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Renormalization-theoretic analysis of non-equilibrium phase transitions: I. The Becker–Döring equations with power law rate coefficients

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Abstract

We study in detail the application of renormalization theory to models of cluster aggregation and fragmentation of relevance to nucleation and growth processes. We investigate the Becker–Döring equations, originally formulated to describe and analyse non-equilibrium phase transitions, and more recently generalized to describe a wide range of physicochemical problems. In this paper we analyse how the systematic coarse-graining renormalization of the Becker–Döring system of equations affects the aggregation and fragmentation rate coefficients. We consider the case of power law size-dependent cluster rate coefficients which we show lead to only three classes of system that require analysis: coagulation-dominated systems, fragmentation-dominated systems and those where coagulation and fragmentation are exactly balanced. We analyse the late-time asymptotics associated with each class.

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1. Introduction

The purpose of this paper is to develop renormalization methods for nucleation and growth processes. Renormalization theory has been applied to various problems in theoretical physics, being widely used in high-energy physics [23] and in the analysis of equilibrium phase transitions in statistical physics [7]. It has also been used in a limited way in asymptotic analysis by Goldenfeld [21]. However, it has not previously been used in the asymptotic analysis of non-equilibrium phase transitions of the kind discussed in this paper, mainly due to the complex nature of these models which often involve nonlinear and non-local features.

In statistical mechanics, the basic idea underlying the concept of renormalization is the systematic filtering out of unwanted degrees of freedom in the transition from the microscopic to the macroscopic description of phenomena. In the case of equilibrium phase transitions, near a critical point the system looks the same on all length scales and this physical insight is translated into mathematical language in terms of 'the renormalization group' (RG), a set of scale-invariant transformations which leave the essential physical properties of the system unchanged. Admittedly, the RG terminology is somewhat inappropriate since the symmetry of such transformations is that of a semi-group (information is lost on coarse-graining), and the methodology comprises many different ideas and distinct methods, rather than being a formal monolithic edifice. Wilson's work on the RG spawned a vast effort in the analysis of equilibrium critical phenomena and quantum field theory [1,38]. Of much more recent interest has been the application of the renormalization methodology to non-equilibrium phenomena. The complexity of far-from-equilibrium dynamics is such that, while the physical motivation behind the RG programme of coarse-graining microscopic models still seems appropriate to obtain the macroscopic properties, it must be shown in each specific case that there may be a suitable scale invariance ('RG') underlying the physics, which can reveal or explain universality in behaviour.

Of central interest in this paper is the asymptotic late-time macroscopic behaviour of complex dynamical systems. Previously, Bricmont and Kupiainen [3–5] have combined asymptotic methods with ideas from renormalization theory to study problems in diffusive processes and special limiting solutions of nonlinear parabolic equations while Woodruff [39–42] has cast multiple-timescale problems in the form of renormalization theory. This allowed the equations governing larger-scale phenomena to be derived from a more general theory and to be separated out from the small-scale dynamics. In his approach, Woodruff separates timescales in the asymptotic limit $\varepsilon \to 0$ by writing the time t as $t = \bar{t}/\varepsilon + \tilde{t}$ where $\tilde{t}$ is the fast timescale and $\bar{t}$ is the slow timescale. The methods we develop in this paper share some of these features.

We apply underlying concepts from renormalization theory to study a simple model of nucleation, namely the Becker–Döring equations. These were originally formulated to study first-order phase transitions, and have been a central pillar in classical nucleation theory. 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. Despite the age of this model, we have only very recently applied generalizations of the Becker–Döring equations to a wide range of physicochemical processes from those involving surfactant self-assembly [14,15] through RNA polymer formation [12,13,32] to cement setting [13,31]. In these studies coarse-graining procedures are derived and used to reduce large systems of equations down to progressively lower-dimensional—'mesoscopic'—dynamical systems capable of theoretical analysis using standard techniques from the modern theory of differential equations. The coarse-grained contraction procedure, which is summarized in section 2, is analogous to other renormalization methods used in statistical physics, and this feature is exploited within this paper.

The Becker–Döring equations have recently been subjected to more conventional analysis using matched asymptotic expansions [36, 37]. Rather than use the coarse-graining approximation, which emphasizes the discrete nature of the equations, that analysis concentrated on the large-time limit where continuum approximations become valid [36]. The key results from this analysis are summarized here in section 3. The large-time limit of the coarse-grained equations was also studied there, and revealed the necessity of combining a change of timescale with the coarse-graining process in order to preserve the accuracy of the dynamics of the system; in the present analysis, this translates into the need to use a dynamical renormalization scheme.

Asymptotic methods have been applied directly to coagulation–fragmentation problems before: for example van Dongen and Ernst [18, 19] and Davies *et al* [17] have elucidated the self-similarity of the pure aggregation form of Smoluchowski's equations. These equations differ from the Becker–Döring equations in allowing clusters arbitrary size to coalesce together whereas the Becker–Döring equations only allow cluster–monomer interactions, but allow both aggregation and fragmentation. The Smoluchowski coagulation–fragmentation problem is much more complex but has been analysed by van Dongen and Ernst [20] and Carr and da Costa [8–10]. The scaling behaviour of the Becker–Döring equations has been studied by several authors: for example, Brilliantov and Krapivsky [6] and Blackman and Marshall [2]. Coarse-grained versions of the Becker–Döring equations have been analysed using matched asymptotic methods [30, 33]. In addition many authors have considered hybrid systems which have combined features of the Smoluchowski equations and the Becker–Döring equations: this approach started with Samsel and Perelson [28] who studied a system in which two clusters of arbitrary size can coalesce, but with a fragmentation step which is strictly Becker–Döring in nature, allowing only monomers to dissociate from clusters. Such models have been investigated further by Krapivsky and Redner [25] and Hendricks and Ernst [22]. Krapivsky [24] considered an alternative modification of the Becker–Döring equations, again concentrating analysis on the large-time scaling laws, while Peliti [26] looked at the scaling behaviour of a very simple model of pure aggregation in various dimensions in order to discover the manner in which the scaling laws depend on spatial dimension.

Our methods fit within the spirit of Woodruff's approach if 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 (mesoscopic and macroscopic) scales. Velazquez [29] 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. His RG differs from ours in several ways, most egregiously in that it separates the monomer concentration from the large-cluster sizes, whereas we retain the monomer concentration as an integral part of the mesoscale model.

Preliminary results of our work were reported in an earlier publication [16]. Here we provide the details omitted from that communication. We also discuss how the coarse-graining procedure affects the large-time kinetic behaviour of the systems under consideration. Various types of system are introduced and analysed, including full and coarse-grained systems of Becker–Döring equations (sections 2 and 3). The underlying renormalization structure is described (section 4), and the large-time asymptotics associated with the fixed points of the renormalization mapping are analysed (section 5). We consider noise-free Becker–Döring systems, by which we mean those with simple analytical formulae for their rate coefficients; in a separate paper [34] we present our analysis of 'noisy' systems in which the rate constants are perturbed by a random amount from the analytical expressions used here. We conclude with a discussion of our results (section 6).

2. The Becker–Döring cluster equations

In this section, we give a basic outline of the Becker–Döring system of equations and their properties. We consider the case for which the monomer concentration (c_1) is held constant; thus the Becker–Döring equations we are concerned with here are

$$\dot{c}_r = J_{r-1} - J_r \quad (r \geqslant 2) \qquad J_r = a_r c_r c_1 - b_{r+1} c_{r+1} \tag{2.1}$$

and we leave the constant mass formulation (in which the monomer concentration may vary) for future study. In this system of equations, $c_r(t)$ represents the concentration of clusters containing r monomers. Clusters of any particular size can be 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 assumption of a constant monomer concentration 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.

There are certain special properties of the Becker–Döring system which are not immediately apparent from the equations (2.1), and which must be preserved under the coarse-graining rescaling if the method is to produce physically relevant results, through approximating the original system in a faithful manner. These are:

(i) There exists a partition function, Q_r, satisfying $a_r Q_r = b_{r+1} Q_{r+1}$, and hence an equilibrium solution $c_r = Q_r c_1^r$. The quantity Q_r is related to the chemical potential of a cluster of size r. If we denote Boltzmann's constant by k, the temperature of the system by T and use the reference state $\mu_r^{\ominus}$ in which $\mu_1^{\ominus} = 0$, then the chemical potential of a cluster of size r (denoted μ_r) is given by $\mu_r = \mu_r^{\ominus} + kT \log c_r$. At equilibrium, this must satisfy $\mu_r = r\mu_1$, thus $\mu_r^{\ominus} = -kT \log Q_r$ and $Q_1 = 1$.

(ii) There exists a Lyapunov function, $V = \sum_{r=1}^{\infty} c_r(\log(c_r/Q_r c_1^r) - 1)$, which is related to the Helmholtz free energy of the system by $F = kT\mathcal{V}V$, where $\mathcal{V}$ is the volume of the system.

(iii) There exists a set of identities (or 'weak form'), $\sum_{r=2}^{\infty} g_r \dot{c}_r = g_1 J_1 + \sum_{r=1}^{\infty} [\, g_{r+1} - g_r \,] J_r$.

(iv) The total density of the system is $\varrho = \sum_{r=1}^{\infty} r c_r$. However, this is not conserved since matter can be added to or removed from the system by the monomer concentration being held constant.

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

$$c_r = Q_r c_1^r \left(1 - J \sum_{k=1}^{r-1} \frac{1}{a_k Q_k c_1^{k+1}}\right) \tag{2.2}$$

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

$$J = 1 \Big/ \sum_{r=1}^{\infty} \frac{1}{a_r Q_r c_1^{r+1}}. \tag{2.3}$$

2.1. Other formulations

An alternative formulation of the Becker–Döring equations has been proposed by Penrose and Lebowitz [27], in which the monomer concentration is allowed to vary, whilst the total mass of material in the system (ϱ) is held constant. The analysis of such a system is in general more complicated since the monomer concentration is unknown and causes the system to become both nonlinear and non-local (in r).

An underlying model in this paper is a constant-mass system in which monomer is added to or removed from the system by way of a precursor chemical P which undergoes a reversible reaction to create monomer C_1. This is modelled by the simple reaction $P \rightleftharpoons C_1$ with forward rate $k_f(p, c_1)$ and reverse rate $k_b(p, c_1)$. Denoting the concentration of P by $p(t)$ we then have the system

$$\dot{p} = k_b(p, c_1)c_1 - k_f(p, c_1)p \tag{2.4}$$

$$\dot{c}_1 = k_f(p, c_1)p - k_b(p, c_1)c_1 - J_1 - \sum_{r=1}^{\infty} J_r \tag{2.5}$$

in addition to (2.1). This system has a conserved quantity $\varrho_{\mathrm{tot}} = p + \sum_{r=1}^{\infty} rc_r$. However, note that the amount of mass in the Becker–Döring part of the system ($\{c_r\}_{r=1}^{\infty}$) is not constant $\varrho_{\mathrm{BD}}(t) = \sum_{r=1}^{\infty} rc_r$. Such an extended system of the Becker–Döring equations has been used previously to model generalized nucleation phenomena [31]. In certain cases analytical progress in the study of such systems can be made using asymptotic techniques, such as in [36] where the constant mass formulation of the Becker–Döring equations are investigated, and in [31] where a generalized constant mass system with inhibition as well as a precursor chemical is analysed.

In studying just the Becker–Döring part of this extended system (2.1), we are assuming that the precursor chemical decays in such a way that the monomer concentration remains constant, that is $\dot{c}_1 = 0$. This requires

$$\dot{p} = -J_1 - \sum_{r=1}^{\infty} J_r. \tag{2.6}$$

Solutions which we describe as *equilibrium* solutions satisfy $J_r = 0$ for all $r \geqslant 1$, thus correspond to $p = k_b c_1/k_f$, and for this specific concentration of precursor chemical the additional reaction which adds or removes matter from the Becker–Döring part of the system will also be in equilibrium. Thus, the equilibrium solution of our extended system is given by $c_r = Q_r c_1^r$ with $c_1 = k_f p/k_b$, and at equilibrium $J_r = 0$ for all $r \geqslant 1$. However, for solutions we describe as *steady states*, the fluxes $J_r = J \neq 0$ where J is independent of size (r), so there is a net flux of matter into the system (assuming $J > 0$, consequently a removal of mass if $J < 0$), and in these cases we assume that there is sufficient precursor chemical to sustain the steady state. In this case, although $\dot{c}_r = 0$ for all r, $\dot{p} \neq 0$ so the precursor chemical is not in equilibrium. Such steady-state solutions can be characterized by the flux associated with them.

3. Coarse-graining procedure

Following a 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

$$\dot{x}_n = L_{n-1} - L_n \quad (r \geqslant 2) \qquad L_n = \alpha_n x_n x_1^{\lambda} - \beta_{n+1} x_{n+1} \tag{3.1}$$

$$\alpha_n = T a_{\Lambda_n} a_{\Lambda_n+1} \ldots a_{\Lambda_{n+1}-1} \qquad \beta_{n+1} = T b_{\Lambda_n+1} b_{\Lambda_n+2} \ldots b_{\Lambda_{n+1}} \tag{3.2}$$

where the retained coarse-grained cluster concentrations are relabelled as $x_n := c_{\Lambda_r}$ with $x_1 := c_1$ the monomer concentration, which is not involved in the coarse-graining since it has a special role in the Becker–Döring theory [14, 16]. 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. In effect, the system models the aggregation–fragmentation processes

$$(\lambda+1)X_1 \rightleftharpoons X_2 \qquad X_n + \lambda X_1 \rightleftharpoons X_{n+1} \quad (n \geqslant 2) \tag{3.3}$$

for coarse-grained clusters of size X_r. 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. This factor was omitted in our original formulation of the coarse-graining procedure [14,32]; its inclusion 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 ($a_r = a$, $b_r = b$). The large-time asymptotics of the constant-monomer-concentration Becker–Döring system with constant coefficients were found by Wattis and King [36] using conventional asymptotic expansion methods. The leading-order solution found there falls into two cases: for $ac_1 < b$ the equilibrium solution $c_r = (a/b)^{r-1}c_1^r$ is approached; whilst for $ac_1 > b$ the steady-state solution $c_r = c_1$ is approached. In both cases the asymptotic solution is realized by a front moving forward into larger r-space ('aggregation space') at speed $\dot{s} = |ac_1 - b|$, ahead of which ($r > s(t)$) the concentrations are all zero, and behind which ($r < s(t)$) the concentrations are either at a steady state or in thermodynamic equilibrium. In order for the coarse-grained contraction to preserve the correct speed of propagation, the timescale T should take the value

$$T = \frac{(ac_1 - b)}{\lambda(a^\lambda c_1^\lambda - b^\lambda)}. \tag{3.4}$$

This temporal rescaling also ensures that the steady-state fluxes in the full and reduced systems coincide. In the terminology of renormalization theory, this makes the coarse-graining procedure a *dynamical renormalization transformation*.

The four properties listed in section 2 above for the full Becker–Döring system of equations are shared by the contracted system of equations (3.1):

$$\begin{aligned} &\overline{x}_n = Q_{\Lambda_n} x_1^{\Lambda_n} \qquad V = \sum_{n=1}^{\infty} x_n \left(\log\left(\frac{x_n}{Q_{\Lambda_n} x_1^{\Lambda_n}} \right) - 1 \right) \\ &\sum_{n=2}^{\infty} g_n \dot{x}_n = g_1 L_1 + \sum_{n=1}^{\infty} (g_{n+1} - g_n) L_n \qquad \varrho = \sum_{n=1}^{\infty} [\,(n-1)\lambda + 1\,]\, x_n \end{aligned} \tag{3.5}$$

where $\alpha_n Q_{\Lambda_n} = \beta_{n+1} Q_{\Lambda_{n+1}}$.

Note that it is also possible to allow the mesh size to vary with aggregation number [31]: that is, putting $\lambda = \lambda_n$ transforms the system with constant rates ($a_r = a$, $b_r = b$) into one with non-constant rates (since $\alpha_r = a^{\lambda_r}$ will be a nontrivial function of r, and similarly for β_{r+1}). For this reason we put to one side such generalized meshes in this paper.

4. Renormalization structure

We now proceed to consider the renormalization of Becker–Döring models in which the cluster rate coefficients are of power law form. As discussed below, this dependence is of immediate relevance to the description of surface-limited nucleation and growth processes in physicochemical systems.

4.1. The Becker–Döring system with power law coefficients

In the case of Becker–Döring systems with power law rate coefficients, the rate coefficients for aggregation and fragmentation are respectively

$$a_r = ar^p \qquad b_{r+1} = br^p \tag{4.1}$$

so that the parameter $\theta = ac_1/b$ which arises in the constant-monomer case remains 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 of rather less physical relevance, but we still study it 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 physical situations [11].

The partition function Q_r is defined by $Q_r = (a/b)^{r-1}$ as in the $p = 0$ case considered earlier [36]. The governing equations are then

$$\dot{c}_r = J_{r-1} - J_r \quad (r \geqslant 2) \qquad J_r = r^p(ac_1c_r - bc_{r+1}) \quad (r \geqslant 1). \tag{4.2}$$

For $\theta \leqslant 1$ the system approaches the steady-state solution (which we also refer to as the equilibrium solution, even though, strictly speaking it may not be, owing to the boundary condition of constant monomer concentration imposed by the pool chemical approximation) given by solving $J_r = 0$, that is

$$c_r = \theta^{r-1}c_1. \tag{4.3}$$

Note that this solution is independent of p, although the way in which the steady-state solution is approached depends on p.

For $\theta > 1$ this solution gives diverging concentrations for large r and is hence unphysical. In this case the system approaches one of a family of time-dependent solutions to equations (4.2), in which all fluxes are equal; $J_r = J$ for all r then implies

$$c_r = \theta^{r-1}c_1\left(1 - J\sum_{k=1}^{r-1}\frac{1}{bc_1k^p\theta^k}\right). \tag{4.4}$$

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

$$J = bc_1\Big/\sum_{k=1}^{\infty}k^{-p}\theta^{-k}. \tag{4.5}$$

The steady-state solution valid for all r is

$$c_r = \frac{J}{b}\sum_{k=r}^{\infty}k^{-p}\theta^{r-k-1}. \tag{4.6}$$

4.2. Repeated application of contraction procedure: renormalization

We have already shown how the full Becker–Döring system of equations can be reduced by a coarse-graining process to the subsystem of equations (3.1), (3.2). We now show that these equations can be further reduced, by applying the contraction procedure to (3.1), (3.2) with mesh size μ, defining the monomer concentration in the new variables by $z_1 = x_1(= c_1)$. The new cluster concentrations z_p are representative of the concentrations x_n for $(M_{p-1}+1) \leqslant p \leqslant M_p$ where $\{M_p\}_{p=1}^{\infty}$ is the grid of retained n values of cluster aggregation numbers, determined by $M_p = (p-1)\mu + 1$. Thus we find

$$\dot{z}_p = I_{p-1} - I_p \quad (p \geqslant 2) \qquad I_p = A_pz_pz_1^{\lambda\mu} - B_{p+1}z_{p+1} \tag{4.7}$$

where I_p is the flux of material from concentration z_p to z_{p+1}, and has aggregation and fragmentation rates determined by

$$A_p = \tilde{T}\alpha_{M_p}\alpha_{M_p+1}\ldots\alpha_{M_{p+1}-1} \qquad B_{p+1} = \tilde{T}\beta_{M_p+1}\beta_{M_p+2}\ldots\beta_{M_{p+1}}. \tag{4.8}$$

We have denoted the change of timescale by $\tilde{T}$. In the case of the model with constant coefficients ($\alpha_n = \alpha$, $\beta_n = \beta$ for all n), in order for the timescales of the approach to steady state or equilibrium to be correctly reproduced, the temporal rescaling factor $\tilde{T}$ should be chosen to be

$$\tilde{T} = \frac{(\alpha x_1^\lambda - \beta)}{\mu(\alpha^\mu x_1^{\lambda\mu} - \beta^\mu)} = \frac{(ac_1 - b)}{\lambda\mu T^\mu(a^{\lambda\mu}c_1^{\lambda\mu} - b^{\lambda\mu})} \tag{4.9}$$

by analogy with (3.4). The rate coefficients satisfy $A_p Q_{(p-1)\lambda\mu+1} = B_{p+1} Q_{p\lambda\mu+1}$. The system satisfies the four properties

$$\begin{gathered}\overline{z}_p = Q_{(p-1)\lambda\mu+1}\overline{z}_1^{(p-1)\lambda\mu+1} \qquad V = \sum_{p=1}^{\infty} z_p\left(\log\left(\frac{z_p}{Q_{(p-1)\lambda\mu+1}}\right) - 1\right) \\ \sum_{p=1}^{\infty} g_p\dot{z}_p = g_1 I_1 + \sum_{r=1}^{\infty}(g_{p+1} - g_p)I_p \qquad \varrho = \sum_{p=1}^{\infty}\left[(p-1)\lambda\mu + 1\right] z_p.\end{gathered} \tag{4.10}$$

So we see that the repeated contraction is identical to a single contraction with mesh parameter $\gamma = \lambda\mu$. The system of equations (4.7) could have been derived by a single coarse-grained contraction, with mesh

$$z_p = c_{\Gamma_r} \qquad z_1 = c_1 \qquad \Gamma_p = (p-1)\gamma + 1. \tag{4.11}$$

Note also that $\Gamma_p = \Lambda_{M_p} = M_{\Lambda_p}$, so that the coarse-graining procedure is commutative.

The combined effect on the rate coefficients and timescale can be verified by noting that in the case of constant coefficients, $A = \tilde{T}\alpha^\mu = \tilde{T}T^\mu a^{\lambda\mu} = \hat{T}a^{\lambda\mu}$, where

$$\hat{T} = \frac{ac_1 - b}{\lambda\mu(a^{\lambda\mu}c_1^{\lambda\mu} - b^{\lambda\mu})} \tag{4.12}$$

which is what one would expect if λ were replaced by $\lambda\mu$ in equation (3.4).

At the heart of renormalization theory is the repeated application of a coarse-graining procedure. The analysis above shows that: (i) a contracted version of the Becker–Döring system can itself be contracted, which is crucial if we are to use ideas from renormalization theory; and (ii) the effect of coarse-graining the Becker–Döring equations with a mesh size λ and then coarse-graining the resultant equations with a mesh size μ is identical to a single application of the coarse-graining process with mesh $\gamma = \lambda\mu$. Thus the limit of repeated applications of the renormalization coarse-graining process corresponds to the $\lambda \gg 1$ limit of equations (3.1). This second property makes the ensuing analysis possible, since we do not have to handle systems of equations more complicated than the Becker–Döring system itself; that is, *the structure of the equations is invariant under this transformation*. Note that as one may have expected *a priori*, the coarse-graining does not introduce cluster–dimer or more general cluster–cluster interactions; rather the theory is generalized so that clusters interact with several monomers in moving from one coarse-grained set of cluster sizes to the next.

4.3. Contraction of power law coefficients

If the rate coefficients in the original formulation in equations (2.1) 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

$$\alpha_n = a^\lambda\left\{[(r-1)\lambda + 1][(n-1)\lambda + 2]\cdots[n\lambda]\right\}^p. \tag{4.13}$$

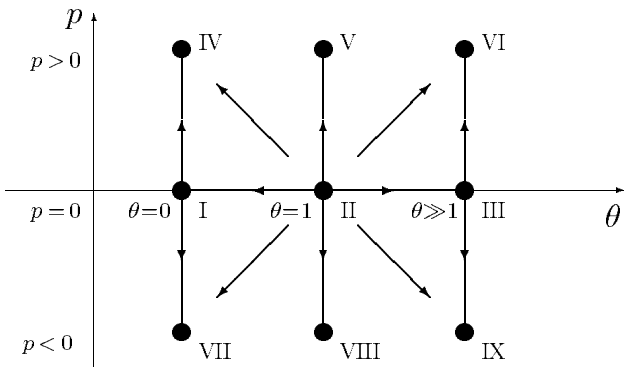

Figure 1. The effect of the coarse-graining contraction or, equivalently, the renormalization mapping, on the parameters θ, p in the Becker–Döring model with power law rate coefficients. The nine fixed points of the map are denoted I–IX, and represent possible universality classes for the dynamics.

Thus

$$\begin{aligned}\log\alpha_n &= \lambda\log a + p\sum_{j=1}^{\lambda}\log(n\lambda-\lambda+j)\\ &\approx \lambda\log a + p\int_0^{\lambda}\log(n\lambda-\lambda+x)\,\mathrm{d}x\\ &= \lambda\log a + p\lambda\left[\log(n\lambda)-1+(1-n)\log\left(1-\frac{1}{n}\right)\right].\end{aligned}\tag{4.14}$$

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 $\beta_{n+1} = (b\lambda^p n^p)^\lambda$. Since contracting a constant density Becker–Döring system leaves the kinetic part of the equations invariant and only affects the coefficients in the 'constitutive equation' for the flux, the steady-state solutions and large-time asymptotics for the contracted systems of equations can be found directly from the above theory.

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 $\theta \mapsto \theta^\lambda$ and $p \mapsto \lambda p$. 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 also be the basis of analysis in subsequent sections of this paper. However, the cases corresponding to $p < 0$ are physically less relevant, since equation (4.1) then assigns the largest rates to the smallest cluster sizes. Figure 1 shows schematically the effect of the contraction on the parameters θ, p.

In phase plane terminology, II has the form of an unstable node, while I, III, V, VIII are saddle points, since they act as attractors in one direction and repellors in the other (although

they are at the limits of the allowable domain, so only have trajectories on one side of the critical point). Cases IV, VI, VII, IX are stable nodes since they act as attractors in both the θ and the p directions.

5. Large-time asymptotics of the nine universality classes

The previous section identified nine special, or limiting, cases which merit more detailed analysis, since following a coarse-grained contraction with large mesh parameter, any model will be approximated by one of these cases. To simplify the analysis we shall always choose a scaling such that $x_1 = 1$, with α and β equal to zero or unity. In this section we present large-time and large-aggregation-number asymptotics. These are developed by means of a continuum limit, which replaces the system of ordinary differential equations by a single partial differential equation, and draws on the results derived by Wattis and King [37]. We apply these results in particular to our nine limiting cases. In a further paper these results will be generalized to systems whose rates are perturbed away from the simple polynomial expressions considered here [34].

5.1. Case I: pure fragmentation at a constant rate

This corresponds to constant fragmentation with rate $\beta_n = 1$ and no aggregation. Hence we expect the system to approach the equilibrium configuration $x_n = 0$ for all $n \geqslant 2$. The governing equation is

$$\dot{x}_n = x_{n+1} - x_n \qquad \text{for} \quad n \geqslant 2. \tag{5.1}$$

If the system is started from the initial conditions $x_n(0) = 0$ for $n \geqslant 2$, then the system does not change. All other initial conditions will approach this state as $t \to \infty$.

5.2. Case II: aggregation and fragmentation at constant rates

This case corresponds to constant rate coefficients but with both coagulation and fragmentation present, and exactly balancing each other, $\alpha_n = 1 = \beta_n$. Thus we expect the system to approach the equilibrium solution $x_r(t) = x_1$. The time evolution follows the equation

$$\dot{x}_n = x_{n-1} - 2x_n + x_{n+1} \qquad \text{for} \quad n \geqslant 2 \tag{5.2}$$

which has the form of a 'discrete diffusion' equation.

In the limit of large time and large n, the discrete system (5.2) can be approximated by the diffusion equation

$$\frac{\partial x}{\partial t} = \frac{\partial^2 x}{\partial n^2} \tag{5.3}$$

whose solution is $x_n = \operatorname{erfc}(n/2\sqrt{t})$. This equilibrium is approached by a purely diffusive mechanism, there being no advective term in (5.3), in contrast to cases I and III (below) where advection is present.

5.3. Case III: pure aggregation at a constant rate

This case corresponds to constant aggregation with rate coefficients $\alpha_n = 1$ for all n, and no fragmentation ($\beta_n = 0$ for all n). Thus we expect the steady-state solution $x_n = x_1$ to be approached, which has steady-state flux $L = \alpha x_n x_1^{\lambda} = 1$. The governing equations

$$\dot{x}_n = x_{n-1} - x_n \qquad \text{for} \quad n \geqslant 2 \tag{5.4}$$

are exactly solved by

$$x_n = 1 - \mathrm{e}^{-t} \sum_{k=0}^{n-2} \frac{t^k}{k!}. \tag{5.5}$$

However, it is not straightforward to see which mechanisms are driving the growth process when the solution is written in this form. An asymptotic approximation gives a much more intuitive idea of the dynamical behaviour. To describe the large-time and large-aggregation-number asymptotics of this case, we approximate (5.4) by

$$\frac{\partial x}{\partial t} = \frac{1}{2}\frac{\partial^2 x}{\partial n^2} - \frac{\partial x}{\partial n} \tag{5.6}$$

from which we can deduce the existence of a front of matter which propagates to larger aggregation numbers with speed unity, the front itself spreading out over a range of aggregation numbers proportional to $t^{1/2}$. This can be shown by transforming to the new independent variable $z = n - t$ yielding $\frac{\partial x}{\partial t} = \frac{1}{2}\frac{\partial^2 x}{\partial z^2}$, which has the similarity solution $x = \frac{1}{2}\mathrm{erfc}(z/\sqrt{t})$. Thus in the limit $t \to \infty$

$$x_n = \frac{1}{2}\mathrm{erfc}\left(\frac{n-t}{\sqrt{2t}}\right) \tag{5.7}$$

which is an asymptotic approximation of (5.5).

5.4. Case IV: pure fragmentation with rates increasing with cluster size

In this case the only process occurring is fragmentation, and the fragmentation rate depends on cluster size, with larger clusters losing monomers at faster rates. So, as in case I the system will tend to $x_n = 0$ for all $n \geqslant 2$. The system is governed by

$$\dot{x}_n = n^{p\lambda} x_{n+1} - (n-1)^{p\lambda} x_n \qquad n \geqslant 2. \tag{5.8}$$

Since the aggregation rates are greater than in case I, the equilibrium solution will be approached more rapidly than in case I. Matter is advected to smaller aggregation sizes, and removed from the system in monomeric form.

5.5. Case V: aggregation and fragmentation with rates increasing with cluster size

In this case we have both coagulation and fragmentation and both rates increase algebraically with aggregation number. The system is governed by the equations

$$\dot{x}_n = (n-1)^{p\lambda} x_{n-1} - (n-1)^{p\lambda} x_n - n^{p\lambda} x_n + n^{p\lambda} x_{n+1}. \tag{5.9}$$

The equilibrium solution is $x_n = 1$ for all n, and by analogy with case II (which also has $\theta = 1$) we might expect the large-time asymptotics to approach this solution. However, if we seek solutions from the wider class of steady-state solutions which are simply characterized by constant flux L (not necessarily equal to zero), then we find a family of solutions

$$x_n = 1 - L \sum_{k=1}^{n-1} \frac{1}{k^{p\lambda}}. \tag{5.10}$$

From this family, we seek the solution which has the fastest possibly decay as $n \to \infty$. This occurs for $L = 1/\zeta(p\lambda)$ (where $\zeta(z) = \sum_{k=1}^{\infty} k^{-z}$ is the Riemann zeta function). Thus for $p \leqslant 1/\lambda$, we have that $L = 0$ and the equilibrium solution determines the large-time asymptotic behaviour of the system; however, for $p > 1/\lambda$ there is a steady-state solution (with $L > 0$) which has a faster decay at large r; hence the evolution will approach this solution rather than the equilibrium solution.

We shall now discuss the manner in which the *equilibrium* solution $x_n = 1$ is approached in the case $p < 1/\lambda$. The continuum limit for $n \gg 1$ is

$$\frac{\partial x}{\partial t} = n^{p\lambda}\left(\frac{\partial^2 x}{\partial n^2} + \frac{p\lambda}{n}\frac{\partial x}{\partial n}\right) \tag{5.11}$$

which immediately yields a similarity solution with variable $\eta = n/t^{1/(2-p\lambda)}$. Assuming $x = f(\eta)$ with $f(0) = 1$ implies

$$f(\eta) = \frac{\int_\eta^\infty u^{-p\lambda}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u}{\int_0^\infty u^{-p\lambda}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u}. \tag{5.12}$$

In this case, there is no travelling diffusive wavefront; rather the balance of coagulation and fragmentation means that the equilibrium solution is reached by a purely diffusive mechanism. However, the similarity variable η shows that the aggregation number at a given concentration increases at a rate $n \propto t^{1/(2-p\lambda)}$, which is faster than the usual spreading rate of $n \propto \sqrt{t}$; this is due to the size-dependent coefficients accelerating mass transfer in the large-n region. The precise details of the special case $p = 1/\lambda$ are not covered by this general solution, but the special case $p = 0$ (case II) can be obtained from the general theory for $p < 1/\lambda$.

When $p > 1/\lambda$ the analysis can be modified for the approach to the steady-state solution

$$x_n^{\mathrm{sss}} = \frac{1}{\zeta(p\lambda)}\sum_{k=n}^{\infty}\frac{1}{k^{p\lambda}}. \tag{5.13}$$

The manner in which such a solution is approached can be found by writing $x_n(t) = x_n^{\mathrm{sss}}\psi_n(t)$. We are then interested in the manner in which $\psi_n \to 1$ as $t \to \infty$. This is governed by the equation

$$\dot{\psi}_n = \left((n-1)^{p\lambda} + \frac{L}{x_n^{\mathrm{sss}}}\right)\psi_{n-1} - n^{p\lambda}\psi_n - (n-1)^{p\lambda}\psi_n + \left(n^{p\lambda} - \frac{L}{x_n^{\mathrm{sss}}}\right)\psi_{n+1} \tag{5.14}$$

where L is the steady-state flux ($L = 1/\zeta(p\lambda)$). For large n and at large times, it is appropriate to take the continuum limit, where x_n^{sss} can be approximated by $1/(p\lambda{-}1)n^{p\lambda-1}\zeta(p\lambda)$, yielding

$$\frac{1}{n^{p\lambda}}\frac{\partial\psi}{\partial t} = \frac{\partial^2\psi}{\partial n^2} + \left(\frac{2-p\lambda}{n}\right)\frac{\partial\psi}{\partial n}. \tag{5.15}$$

This equation possesses a similarity solution of the form $\psi(r,t) = f(\eta)$ where $\eta = r/t^{1/(2-p\lambda)}$ and

$$f(\eta) = \frac{\int_\eta^\infty u^{p\lambda-2}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u}{\int_0^\infty u^{p\lambda-2}\exp(-u^{2-p\lambda}/(2-p\lambda)^2)\,\mathrm{d}u}. \tag{5.16}$$

However, this solution is only defined for $1/\lambda < p < 2/\lambda$ and is not valid for the case $p = 1/\lambda$. In the special case $p = 2/\lambda$ equation (5.15) is solved by

$$\psi = \frac{1}{2}\mathrm{erfc}\left(\frac{\log(n) - t}{2\sqrt{t}}\right). \tag{5.17}$$

Although different states are approached in the cases $p < 1/\lambda$ and $p > 1/\lambda$, in both cases the asymptotics are governed by a similarity solution of the form $\eta = n/t^{1/(2-p\lambda)}$.

5.6. Case VI: pure aggregation with rates increasing with cluster size

This case corresponds to pure aggregation, the rate of aggregation growing with cluster size. There is thus no equilibrium solution; instead the system approaches the steady-state solution $x_n = n^{-p\lambda}$ according to

$$\dot{x}_n = (n-1)^{p\lambda}x_{n-1} - n^{p\lambda}x_n \qquad n \geqslant 2. \tag{5.18}$$

The substitution $\psi(n,t) = n^{p\lambda}x_n$ enables progress to be made. From the initial conditions $\psi_n = 0$ for $n \geqslant 2$, the steady-state solution $\psi_n \equiv 1$ will be reached as time progresses. For $p > 1/\lambda$ the system is ill-posed due to the instantaneous transport of material to large aggregation numbers.

For $p < 1/\lambda$ we assume that the equilibrium state is reached by a front moving from $n = 1$ to large n as time increases. To find the form of this wave at large times, we take the large-n and large-t limits, replacing equation (5.18) by

$$\frac{\partial\psi}{\partial t} = n^{p\lambda}\left(\frac{1}{2}\frac{\partial^2\psi}{\partial n^2} - \frac{\partial\psi}{\partial n}\right). \tag{5.19}$$

We define the position of the front by $n = s(t)$, and transform to a moving coordinate frame $z = n - s(t)$. We now show that the two 'outer' solutions $\psi = 1$ valid for $z \to -\infty$ (that is $n/s(t) < 1$) and $\psi = 0$ which holds in the limit $z \to +\infty$ (that is $n/s(t) > 1$) can be joined smoothly by a transition layer. Equation (5.19) implies that $\psi(z,t)$ is determined by

$$\frac{\partial\psi}{\partial t} - \dot{s}\frac{\partial\psi}{\partial z} = s^{p\lambda}\left(1+\frac{z}{s}\right)^{p\lambda}\left(\frac{1}{2}\frac{\partial^2\psi}{\partial z^2} - \frac{\partial\psi}{\partial z}\right). \tag{5.20}$$

The leading-order terms are those involving $\frac{\partial\psi}{\partial z}$, giving $\dot{s} = s^{p\lambda}$, which is solved by

$$s(t) \sim [(1-p\lambda)t]^{1/(1-p\lambda)} \qquad \text{as} \quad t \to \infty. \tag{5.21}$$

This result can be verified by considering the density, $\varrho = \sum_{n=1}^{\infty} nx_n \sim \sum_1^s n^{1-p\lambda} \sim (1 - s^{2-p\lambda})/(p\lambda - 2)$, which implies that the density asymptotically increases according to $\dot{\varrho} \sim s^{1-p\lambda}\dot{s}$. However, the formula for the density also satisfies $\dot{\varrho} = 1 + \sum_{n=1}^{\infty} n^{p\lambda}x_n = s$. Thus this calculation also gives $\dot{s} = s^{p\lambda}$, confirming equation (5.21).

The first correction terms in (5.20) are

$$\frac{1}{s^{p\lambda}}\frac{\partial\psi}{\partial t} = \frac{1}{2}\frac{\partial^2\psi}{\partial z^2} - \frac{p\lambda z}{s}\frac{\partial\psi}{\partial z}. \tag{5.22}$$

Since $s(t)$ is monotonically increasing, we simplify further calculations by using s as our temporal variable. The next stage of the calculation is straightforward if $p < 1/2\lambda$, since in this case $z \sim \sqrt{s}$ and (5.22) reduces to $\frac{\partial\psi}{\partial s} = \frac{1}{2}\frac{\partial^2\psi}{\partial z^2}$. Thus we find

$$x_n = \frac{1}{2}n^{-p\lambda}\operatorname{erfc}\left(\frac{(n-s)\sqrt{1-2p\lambda}}{\sqrt{2s}}\right). \tag{5.23}$$

For $p > 1/2\lambda$, advection of the front dominates the diffusion processes and so the front retains its memory of the initial conditions. An alternative way of visualizing this process is that the front moves so fast that it reaches $n = \infty$ before it has had time to adjust its shape to that of the erfc function. Thus we cannot specify in detail the shape of the front. More details of the special case $p = 1/2\lambda$ can be found in [37].

5.7. Case VII: pure fragmentation with rates decreasing with cluster size

Here there is no aggregation, so fragmentation will cause all clusters to break up, and as in cases I and IV, the system will approach the state where all matter is in monomeric form ($x_n = 0$ for $n \geqslant 2$). Since the fragmentation decays rapidly with size, large clusters will take a very long time to break up. The determining equations are

$$\dot{x}_n = n^{p\lambda}x_{n+1} - (n-1)^{p\lambda}x_n \qquad n \geqslant 2. \tag{5.24}$$

Since fragmentation is weaker than in cases I and IV, case VII takes longer to reach equilibrium.

5.8. Case VIII: aggregation and fragmentation with rates decreasing with cluster size

This corresponds to coagulation and fragmentation being equally balanced, both decaying as the aggregation number increases. As in cases II and V (with $p < 1/\lambda$), the system approaches the equilibrium solution $x_n \equiv 1$ in the large-time limit. The similarity solution valid for $p < 1/\lambda$ derived in case V is valid for this case too. The balance of coagulation and fragmentation forces means that the equilibrium solution is reached by a predominantly diffusive process.

5.9. Case IX: pure aggregation with rates decreasing with cluster size

The final case has no fragmentation, only an aggregation term which decays with increasing particle size. The system thus has no equilibrium solution, and will evolve to the divergent steady-state solution $x_n = n^{-p\lambda}$ according to

$$\dot{x}_n = (n-1)^{p\lambda} x_{n-1} - n^{p\lambda} x_n \qquad n \geqslant 2. \tag{5.25}$$

The substitution $\psi_n = n^{p\lambda} x_n$ yields $n^{-p\lambda}\dot{\psi}_n = \psi_{n-1} - \psi_n$, and progress can be made by forming a continuum approximation

$$n^{-p\lambda}\frac{\partial \psi}{\partial t} = \frac{1}{2}\frac{\partial^2 \psi}{\partial n^2} - \frac{\partial \psi}{\partial n}. \tag{5.26}$$

As in previous pure aggregation cases, the large-time asymptotic approach to the steady state is governed by a diffusive wave moving in the n-domain from $n = 1$ to large n; also as t increases the wavefront widens. The speed of propagation can be found by considering the density injected into the system, or by substituting $n = s(t) + z$ into equation (5.26) and expanding in z. The leading-order terms are

$$\frac{1}{s(t)^{p\lambda}}\frac{\partial \psi}{\partial t} = \frac{1}{2}\frac{\partial^2 \psi}{\partial z^2} + \frac{\partial \psi}{\partial z}\left(s(t)^{-p\lambda}\dot{s}(t) - 1 - \frac{p\lambda z}{s}\right). \tag{5.27}$$

At leading order the dominant terms are those involving $\frac{\partial \psi}{\partial z}$, giving $\dot{s} = s^{p\lambda}$ since we assume $z/s \ll 1$. The position of the front is given by

$$s(t) \simeq [(1-p\lambda)t]^{1/(1-p\lambda)} \qquad \text{as} \quad t \to \infty \tag{5.28}$$

and we now use s as a new timescale to solve the next order terms in (5.27), which yield $\psi = \frac{1}{2}\mathrm{erfc}(z\sqrt{((1-2p\lambda)/(2s))})$. Thus

$$x_n(t) \sim \frac{1}{2}n^{-p\lambda}\mathrm{erfc}\left(\frac{[n-s(t)]\sqrt{1-2p\lambda}}{\sqrt{2s(t)}}\right) \qquad \text{as} \quad t \to \infty \quad \text{with} \quad n - s(t) = \mathcal{O}(\sqrt{t}). \tag{5.29}$$

From equation (5.28) it is seen that the effect of λ is to reduce the exponent with which the position of the wavefront scales with time. Equation (5.29) shows that λ increases the decay exponent of the steady-state solution from p to $p\lambda$, and alters the scaling of the width of the wave. In the fully detailed system of equations the width asymptotes to $\sqrt{2s/(1-2p)}$, which, under coarse-graining, one might expect to be mapped to $\sqrt{2s/(1-2p)}/\lambda$; however, solving the coarse-grained equations yields $\sqrt{2s/(1-2p\lambda)}$ instead.

6. Discussion

We have described in detail the nine archetypal classes of behaviour into which the asymptotic dynamics of the Becker–Döring equations with power law coefficients falls. These nine classes

('cases I–IX' of section 5) arise as a result of the application of a systematic renormalization procedure to the fine-grained Becker–Döring equations and capture qualitatively different physical properties which are shared by all the models within the class, regardless of their microscopic differences. This amounts to a massive simplification of the original problem. In this paper, we have concentrated on the detailed large-time asymptotic analysis of these nine cases.

One specific detailed feature is worthy of note here. Our analysis of cases IV, V and VI shows that coarse-graining retains the correct leading-order structure of the problem, though critical exponents of $p = 1$ where the behaviour changes from fragmentation to aggregation dominated are mapped to $p = 1/\lambda$. Thus if $p < 1$, to retain the correct qualitative behaviour one is limited to taking $\lambda < 1/p$: taking the limit $\lambda \to \infty$ causes the correct form of the kinetics to be lost, although the correct solution is still approached in cases IV and VI. In case V, the equilibrium solution $x_n = 1$ is approached if $\lambda < 1/p$, and a steady-state solution if $p > 1$. However, if $\lambda > 1/p > 1$, the coarse-grained system approaches a steady-state solution whereas the microscopic model approaches the equilibrium solution.

In a companion paper [34] we analyse the effect that random perturbations to the rate coefficients have on the above analysis. There we consider the modifications such perturbations make to the steady-state solutions, the kinetics of approach to these states and their effects on the coarse-graining process itself. That analysis is necessary to confirm the existence and number of distinct universality classes in these Becker–Döring systems; as we have previously announced, all nine classes of behaviour may indeed be described as such (modulo, in cases VII–IX, a particular requirement on the behaviour of the noise) [16].

The renormalization programme described here is of direct relevance to many of our recent publications on the application of generalized Becker–Döring models to a wide range of problems of physicochemical interest. A further paper currently in preparation [35] explores several of these nucleation and growth problems in which the renormalization scheme is *exact*.

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