COAGULATION-FRAGMENTATION DYNAMICS

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1. INTRODUCTION

The dynamics of cluster growth has attracted considerable interest in many apparently unrelated areas of pure and applied science. Examples include polymer science, colloidal and aerosol physics, atmospheric science, astrophysics and the kinetics of phase transformations in binary alloys [5,6,8,10,12,13]. The common link in all these examples is that they can be considered as a system of a large number of clusters of particles that can coagulate to form larger clusters or fragment to form smaller ones.

If $c_r(t) \geq 0$, $r = 1,2,\ldots,$ denotes the expected number of r-particle clusters per unit volume at time t, then the discrete coagulation-fragmentation equations are

$$\dot{c}_r = \frac{1}{2}\sum_{s=1}^{r-1}[a_{r-s,s}c_{r-s}c_s - b_{r-s,s}c_r] - \sum_{s=1}^{\infty}[a_{r,s}c_rc_s - b_{r,s}c_{r+s}] \quad (1.1)$$

for $r = 1,2,\ldots,$ where the first sum is absent if $r = 1$. The coagulation rates $a_{r,s}$ and fragmentation rates $b_{r,s}$ are non-negative constants with $a_{r,s} = a_{s,r}$ and $b_{r,s} = b_{s,r}$. This model neglects (among other things) the geometric location of clusters and considers only binary collisions of clusters. For derivations of this and similar equations see [10].

The dependence of the rate coefficients $a_{r,s}, b_{r,s}$ on r and s depends on the particular application. In this paper we shall concentrate on the Becker-Döring equations in which $a_{r,s} = b_{r,s} = 0$ if both r and s are greater than 1. In this case we can write the equations in the form

$$\dot{c}_r = J_{r-1} - J_r, \quad r \geq 2,$$
$$\dot{c}_1 = -J_1 - \sum_{r=1}^{\infty} J_r \tag{1.2}$$

where $J_r = a_r c_1 c_r - b_{r+1} c_{r+1}$. To see that (1.2) is a special case of (1.1) take $a_r = a_{r,1}, b_{r+1} = b_{r,1}$ for $r \geq 2$ and $2a_1 = a_{1,1}$, $2b_2 = b_{1,1}$. For ease of notation, from now on all summations will be over the positive integers unless stated otherwise.

In sections 2-3 we discuss equation (1.2). The asymptotic behaviour of solutions is especially interesting, both mathematically and for applications. For example, in the binary alloy problem the essence of the phase transition is the formation of larger and larger clusters as t increases. Mathematically this can be identified with a weak but not strong convergence as $t \to \infty$. We only outline the main ideas involved in this investigation; full details appear in [3]. The general equation (1.1) is more difficult to analyse since solutions may have singularities not present in (1.2). In section 4 we briefly discuss some of the difficulties and state a new result on density conservation.

2. BASIC IDEAS

We first review some facts concerning convergence in a space of sequences. Let $X = \{c = (c_r): \Sigma r|c_r| < \infty\}$ and let $\{c^j\}$ be a sequence of elements in X. We say that c^j converges strongly to $c \in X$ (symbolically $c^j \to c$) if $\Sigma r|c_r^j - c_r| \to 0$ as $j \to \infty$. It is also useful to have another notion of convergence in X. We say that c^j converges weak * to $c \in X$ (symbolically $c^j \xrightarrow{*} c$) if (i) $\sup\{\Sigma r|c_r^j|; j = 1,2,\ldots\} < \infty$ and (ii) $c_r^j \to c_r$ as $j \to \infty$ for each $r = 1,2,\ldots$. Thus weak * convergence is in a sense pointwise convergence. The justification of the terminology comes from functional analysis (cf. [9], p374). Clearly strong convergence implies weak * convergence. However, the converse is false in general; for example take $c^j = (j^{-1}\delta_{rj})$ where $\delta_{rj} = 1$ if $r = j$ and 0 otherwise. Then c^j converges weak * to the zero sequence but it does not converge strongly. We can express the weak * convergence as convergence in a metric space. For $\rho > 0$ let $B_\rho = \{(y_r) \in X; \Sigma r|y_r| \leq \rho\}$. Then (B_ρ, d) is a metric space where $d(y,z) = \Sigma |y_r - z_r|$. Clearly a sequence $\{y^j\} \subset B_\rho$ converges weak * to $y \in X$ if and only if $y \in B_\rho$ and $d(y^j, y) \to 0$ as $j \to \infty$. Weak * convergence is useful because B_ρ is compact; equivalently, any bounded sequence in X has a weak * convergent subsequence.

In order to arrive quickly at the most interesting questions concerning (1.2) we give a rapid review of its properties. The density is given by $\Sigma rc_r(t)$ and since matter is neither created or destroyed in an interaction it is a conserved quantity. Thus we look for equilibrium solutions $c^\rho = (c_r^\rho)$ with $\rho = \Sigma rc_r^\rho$. From (1.2) we must have $J_r(c^\rho) = 0$ for all r so that

$$c_r^\rho = Q_r (c_1^\rho)^r \tag{2.1}$$

where $Q_1 = 1$, $Q_{r+1} = Q_r a_r / b_{r+1}$, $r \geq 1$. It remains to identify c_1^ρ. To do this let

$$F(z) = \Sigma rQ_r z^r$$

In the binary alloy problem the above series has finite radius of convergence z_s and $F(z_s) = \rho_s < \infty$. In this paper we shall describe our results for this case; for other cases see [3]. Since F is an increasing function of z, the equation $F(z) = \rho$ has a unique solution $z = c_1^\rho$ if $0 \leq \rho \leq \rho_s$ and no solution if $\rho > \rho_s$. Thus if $0 \leq \rho \leq \rho_s$ there is a unique equilibrium c^ρ with density ρ, while if $\rho > \rho_s$ there is no equilibrium with density ρ. Let

$$V(c) = \Sigma c_r[\ln(c_r/Q_r) - 1]. \tag{2.2}$$

The 'free-energy' function V is a Lyapunov function for (1.2), that is it is non-increasing along solutions. Also, for $0 \leq \rho \leq \rho_s$, the equilibrium c^ρ is the unique minimizer of V on the set $X^\rho = \{c = (c_r): c_r \geq 0$ for all r, $\Sigma rc_r = \rho\}$.

Suppose that the initial data for (1.2) has density ρ_o. If $\rho_o \leq \rho_s$ the above results suggest that the corresponding solution $c(t) \to c^\rho$ strongly in X as $t \to \infty$ and this is indeed the case. If $\rho_o > \rho_s$ the asymptotic behaviour is not so clear since there is no equilibrium with density ρ_o. Since V is non-increasing along solutions it is natural to consider the behaviour of minimizing sequences of V on X^{ρ_o}. The basic result here is that if $\rho_o > \rho_s$ and c^j is a minimizing sequence of V on X^{ρ_o} then c^j converges weak * to c^{ρ_s} in X but not strongly. The main result on asymptotic behaviour says that the solution $c(t)$ of (1.2) with density ρ_o is minimizing for V on X^{ρ_o} as $t \to \infty$, so that, for $0 \leq \rho_o \leq \rho_s$, $c(t) \to c^{\rho_o}$ strongly in X and, for $\rho_o > \rho_s$, $c(t) \xrightarrow{*} c^{\rho_o}$ in X. Note that for the case $\rho_o > \rho_s$ we have that

$$\rho_o = \Sigma\, rc_r(t) > \Sigma\, r \lim_{t\to\infty} c_r(t) = \Sigma\, rc_r^{\rho_s} = \rho_s.$$

The excess density $\rho_o - \rho_s$ corresponds to the formulation of larger and larger clusters as t increases, i.e. condensation.

To obtain results on the asymptotic behaviour of a solution $c(t)$ we have to exploit the Lyapunov function V. To do this we apply the invariance principle for evolution equations endowed with a Lyapunov function (cf. [7] for a survey). To apply this method we need to find a metric with respect to which V is continuous, the positive orbit $\{c(t): t \geq 0\}$ is relatively compact and solutions depend continuously on initial data. It might seem natural to try and use the metric induced by strong convergence on X, that is $d(y,z) = \Sigma\, r|y_r - z_r|$. However, in the case $\rho_o = \Sigma\, rc_r(0) > \rho_s$ the positive orbit cannot be relatively compact with this metric since there is no equilibrium with density ρ_o. Moreover, since the only obvious global estimate is density conservation we have to use the metric induced by weak * convergence on bounded subsets of X to achieve relative compactness of positive orbits. Unfortunately, V defined by (2.2) is not continuous in this metric. Fortunately, however, because density is conserved,

$$V_z(c) = V(c) - \ln z\, \Sigma\, rc_r$$

is a Lyapunov function for each z, and for exactly one value of z, namely $z = z_s$, V_z is sequentially weak * continuous. Thus we can apply the invariance principle to prove that $c(t) \xrightarrow{*} c^{\rho}$ as $t \to \infty$ for some ρ, $0 \leq \rho \leq \min(\rho_o, \rho_s)$ where ρ_o is the density of the initial data. We then prove the result described above by using a maximum principle for (1.2) in the case $\rho < \rho_s$. At this stage of the proof in [3] we made certain hypotheses on the initial data; a more refined argument shows that these hypotheses are not needed [4].

3. EXISTENCE AND DENSITY CONSERVATION

We prove existence of solutions to (1.2) by taking a limit of solutions of the finite-dimensional system

$$\begin{aligned} \dot{c}_r &= J_{r-1} - J_r, \quad 2 \leq r \leq n-1 \\ \dot{c}_1 &= -J_1 - \sum_{r=1}^{n-1} J_r, \quad \dot{c}_n = J_{n-1}. \end{aligned} \tag{3.1}$$

Solutions of (3.1) satisfy $\sum_{r=1}^{n} rc_r(t) = \sum_{r=1}^{n} rc_r(0)$ so that $c_r = O(r^{-1})$ for all n. Hence if $a_r, b_r = o(r)$ then for each r, $\dot{c}_r$ is bounded. Thus by applying the Arzela-Ascoli Theorem and passing to the limit in the equations we get a simple global existence proof. In fact since fragmentation can be thought of as a dissipative mechanism we do not need any hypotheses on b_r and by working harder we need only assume $a_r = O(r)$ to get global existence. If $r^{-1}a_r \to \infty$ as $r \to \infty$, there is in general no solution of (1.2) even on a short time interval.

We remarked earlier that formally the density $\Sigma\, rc_r(t)$ is a constant of the motion. This is always true for (1.2); it is not true in general for (1.1) (cf. section 4). To prove it for (1.2) we consider partial sums. Now

$$\sum_{r=1}^{n} r[c_r(t) - c_r(0)] = -\int_0^t \Big[nJ_n(c(s)) + \sum_{r=n}^{\infty} J_r(c(s))\Big] ds. \tag{3.2}$$

For a solution of (1.2) we require that $\Sigma\, J_r(c)$ converges so that

$$\int_0^t \sum_{r=n}^{\infty} J_r(c(s))ds \to 0 \quad \text{as } n \to \infty.$$

Also, from (1.2)

$$n\int_0^t J_n(c(s))ds = n \sum_{r=n+1}^{\infty} (c_r(t) - c_r(0)) \to 0 \quad \text{as } n \to \infty$$

since $n \sum_{r=n+1}^{\infty} c_r \leq \sum_{r=n+1}^{\infty} rc_r$. Thus letting $n \to \infty$ in (3.2) proves that the density is conserved.

4. THE GENERAL DISCRETE COAGULATION-FRAGMENTATION EQUATIONS

We first discuss equations (1.1) when both coagulation and fragmentation are included. In this case it is usual to assume the detailed balance condition. This demands that (i) an equilibrium solution $\bar{c} = (\bar{c}_r)$ with $\bar{c}_r > 0$ exists and (ii) at equilibrium the net rate of conversion of r and s clusters to $r + s$ clusters is zero, so that $b_{r,s}\bar{c}_{r+s} = a_{r,s}\bar{c}_r\bar{c}_s$. This places the following restriction on $a_{r,s}$, $b_{r,s}$;

$$a_{r,s}Q_rQ_s = b_{r,s}Q_{r+s} \tag{4.1}$$

for some Q_r. Assuming (4.1), it follows that equilibria of (1.1) have the form $c_r = Q_r(c_1)^r$ and a formal calculation shows that $V(c) = \Sigma\, c_r[\ln(c_r/Q_r) - 1]$ is a Lyapunov function for (1.1). This is the same as for the Becker-Döring equation (cf. equations (2.1) and (2.2)) and so we expect to get similar results. The analysis for (1.1) however is even more complicated than that needed for (1.2). Most of the analysis has been completed [4] but there are still some technicalities to be finalised. To reveal some of these difficulties we look at some special cases of (1.2). In particular, we show that the density $\Sigma\, rc_r(t)$, which formally is a constant of the motion, need not in fact be conserved.

(a) Let $a_{r,s} = 0$, $b_{r,s} = 1$ for all r and s so that

$$\dot{c}_r = \sum_{s=1}^{\infty} c_{r+s} - \frac{1}{2}(r-1)c_r. \tag{4.2}$$

A solution of (4.2) is

$$c_r(t) = (e^{-t/2})^{r-1}\left[c_r(0) + \sum_{n=r+1}^{\infty} c_n(0)(2(1-e^{-t/2}) + (1-e^{-t/2})^2(n-r-1))\right] \tag{4.3}$$

and it is easy to check that for this solution the density is a conserved quantity [2]. However, for any $\lambda > 0$, (4.2) has a solution

$$c_r = e^{\lambda t}r^{-3}x_r, \tag{4.4}$$

where x_r is defined by $x_1 = 1$, $x_{r+1} = (1 + \alpha_r)x_r$, and

$$\alpha_r = \frac{6\lambda r^2 + (6\lambda - 2)r + 2\lambda - 1}{r^3(2 + r + 2\lambda)}.$$

Since $\alpha_r = O(r^{-2})$, x_r is bounded and $\Sigma\, rc_r(t) = e^{\lambda t}\Sigma\, rc_r(0)$. The special solutions (4.4) also show that for any initial data, solutions of (4.2) are not unique. Clearly, the solutions given by (4.4) are unphysical. In this case it is easy to pick out the correct unique solution by placing extra requirements on the definition of a solution (cf. [1] for the continuous case of (4.2)). However, in more complicated situations it is useful to know conditions on the fragmentation coefficients which prohibit non-uniqueness.

(b) Let $b_{r,s} = 0$ for all r and s so that we are only considering coagulation processes. In this case the density conservation can break down at a finite time t_c, a phenomenon known as gelation [11]. The gel point t_c is characterised as the first time for which $\sum_{r,s} ra_{r,s}c_rc_s$ diverges and is interpreted as the formation of a super-particle (gel phase). In particular, this phenomenon occurs when $a_{r,s} = (rs)^\alpha$, $\alpha > 1/2$. For $t > t_c$ it may be necessary to modify the equations to account for interactions of the gel phase with finite clusters.

For applications to phase transitions, one set of conditions suggested by O. Penrose on the coagulation and fragmention rates is that $a_{r,s} = O(r^{1/3} + s^{1/3})$ and that $b_{r,s} = a_{r,s}Q_{r+s}^{-1}Q_rQ_s$, where $Q_r \sim z_s^{-r}\exp(-\alpha r^{1/3})$ with α, z_s positive constants. Note that in this case $b_{r,s} \sim r^{1/3}$ for r large and s bounded while for r and s large with $r - s$ small, $b_{r,s}$ is small. The physical motivation here is that surface area considerations show that it is unlikely that a large cluster of size $r + s$ will split into two large clusters of size r and s (and hence increase the surface energy by a large amount). It turns out that under these conditions we can show that density is conserved. More generally we have:

<u>Theorem</u>

Suppose that for some $n_0 \geq 1$ and $k > 0$ we have that

(i) $a_{r,s} \leq k(r + s)$ for all $r,s \geq n_0$,

(ii) $\frac{n}{r}\sum_{j=n}^{r-n} b_{r-j,j} \leq k$ for all r,n with $r \geq 2n \geq 2n_0$,

(iii) $\frac{1}{r}\sum_{j=n_0}^{m} j b_{r-j,j} \leq k$ for all r and n with $r \geq n + n_0$

where $m = \min(n, r - n)$.

Then if c is a solution of (1.1) on $[0,T)$ with $\rho_0 = \Sigma\, r c_r(0) < \infty$, $\Sigma\, r c_r(t) = \rho_0$ for all $t \in [0,T)$.

The proof of the above result is given in [4].

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