J L 1998 The Becker–Döring equations and the Lifshitz–Slyozov theory of coarsening *J. Stat. Phys.* **92** 195–236
[17] Wattis J A D and Coveney P V 1997 General nucleation theory with inhibition for chemically reacting systems *J. Chem. Phys.* **106** 9122–40
[18] Wattis J A D and Coveney P V 1999 The origin of the RNA world: a kinetic model *J. Phys. Chem.* B **103** 4231–50
[19] Wattis J A D and Coveney P V 2001 Renormalization-theoretic analysis of non-equilibrium phase transitions: I. The Becker–Döring equations with power law rate coefficients *J. Phys. A: Math. Gen.* **34** 8679–95 (preceding paper)
[20] Wattis J A D and Coveney P V 2001 Exact renormalisation theory for the Becker–Döring equations with size-dependent rate coefficients, in preparation
[21] Wattis J A D and King J R 1998 Asymptotic solutions to the Becker–Döring equations *J. Phys. A: Math. Gen.* **31** 7169–89
[22] Woodruff S L 1993 The use of an invariance condition in the solution of multiple-scale singular perturbation problems: ordinary differential equations *Stud. Appl. Math.* **90** 225–48
[23] Woodruff S L 1995 A uniformly valid asymptotic solution to a matrix system of ordinary differential equations and a proof of its validity *Stud. Appl. Math.* **94** 393–413
[24] Woodruff S L 1995 Multiple-scale perturbation analysis of the direct interaction approximation for inertial-range turbulence *Phys. Rev.* E **52** 3245–8
[25] Woodruff S L and Messiter A F 1994 A perturbation analysis of an interaction between long and short surface waves *Stud. Appl. Math.* **92** 159–89