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Metastable States for the Becker–Döring Cluster Equations

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Abstract. The Becker–Döring equations, in which $c_l(t)$ can represent the concentration of l-particle clusters or droplets in (say) a condensing vapour at time t, are

$$dc_l(t)/dt = J_{l-1}(t) - J_l(t) \quad (l = 2, 3, \dots)$$

with

$$J_l(t) := a_l c_1(t) c_l(t) - b_{l+1} c_{l+1}(t)$$

and either $c_1 = \text{const.}$ ('case A') or $\rho := \sum_1^\infty l c_l = \text{const.}$ ('case B'). The equilibrium solutions are $c_l = Q_l z^l$, where $Q_l := \prod_2^l (a_{r-1}/b_r)$. The density of the saturated vapour, defined as $\rho_s := \sum_1^\infty l Q_l z_s^l$, where z_s is the radius of convergence of the series, is assumed finite. It is proved here that, subject to some further plausible conditions on the kinetic coefficients a_l and b_l, there is a class of "metastable" solutions of the equations, with $c_1 - z_s$ small and positive, which take an exponentially long time to decay to their asymptotic steady states. (An "exponentially long time" means one that increases more rapidly than any negative power of the given value of $c_1 - z_s$ (or, in case B, $\rho - \rho_s$) as the latter tends to zero). The main ingredients in the proof are (i) a time-independent upper bound on the solution of the kinetic equations (this upper bound is a steady-state solution of case A of the equations, of the type used in the Becker–Döring theory of nucleation), and (ii) an upper bound on the total concentration of particles in clusters greater than a certain critical size, which (with suitable initial conditions) remains exponentially small until the time becomes exponentially large.

1. Introduction

In 1979 an article entitled "towards a rigorous theory of metastability" was published by J. L. Lebowitz and this author (Penrose and Lebowitz 1979, 1987).

Just how difficult it has been to make progress in the suggested direction is shown by the fact that the same article could be reprinted 8 years later with only a few pages added to bring it up to date.

The approach described in that article is the one used by Penrose and Lebowitz (1971), Capocaccia et al. (1974) and Cassandro & Oliveri (1977) in which a metastable state, associated with a first-order phase transition in some macroscopic thermodynamic system, is represented by a region R in phase space characterized by three criteria: (i) only one thermodynamic phase is present; (ii) the metastable state has a very long lifetime; (iii) once the system has left the metastable state, it is very unlikely to return. In the papers mentioned, the main part of the work was to estimate the lifetime of the metastable state by estimating the rate of escape from R for a system started in the "restricted canonical ensemble"—one whose phase-space density is canonical within R but zero outside. Unfortunately, in neither paper was it possible to obtain an estimate which was valid in the thermodynamic limit; that is to say, the estimated rate of escape from R is proportional to the size of the system, so that in the thermodynamic limit the rate of escape becomes infinite and the estimated lifetime goes to zero. The difficulty can be eased somewhat by using a different definition for the lifetime (Vanheuverzwijn 1979) but the rigorous estimates which have so far been obtained for this lifetime, though greater than zero, are still unrealistically short. One response to the difficulties with the infinite-system limit is to argue that it is the finite rather than the infinite model which most properly represents the essential features of metastability (Sewell 1986). The viewpoint of the present paper, however, is that these difficulties can be overcome by improvements in the infinite-system theory.

The root of the difficulty we have been discussing is the unrealistic picture of the breakdown of metastability used in the first four papers cited above. According to that picture, at the moment when the condition defining the phase-space region R is violated in some particular part of the system the metastable state breaks down throughout the whole of the region of three-dimensional space occupied by the system—as if the whole of the very large system immediately "knows" when a super-critical nucleus of the new thermodynamic phase has formed in some other part of it, no matter how distant. Such a thing would make sense if the super-critical nucleus immediately grew in a catastrophic or explosive way as soon as it formed. But in reality super-critical nuclei grow very slowly, and so even if a super-critical nucleus has formed in one part of the system the rest of the system is likely to go on as usual for a long time. The real breakdown of metastability comes only when the density of super-critical nuclei has become significant over the whole system—quite a different thing from the formation of just one super-critical nucleus at one place in it. Thus we may expect that if we explicitly take into account the density of super-critical nuclei we can get a more realistic estimate of the lifetime.

In order to make such estimates we need a specific kinetic model from which to estimate the rate of growth of the super-critical clusters. One would like to do this for a specific molecular model, such as the Ising model with Glauber (1963) stochastic dynamics considered by Capocaccia et al., or even the simpler "bootstrap percolation" model considered by Aizenman and Lebowitz (1988) but the aim of the present paper is less ambitious. Instead of using a microscopic model we shall work from a system of kinetic equations of the type introduced by Becker and Döring (1935) in their pioneering treatment of this topic. In these equations the system is modelled as a collection of droplets of one thermodynamic phase embedded in an otherwise uniform matrix of the other. These droplets (also called *clusters*) are assumed to change size through the gain or loss of just one particle at a time. The resulting changes in their concentrations are assumed to satisfy a system of kinetic equations similar to the ones used in chemical kinetics.

There are two versions of the Becker–Döring equations: the original version used by Becker and Döring themselves, in which the concentration of monomers (one-particle clusters) is taken to be constant while the overall concentration of particles can vary, and the modified version (Penrose & Lebowitz 1979, Burton 1977) which takes account of the depletion of monomers as larger clusters form, by requiring the overall concentration of particles in all clusters to be constant. In the present paper, the original version will be referred to as version A, or as the constant-c_1 version (the symbol c_1 representing the concentration of monomers), and the modified version will be referred to as version B, or as the constant-density version. The constant-c_1 version leads, as shown in Becker and Döring's original paper, to a simple representation of the metastable state as a steady-state solution of the kinetic equations. This representation, outlined in Sect. 3 below, is not free of difficulties: the overall concentration of particles diverges (Penrose 1978, or see Eq. (10.5) below), and the method does not give a direct estimate of the lifetime of the metastable state; but it is good enough to form the basis of a very successful physical theory. In the constant-density version, however, the Becker–Döring representation of the metastable state cannot consistently be applied at all, since it is not a solution of the kinetic equations.

What we shall do here, therefore, is to go beyond the theory based on steady-state solutions of the kinetic equations, and instead study time-dependent solutions. The main result is to prove the existence of a class of solutions which have (in a well-defined sense) very long lifetimes. These solutions provide a description of the metastable state which avoids the difficulties mentioned above.

2. The Model

We start from the Becker–Döring cluster equations, as given in (for example Sect. 9 of Penrose & Lebowitz (1979, 1987),

$$\frac{dc_l(t)}{dt} = J_{l-1}(t) - J_l(t) \qquad (l = 2, 3, 4, \ldots), \tag{2.1}$$

$$J_l(t) = a_l c_1(t) c_l(t) - b_{l+1} c_{l+1}(t) \quad (l = 1, 2, 3, \ldots). \tag{2.2}$$

Here $c_l(t)$ denotes the concentration of l-particle clusters at time t and $J_l(t)$ denotes the net rate per unit volume at which l-particle clusters are being converted into $(l+1)$-particle clusters. The kinetic coefficients $a_1, a_2, \ldots$ and $b_2, b_3, \ldots$ are positive constants. To complete the system of equations we need an equation for dc_1/dt.

As already mentioned in the Introduction, there are two cases to consider:

$$\left.\begin{aligned} \frac{dc_1(t)}{dt} &= 0 && \text{(case A: constant } c_1) \\ \frac{dc_1(t)}{dt} &= -J_1(t) - \sum_{l=1}^{\infty} J_l(t) && \text{(case B: constant } \rho) \end{aligned}\right\}. \tag{2.3}$$

A third version of the equations, which is suitable in cases where there is no conserved order parameter, will be considered in Sect. 12. It does not lead to anything really new since it can be transformed into case A.

The simplest solutions of Eq. (2.1–3) are the ones where the J_l are all zero and the c_l are independent of t. We may call these the *equilibrium* solutions. They have the form

$$c_l = Q_l z^l \quad (l = 1, 2, \ldots), \tag{2.4}$$

where $Q_1, Q_2, \ldots$ are 'cluster partition functions,' defined here by

$$Q_1 := 1 \tag{2.5}$$

$$Q_l := \frac{a_1 a_2 \cdots a_{l-1}}{b_2 b_3 \cdots b_l} \quad (l = 2, 3, \ldots), \tag{2.6}$$

and z is an arbitrary positive number, which can be interpreted as the activity or fugacity of the equilibrium state (2.4).

We shall assume that the constants a_l, b_l satisfy the following conditions

(i) there exist positive constants A, A', α, with $0 < \alpha < 1$, such that

$$A' < a_l < A l^{\alpha} \quad (l = 1, 2, \ldots); \tag{2.7}$$

(ii)

$$\lim_{l \to \infty} b_{l+1}/b_l = 1; \tag{2.8}$$

(iii) the sequence b_l/a_l is monotonic decreasing, with a positive limit which we shall call z_s (it can be interpreted as the fugacity of the saturated vapour)

$$b_{l+1}/a_{l+1} \leqq b_l/a_l \quad (l = 2, 3, \ldots), \tag{2.9}$$

$$\lim_{l \to \infty} b_l/a_l =: z_s > 0; \tag{2.10}$$

(iv) the sequence b_l/a_l converges to its limit like a negative power of l, but not as rapidly as l^{-1}; that is to say, there exist positive constants γ, γ', G, G' satisfying the conditions

$$0 < \gamma < 1 \quad \text{and} \quad 0 < \gamma', \tag{2.11}$$

such that

$$z_s \exp(G l^{-\gamma}) < b_l/a_l < z_s \exp(G' l^{-\gamma'}). \tag{2.12}$$

This last assumption can be given the following physical interpretation: the chemical potential inside an l-particle cluster or droplet, $kT \log(Q_l/Q_{l+1})$, is by (2.6) proportional to $\log(b_{l+1}/a_l)$; so, if we approximate b_{l+1} by b_l in accordance with

(2.8), Eq. (2.12) is telling us that the chemical potential inside a cluster of size l exceeds that of the saturated vapour by an amount which (assuming $\gamma = \gamma'$) is asymptotically proportional to $l^{-\gamma}$. According to Thomson's formula (see Frenkel 1946, Sect. VII.1) it is also inversely proportional to the radius of the cluster, so that if the clusters are approximately spherical we expect (in 3 dimensions) $\gamma = \gamma' = 1/3$. This estimate for γ and γ' also appears in the simplest version of the droplet theory of condensation (Andreev 1963, Fisher 1967, Langer 1967).

The conditions (i)–(iv) are all satisfied by the choice of a_l, b_l used by Penrose et al. (1983), (1984), appropriate values for the exponents being $\alpha = \gamma = \gamma' = 1/3$.

One consequence of the assumptions (i)–(iv) is that the series for the equilibrium density,

$$\sum_{l=1}^{\infty} lQ_l z^l \tag{2.13}$$

has (by (2.6), (2.8) and (2.10)) the positive radius of convergence $\lim_{l\to\infty}(b_{l+1}/a_l) = z_s$. Moreover, it follows from (2.12) (for details see Theorem 2) that this series converges when $z = z_s$. Its sum will be denoted by ρ_s:

$$\rho_s := \sum_{l=1}^{\infty} lQ_l z_s^l < \infty. \tag{2.14}$$

This sum may be interpreted as the density of the saturated vapour. In this paper we shall be mainly interested in values of z and ρ which exceed the saturation values z_s and ρ_s.

3. The Becker–Döring Theory

As mentioned earlier, the original Becker–Döring theory of metastability applies to the constant-c_1 version of the kinetic equations. Suppose we give c_1 some value just greater than z_s, and look for a steady state solution, i.e. one where $dc_l/dt = 0$ ($l = 1, 2, \ldots$). The relevant equilibrium solution, with all $J_l = 0$, is given by (2.4) with $z = c_1$. This solution may well be a good approximation to the steady state for small l, but it cannot be right for large l, because if $z > z_s$ the right side of (2.4) becomes very large for large l. A more sensible steady-state solution can be obtained by relaxing the condition $J_l = 0$, in which case the J_l are independent of l but not zero. Their common value, denoted here by $J(c_1)$, is determined by using the condition that c_l be bounded for large l. The quantity $J(c_1)$ is called the *nucleation rate*; it gives the rate per unit volume at which clusters are acquiring new particles in the steady state. The resulting steady-state solution will be denoted here by

$$c_l = f_l(c_1) \quad (l = 1, 2, \ldots). \tag{3.1}$$

Explicit formulas for $J(c_1)$ and $f_l(c_1)$ are given in Eqs. (5.8) and (5.9) below.

The crux of the Becker–Döring theory of metastability is that, for moderately small values of $c_1 - z_s$, the nucleation rate $J(c_1)$ can be extremely small, so small as to be completely undetectable experimentally. This makes it possible to think of (3.1) as representing a metastable state in which large clusters (i.e. the new phase) are being formed extremely slowly. The mathematical feature responsible for these very small nucleation rates, proved in Theorem 2 below, is that $J(z)$ is *exponentially small* in the limit $z \searrow z_s$. This means that, as $z - z_s$ becomes small, $J(z)$ goes to zero more rapidly than any power of $z - z_s$.

4. The Main Results

In this paper, we shall go beyond the Becker–Döring theory by treating metastability as a time-dependent rather than a steady-state phenomenon. We shall show that there exist solutions of the kinetic equations which, although not equilibrium or even steady-state solutions, persist for an exponentially long time. The main results can be summarized in four theorems, which are stated in the present section and proved in Sects. 5–11. Theorem 1 puts an upper bound on the rate of increase of the number of clusters larger than a certain critical size l^*. Theorem 2 gives estimates showing that, under suitable conditions, this rate of increase is exponentially small, so that the time necessary for the number of particles in super-critical clusters to become appreciable is exponentially large. Theorems 3 and 4 contain the explicit construction of metastable states, with lifetimes which are exponentially long but not infinite.

Theorem 1. *Let z be chosen greater than z_s, and let the initial data in a solution $c_l(t)$ of the Becker–Döring equations (2.1–3A or B) satisfy*

$$0 \leqq c_l(0) \leqq f_l(z) \quad (l = 1, 2, \ldots) \tag{4.1}$$

and

$$\sum_1^\infty l^2 c_l(0) < \infty, \tag{4.2}$$

where $f_l(z)$ is the unique solution (given explicitly in (5.9), the symbol $J(z)$ appearing there being defined in (5.8)) of the difference equation

$$a_{l-1} z f_{l-1}(z) - (b_l + a_l z) f_l(z) + b_{l+1} f_{l+1}(z) = 0 \quad (l = 2, 3, \ldots) \tag{4.3}$$

with the end conditions

$$f_1(z) = z \tag{4.4}$$

and

$$f_l(z) \quad \text{is bounded as} \quad l \to \infty. \tag{4.5}$$

Then for all $t \geqq 0$ we have

$$0 \leqq c_l(t) \leqq f_l(z) \quad (l = 1, 2, \ldots), \tag{4.6}$$

$$M_0(t) \leqq M_0(0) + J^* t, \tag{4.7}$$

$$M_1(t) \leqq 2^{\beta - 2}\{M_1(0) + t_0 J^* + t_0 J^*[(l^* + 1)/\beta]^{\beta - 1}[1 + M_0(0)/t_0 J^* + t/t_0]^\beta\}, \tag{4.8}$$

where $M_r(t)$, β and t_0 are defined by

$$M_r(t) := \sum_{l = l^* + 1}^\infty l^r c_r(t) \quad (r = 0, 1), \tag{4.9}$$

$$\beta := (2-\alpha)/(1-\alpha), \quad \text{i.e.} \quad (\beta-1)(1-\alpha)=1, \tag{4.10}$$

$$t_0 := (l^*+1)/Az \tag{4.11}$$

with A the constant in (2.7), J^* is defined by

$$J^* := a_{l^*}Q_{l^*}z^{l^*+1}, \tag{4.12}$$

and l^* is the critical cluster size, defined as the value of l that minimizes the quantity $a_lQ_lz^l$.

By (2.6) and the monotonic decrease of b_l/a_l, this value of l is the unique solution of

$$b_{l^*}/a_{l^*} \geqq z > b_{l^*+1}/a_{l^*+1} \tag{4.13}$$

with the convention $b_1=\infty$ to take care of the case where $z > b_2/a_2$. By (2.10) this definition implies that l^* increases without bound as $z \searrow z_s$; further information about l^* and related quantities will be found in Theorem 2.

The proof of Theorem 1 is given in Sects. 7 and 8. It depends on two lemmas, which are stated and proved in Sects. 5 and 6. Before embarking on this proof, however, we state the other three theorems. The following terminology will be used, where $q(z)$ stands for any quantity depending on z.

"$q(z)$ is exponentially small": for all positive m we have
$q(z)=O(z-z_s)^m$ (i.e. $q(z)/(z-z_s)^m$ is bounded as $z \searrow z_s$)

"$q(z)$ is at most algebraically large": for some positive m we have
$q(z)=O(z-z_s)^{-m}$

Theorem 2. This theorem is about the orders of magnitude of the quantities l^*, J^* and $M_0(0)$ appearing in Theorem 1. *Let z be any number greater than z_s. Then the following results hold*:

(i) *l^*, defined in (4.13), is at most algebraically large.*

(ii) *All moments of the equilibrium cluster size distribution converge when $z=z_s$:*

$$\sum_{l=1}^{\infty} l^n Q_l z_s^{\,l} < \infty. \quad (n=0,1,2,\ldots); \tag{4.14}$$

in particular, the case $n=1$ gives Eq. (2.14).

(iii) *The quantities $J^*(z)$, defined by*

$$J^*(z) := a_{l^*}Q_{l^*}z^{l^*+1} \tag{4.15}$$

and $J(z)$, defined by

$$J(z) = \left[\sum_{l=1}^{\infty} \frac{1}{a_lQ_lz^{l+1}}\right]^{-1} \tag{4.16}$$

are exponentially small.

(iv) *The ratio $\rho^*(z)/J^*(z)$, where*

$$\rho^*(z) := \sum_{l^*+1}^{\infty} lQ_lz_s^{\,l}, \tag{4.17}$$

is at most algebraically large; moreover, $\rho^*(z)$, being the product of $\rho^*(z)/J^*(z)$ with the exponentially small quantity $J^*(z)$, is itself exponentially small.

The proof of this theorem is given in Sect. 9.

The final pair of theorems use Theorems 1 and 2 to construct a metastable solution of the Becker–Döring equations (2.1–3)—more precisely, a family of solutions, one for each $z > z_s$, such that as $z - z_s$ becomes small a quantity which we can interpret as the lifetime of the solution becomes exponentially large. Theorem 3 applies to version A of the equations, and shows that in this case the concentration of super-critical clusters eventually grows beyond all bounds, but takes an exponentially long time to do so. Theorem 4 applies to version B; in addition to containing the analogous result that the number of super-critical clusters takes an exponentially long time to reach its final equilibrium value, the theorem also shows that the entire distribution of sub-critical clusters in the metastable state changes exponentially slowly.

The particular cluster distribution investigated is given in (4.18). For clusters smaller than the critical size l^* it is identical with the one given by Becker and Döring; but for larger clusters a different formula is used, chosen so as to ensure that the condition $\sum l^2 c_l < \infty$ (Eq. (4.2)) is satisfied and that the initial number of particles in super-critical clusters is exponentially small. The exact choice is not very significant; it was made so as to give a total concentration of particles which was manifestly greater than the critical concentration ρ_s.

Theorem 3. *Consider the solution $c_l(t)$ of the Becker–Döring constant-c_1 kinetic equations ('case A') with initial conditions*

$$c_l(0) = \begin{Bmatrix} f_l(z) & \text{for} & l \leqq l^* \\ Q_l z_s^{\,l} & \text{for} & l > l^* \end{Bmatrix}. \tag{4.18}$$

This solution has an exponentially long lifetime, in the sense that

(i) *If t is at most algebraically large then $M_1(t)$, the concentration of particles in super-critical clusters as defined in (4.9), is exponentially small.*

(ii) *In the limit of large t, $M_1(t)$ grows beyond all bounds.*

That is to say, the number of super-critical clusters remains exponentially small until an exponentially long time has elapsed; but eventually it does become large—large enough, indeed, to invalidate the low-density approximations upon which the derivation of the Becker–Döring equations was based in the first place.

Theorem 4. *For constant-density kinetics ('case B'), the solution of the kinetic equations with initial conditions (4.18) has an exponentially long lifetime in the sense that for each fixed l the following two results hold in the limit $z \searrow z_s$ (which implies $l^* \to \infty$):*

(i) *If t is at most algebraically large, then $c_l(t) - c_l(0)$ is exponentially small*

(ii) $\lim_{t \to \infty} [c_l(t) - c_l(0)]$ *is not exponentially small.*

That is to say, cluster concentrations with $l \ll l^*$ remain exponentially close to their initial values until an exponentially long time has elapsed; but eventually they do change.

The proofs of Theorems 3 and 4 are given in Sects. 10 and 11.

5. Properties of the Becker–Döring Steady State

To prove Theorem 1 we need some preliminary results. These will take the form of two lemmas. Lemma 1 gives some useful properties of the steady-state solution f_l which forms the basis of the Becker–Döring theory of metastability

Lemma 1.

(i) *For each $z > z_s$ the conditions (4.3–4.5) define a unique sequence $f_l(z)$ $(l = 1, 2, \ldots)$.*

(ii) *For fixed z, $a_l f_l(z)$ decreases monotonically with l:*

$$a_{l+1} f_{l+1}(z) \leqq a_l f_l(z) \qquad (l = 1, 2, \ldots). \tag{5.1}$$

(iii) *For fixed l, $f_l(z)/z$ increases monotonically with z, and hence $f_l(z)$ increases strictly monotonically with z:*

$$\text{if} \quad z' > z \quad \text{then} \quad f_l(z') > f_l(z) \quad (l = 1, 2, \ldots). \tag{5.2}$$

(iv) *The sequence $f_l(z)$ $(l = 1, 2, \ldots)$ has the upper bound*

$$f_l(z) \leqq Q_l z^l. \tag{5.3}$$

(v) *In the limit $z \searrow z_s$, the sequence $f_l(z)$ becomes the equilibrium cluster distribution at $z = z_s$:*

$$\lim_{z \searrow z_s} f_l(z) = Q_l z_s^{\,l} \quad (l = 1, 2, \ldots) \tag{5.4}$$

so that, by (5.2),

$$f_l(z) > Q_l z_s^{\,l} \quad \text{for} \quad z > z_s \quad (l = 1, 2, \ldots). \tag{5.5}$$

Proof of Lemma 1. First we obtain the explicit solution of the difference Eq. (4.3). The method is essentially that of Becker and Döring (1935). To start, we note that the difference equation is equivalent to the statement that $J(z)$, defined for the moment by

$$J(z) := a_l z f_l(z) - b_{l+1} f_{l+1}(z) \quad (l = 1, 2, \ldots) \tag{5.6}$$

is independent of l. Dividing both sides of the above equation by $a_l Q_l z^{l+1}$ and using the identity $a_l Q_l = b_{l+1} Q_{l+1}$ derived from (2.6), we obtain

$$\frac{J(z)}{a_l Q_l z^{l+1}} = \frac{f_l(z)}{Q_l z^l} - \frac{f_{l+1}(z)}{Q_{l+1} z^{l+1}}. \tag{5.7}$$

Now, as we saw when discussing (2.13), the ratio of successive terms of the series $\sum_1^\infty Q_l z^l$, in the limit of large l, is z/z_s. Since we are requiring $z > z_s$, the denominators on the right of (5.7) grow without bound as $l \to \infty$. Hence, by the condition (4.5) in the definition of f_l, both terms on the right of (5.7) tend to zero as $l \to \infty$. Summing both sides of (5.7) from $l=1$ to ∞, and using (2.5) and (4.4) to show that $f_1/Q_1 z = 1$, we conclude that

$$J(z) = \left[\sum_{l=1}^{\infty} \frac{1}{a_l Q_l z^{l+1}}\right]^{-1}. \tag{5.8}$$

The series is a convergent sum of positive terms, so that we can be sure $J(z) > 0$. Equation (5.8) is the formula for $J(z)$ used in Theorem 2 (Eq. (4.16)).

To obtain $f_l(z)$ explicitly, we sum both sides of (5.7) from l to infinity and obtain

$$f_l(z) = J(z) Q_l z^l \sum_{r=l}^{\infty} \frac{1}{a_r Q_r z^{r+1}}. \tag{5.9}$$

If the conditions (4.3–5) have a solution at all, this is it; but we must still show that $f_l(z)$ as given by (5.9) does indeed satisfy the conditions. For (4.3) and (4.4) this is a matter of substitution. For (4.5) we use part (ii) of the lemma (proved just below) to show that $a_{l+1} f_{l+1}(z) \leqq a_1 f_1(z)$, and hence that $f_{l+1}(z) \leqq a_1 f_1(z)/A' =$ const. by (2.7); if (as is normally the case) the coefficients a_l increase without bound as $l \to \infty$, then we have in addition $\lim_{l\to\infty} f_l(z) = 0$.

Part (ii) of the lemma concerns the monotonic decrease of $a_l f_l(z)$. From (5.9) it follows that

$$\begin{aligned} z a_l f_l(z) &= J(z)\left[1 + \sum_{r=l+1}^{\infty} \frac{a_l Q_l}{a_r Q_r} z^{l-r}\right] \\ &= J(z)[1 + h_{l+1} z^{-1} + h_{l+1} h_{l+2} z^{-2} + \cdots], \end{aligned} \tag{5.10}$$

where

$$h_{l+1} := \frac{b_{l+1}}{a_{l+1}} = \frac{a_l Q_l}{a_{l+1} Q_{l+1}}. \tag{5.11}$$

By our hypothesis (2.9), h_l is a decreasing function of l and hence every term in the series for $a_l f_l(z)$ is a decreasing function of l; so part (ii) of the lemma is proved.

To prove part (iii) of the lemma we define, for any given z and z' both greater than z_s, two new sequences

$$\tilde{f}_l(z', z) := z' f_l(z) - z f_l(z') \qquad (l = 1, 2, \ldots), \tag{5.12}$$

$$\tilde{J}_l(z', z) := a_l z' \tilde{f}_l(z', z) - b_{l+1} \tilde{f}_{l+1}(z', z) \quad (l = 1, 2, \ldots). \tag{5.13}$$

Using these definitions and then the difference equations (4.3) for $f_l(z)$ and $f_l(z')$, we calculate (for $l \geqq 2$)

$$\begin{aligned} \tilde{J}_{l-1}(z', z) - \tilde{J}_l(z', z) &= a_{l-1} z' \tilde{f}_{l-1}(z', z) - (b_l + a_l z')\tilde{f}_l(z', z) + b_{l+1} \tilde{f}_{l+1}(z', z) \\ &= z'\{a_{l-1} z' f_{l-1}(z) - (b_l + a_l z') f_l(z) + b_{l+1} f_{l+1}(z)\} \\ &\quad - z\{a_{l-1} z' f_{l-1}(z') - (b_l + a_l z') f_l(z') + b_{l+1} f_{l+1}(z')\} \\ &= z'(z' - z)(a_{l-1} f_{l-1}(z) - a_l f_l(z)) \\ &\geqq 0 \quad \text{if} \quad z' > z, \end{aligned} \tag{5.14}$$

the last line being a consequence of (5.1). Thus (assuming from now on that $z' > z$)

the sequence $\tilde{J}_1, \tilde{J}_2, \ldots$ is monotonic decreasing, and can therefore change sign at most once.

Let $\tilde{l}$ be the (unique) value of l at which this sequence changes sign, so that

$$\tilde{J}_l \begin{Bmatrix} \geqq 0 & \text{if} & l < \tilde{l} \\ < 0 & \text{if} & l \geqq \tilde{l} \end{Bmatrix}, \tag{5.15}$$

where we take $\tilde{l} = 0$ if all terms are negative and $\tilde{l} = \infty$ if all are non-negative. By the same manipulations as in the derivation of (5.9) from (5.6), we can solve the system of equations (5.13) for $\tilde{f}_l$, obtaining

$$\tilde{f}_l(z', z) = Q_l z'^l \sum_{r=l}^{\infty} \frac{\tilde{J}_l(z', z)}{a_r Q_r z'^{r+1}}. \tag{5.16}$$

Setting $l = 1$ and noting that (by (5.12) and (4.4)) $\tilde{f}_1(z', z) = 0$, we obtain

$$\sum_{r=1}^{\tilde{l}-1} \frac{\tilde{J}_l(z', z)}{a_r Q_r z'^{r+1}} + \sum_{r=\tilde{l}}^{\infty} \frac{\tilde{J}_l(z', z)}{a_r Q_r z'^{r+1}} = 0. \tag{5.17}$$

By (5.15), the first sum consists entirely of non-negative terms and the second consists entirely of negative terms.

Now we can complete the proof of part (iii) of the lemma by using (5.16) to show that $\tilde{f}_l(z', z)$ is non-positive. There are two cases to consider. If $l \geqq \tilde{l}$, then by (5.15) all terms of the sum in (5.16) are negative, and so $\tilde{f}_l(z', z)$ is negative. If $l < \tilde{l}$, then there may be some positive terms in the sum as well, but by (5.17) these terms can at most cancel the contribution of the negative terms. Thus in either case we have

$$\tilde{f}_l(z', z) \leqq 0. \tag{5.18}$$

Referring back to the definition (5.12) of $\tilde{f}_l(z', z)$, and remembering that we have been assuming $z' > z$, we obtain part (iii) of the lemma.

Part (iv) of the lemma follows immediately from the fact that the series in (5.9) is a subset of the series in (5.8) for $1/J(z)$, in which all terms are positive.

For part (v) of the lemma we first show that

$$\lim_{z \searrow z_s} J(z) = 0. \tag{5.19}$$

From (2.6), (2.9) and (2.10) we have

$$a_l Q_l / a_{l+1} Q_{l+1} = b_{l+1} / a_{l+1} \geqq z_s, \tag{5.20}$$

and hence

$$a_1 Q_1 / a_l Q_l = \prod_{r=1}^{l-1} a_r Q_r / a_{r+1} Q_{r+1} \geqq z_s^{l-1}. \tag{5.21}$$

Putting this estimate into (5.8) we have

$$J(z)^{-1} \geqq \sum_{l=1}^{\infty} \frac{1}{z z_s a_1 Q_1} \left(\frac{z_s}{z} \right)^l = \frac{1}{z(z - z_s) a_1 Q_1}, \tag{5.22}$$

from which (5.19) follows immediately.

Taking the limit $z \searrow z_s$ in (5.6) we obtain

$$a_l z_s f_l(z_s) - b_{l+1} f_{l+1}(z_s) = 0, \tag{5.23}$$

where $f_l(z_s)$ means $\lim_{z \searrow z_s} f_l(z)$. Solving this recurrence relation, as in the derivation of (2.4), we obtain (5.4) and so complete the proof of the lemma.

6. Approximation by a Finite System of Equations

Lemma 2 is concerned with some properties of the infinite system of differential equations (2.1–3), of which the most basic are the existence and uniqueness of solutions. Unfortunately it is not possible to apply the standard existence and uniqueness theory of ordinary differential equations in Banach space because the coefficients a_l and b_l are not bounded; some kind of limiting process in which the infinite system is approximated by a sequence of more tractable equations has to be used. The method we shall use here follows earlier work on infinite systems of equations of this kind (Reuter & Ledermann 1953; McLeod 1962, Ball et al. 1986 etc.) in which the infinite system is approximated by an auxiliary finite system with only n non-zero dependent variables, where n can take any positive integral value. The approximating system we shall use is

$$\frac{dc_l^{(n)}(t)}{dt} = J_{l-1}^{(n)}(t) - J_l^{(n)}(t) \qquad (l = 2, 3, \ldots, n), \tag{6.1}$$

$$c_l^{(n)}(t) = 0 \qquad (l = n+1, n+2, \ldots), \tag{6.2}$$

$$J_l^{(n)}(t) = a_l c_1^{(n)}(t) c_l^{(n)}(t) - b_{l+1} c_{l+1}^{(n)}(t) \quad (l = 1, 2, 3, \ldots, n), \tag{6.3}$$

$$\left.\begin{aligned} \frac{dc_1^{(n)}(t)}{dt} &= 0 && \text{(case A: constant } c_1) \\ \frac{dc_1^{(n)}(t)}{dt} &= -J_1^{(n)}(t) - \sum_{l=1}^{n} J_l^{(n)}(t) && \text{(case B: constant } \rho) \end{aligned}\right\}, \tag{6.4}$$

with the initial conditions

$$c_l^{(n)}(0) = C_l \quad (l = 1, \ldots, n), \tag{6.5}$$

where n is an arbitrary positive integer. The non-negative constants $C_1, C_2, \ldots$ are independent of n and correspond to a finite total density, denoted by ρ:

$$\rho := \sum_1^{\infty} l C_l < \infty. \tag{6.6}$$

This auxiliary system of equations is similar to the one used in Ball et al. (1986), but with the difference that the method used there is equivalent to setting $J_n = 0$, whereas here we set $c_{n+1} = 0$. The method used here gives a little more information about the values of the c_l variables and so enables us to apply a maximum principle to these variables (see Eq. (7.8) below).

Lemma 2.

(i) *For each positive integer n the system of equations* (6.1–6) *has a unique continuous solution* $c_l^{(n)}(t)$ $(l = 1, 2, \ldots; t \in [0, \infty))$.

(ii) *This solution is non-negative*

$$c_l^{(n)}(t) \geqq 0 \quad (l=1,2,\ldots). \tag{6.7}$$

(iii) *The density at time t has an upper bound independent of n, given by*

$$\sum_1^n l c_l^{(n)}(t) \leqq \left\{\begin{matrix} \rho \exp(2AC_1 t) & \text{(case A: constant } c_1) \\ \rho & \text{(case B: constant } \rho\ ) \end{matrix}\right\}. \tag{6.8}$$

(The inequality (6.8A) and its relevance to this work were pointed out to me by J. M. Ball (1988)).

(iv) *If the initial data $C_1, C_2, \ldots$ have a finite second moment*

$$\sigma := \sum_1^\infty l^2 C_l < \infty, \tag{6.9}$$

then the second moment at time t has an upper bound independent of n, given by

$$\sum_1^n l^2 c_l^{(n)}(t) \leqq \left\{\begin{matrix} \sigma \exp(4AC_1 t) & \text{(case A: constant } c_1) \\ \sigma \exp(2A\rho t) & \text{(case B: constant } \rho\ ) \end{matrix}\right\}. \tag{6.10}$$

(v) *If (6.9) holds then there exists an increasing sequence of positive integers $n_1, n_2, \ldots$ such that as n tends to ∞ through these values the solutions to the approximating system of equations converge to the unique non-negative solution $c_l(t)$ of the full system of kinetic equations (2.1–3) with initial conditions $c_l(0) = C_l$ $(l=1,2,\ldots)$:*

$$\lim_{k\to\infty} c_l^{(n_k)}(t) = c_l(t) \quad (l=1,2,\ldots; 0 \leqq t < \infty), \tag{6.11}$$

the convergence being, for each fixed l, uniform on compact intervals of the positive real t-axis.

Proof of Lemma 2. For parts (i) and (ii) the method of proof is just the same as in Lemma 2.1 of Ball et al. (1986).

For part (iii) the method is to calculate the rate of change of the sum we are interested in, using the given differential equations (6.1, 2 and 4), and then to estimate this rate of change using the upper bound

$$J_l^{(n)} \leqq A l^\alpha c_1^{(n)} c_l^{(n)} \leqq A l c_1^{(n)} c_l^{(n)} \quad (l=1,2,\ldots,n), \tag{6.12}$$

which follows from (6.3), (2.7) and (6.7), and the lower bound

$$J_n^{(n)} \geqq 0, \tag{6.13}$$

which follows from (6.3), (6.2) and (6.7). Thus, in case A we have (omitting the superscripts (n) for easier reading)

$$\begin{aligned} (d/dt)\sum_1^n l c_l(t) &= \sum_2^n l(J_{l-1} - J_l) \quad \text{by (6.1)} \\ &= 2J_1 + J_2 + J_3 + \cdots + J_{n-1} - nJ_n \\ &\leqq 2Ac_1(t) \sum_1^n l c_l(t) \quad \text{by (6.12).} \end{aligned} \tag{6.14}$$

From (6.4A) and (6.5) we know that $c_1(t) = C_1$ for all $t \geqq 0$; putting this value for $c_1(t)$ into (6.14) we obtain a differential inequality for $\sum lc_l(t)$. Dividing both sides by $\sum lc_l(t)$, integrating from 0 to t, and noting that (because of (6.5) and (6.6)) the initial condition satisfies $\sum_1^n lc_l(0) \leqq \rho$, we obtain (6.8A).

For case B, the corresponding calculation, using (6.4B), gives

$$\begin{aligned}(d/dt)\sum_1^n lc_l(t) &= \sum_2^n l(J_{l-1} - J_l) - J_1 - \sum_1^n J_l \\ &= -(n+1)J_n \\ &\leqq 0 \quad \text{by (6.13).}\end{aligned} \tag{6.15}$$

Solving this differential inequality, with initial condition satisfying $\sum_1^n lc_l(0) \leqq \rho$ as before, we obtain (6.8B).

The method for proving part (iv) of the lemma is very similar. In case A we have

$$\begin{aligned}(d/dt)\sum_1^n l^2 c_l(t) &= \sum_2^n l^2(J_{l-1} - J_l) \\ &= 4J_1 + 5J_2 + 7J_3 + \cdots + (2n-1)J_{n-1} - n^2 J_n \\ &\leqq 4Ac_1(t)\sum_1^n l^2 c_l(t) \quad \text{by (6.12 and 13)}\end{aligned} \tag{6.16}$$

with the initial condition $\sum_1^n l^2 c_l(0) = \sum_1^n l^2 C_l \leqq \sigma$, from which (recalling that $c_1(t)$ is equal to the constant C_1), we obtain (6.10A). In case B the corresponding calculation gives

$$\begin{aligned}(d/dt)\sum_1^n l^2 c_l(t) &= 2J_1 + 4J_2 + 6J_3 + \cdots + (2n-2)J_{n-1} - (n^2+1)J_n \\ &\leqq 2Ac_1(t)\sum_1^n l^2 c_l(t).\end{aligned} \tag{6.17}$$

From (6.8B) and (6.7), we have $c_1(t) \leqq \rho$. Substituting this bound into (6.17) and then solving the differential inequality, we obtain (6.10B).

To prove part (v) we apply the methods used in Ball et al. (1986). For each l, inequalities (6.7) and (6.8) and the constitutive relation (6.3) show that the right-hand sides of the differential equations (6.1) and (6.4) are uniformly bounded as $n \to \infty$. The sequence of functions $c_l^{(n)}(t)$ $(n = 1, 2, \ldots)$ is therefore equicontinuous, and so we can apply Ascoli's theorem together with the "diagonal" argument described by McLeod (1962) to show that it has a sub-sequence converging uniformly to a solution of the full system of differential equations. To do this, consider first case A. Let T be any positive number. Ascoli's theorem shows that there is a sequence of integers $S_2 \subset \{1, 2, 3, \ldots\}$ such that the sequence of functions $c_2^{(n)}(t)$ $(n \in S_2)$ converges uniformly on the interval $[0, T]$ of the real t-axis to a continuous function $c_2(t)$; a second application of Ascoli's theorem shows that there is a sub-sequence $S_3 \subset S_2$ such that $c_3^{(n)}(t)$ $(n \in S_3)$ also converges uniformly to a continuous function c_3; a third application shows that there is a $S_4 \subset S_3$ such that $c_4^{(n)}(t)$ $(n \in S_4)$ also converges, and so on. Then we can take n_k in (6.11) to be the k^{th} member of S_{k+1}, so that (6.11) gives a continuous function $c_l(t)$ for every l. By the constitutive relations (6.3) and (2.2), the sequence of functions $J_l^{(n_k)}(t)$ $(k = 1, 2, \ldots)$ also converges as $k \to \infty$ to a continuous function $J_l(t)$, uniformly on $[0, T]$, for each value of l. Integrating both sides of (6.1) from 0 to T, taking the limit $n \to \infty$ on both sides of the equation, setting $T = t$ and finally differentiating with respect to t, we conclude that the functions $c_l(t)$ defined by (6.11) do satisfy the infinite system of differential equations (2.1–3A).

In case B, the method of constructing the continuous functions $c_l(t)$ is the same except that we start with c_1 rather than c_2. The method of proving that these functions satisfy the differential equations is also the same in the case of $c_2, c_3, \ldots$. In the case of the differential equation for $c_1(t)$ we also need to show that as $n \to \infty$ the sum of the series in (6.4B) converges to the sum of the series in (2.3B) uniformly on $[0, T]$. Now we know from (6.7), (6.8B) and (6.10B) that

$$\left.\begin{cases} 0 \leqq c_1^{(n)}(t) \leqq \rho & \\ 0 \leqq c_l^{(n)}(t) \leqq \sigma \exp(2A\rho t)/l^2 & (l = 2, 3, \ldots) \end{cases}\right\}, \tag{6.18}$$

and hence, from (6.3) and (2.7), that

$$J_l^{(n)}(t) \leqq A\rho\sigma \exp(2A\rho t)/l^{2-\alpha} \quad (l = 2, 3, \ldots), \tag{6.19}$$

and (from (2.12)) that

$$J_l^{(n)}(t) \geqq -Az_s \exp(G')\sigma \exp(2A\rho t)/l^{2-\alpha} \quad (l = 2, 3, \ldots). \tag{6.20}$$

Thus we have, for all t in $[0, T]$,

$$|J_l^{(n)}(t)| \leqq K(T)/l^{2-\alpha} \quad (t \in [0, T]) \quad (l = 2, 3, \ldots), \tag{6.21}$$

where $K(T) = \text{const.} \exp(2A\rho T)$. Since the series $\sum_1^\infty 1/l^{2-\alpha}$ converges we can, given any small positive number ε, choose L large enough to make $\sum_{L+1}^\infty |J_l^{(n)}(t) - J_l(t)| < \varepsilon/2$ for all $t \in [0, T]$, and then (by the uniform convergence in Ascoli's theorem) choose n large enough to make $\sum_1^L |J_l^{(n)}(t) - J_l(t)| < \varepsilon/2$ for all $t \in [0, T]$; so the sum of the infinite series in (6.4B) converges as $n \to \infty$, uniformly on $[0, T]$, to the sum of the infinite series in (2.3B). Then at last we can, as before, integrate both sides of (6.4B) from 0 to T, take the limit $n \to \infty$ on both sides, and differentiate again (using the continuity of the functions $J_l(t)$ and the uniformity of the convergence as $n \to \infty$) to show that the function $c_1(t)$ defined by (6.11) satisfies Eq. (2.3B).

It remains to show that the solution of (2.1–3) constructed in this way is unique. For case B, a proof is given in Theorem 3.6 of Ball et al. (1986). For case A the following version of their argument applies. Let c_l and c_l' be any two solutions of the full Becker–Döring system (2.1–3A) with the same initial conditions satisfying (4.2). Define

$$x_l(t) = c_l(t) - c_l'(t) \quad (l = 1, 2, \ldots). \tag{6.22}$$

Let N be any positive integer and define the function sgn by

$$\operatorname{sgn}(x) := \begin{Bmatrix} +1 & \text{if} & x>0 \\ 0 & \text{if} & x=0 \\ -1 & \text{if} & x<0 \end{Bmatrix}, \tag{6.23}$$

so that $d|x|/dt = \operatorname{sgn}(x)dx/dt$ a.e.. Then we have from (2.1–2),

$$\begin{aligned}(d/dt)\sum_2^N |x_r| &= \sum_2^N \operatorname{sgn}(x_r)[a_{r-1}c_1x_{r-1} - (a_rc_1 + b_r)x_r + b_{r+1}x_{r+1}] \\ &= \sum_2^N [a_rc_1 \operatorname{sgn}(x_{r+1}) - (a_rc_1 + b_r)\operatorname{sgn}(x_r) + b_r \operatorname{sgn}(x_{r-1})]x_r \\ &\quad - a_Nc_1 \operatorname{sgn}(x_{N+1})x_N + b_{N+1}x_{N+1}\operatorname{sgn}(x_N) \\ &\leqq a_Nc_1|x_N| + b_{N+1}|x_{N+1}|,\end{aligned} \tag{6.24}$$

since the summand is always non-positive, regardless of the signs of x_{r-1}, x_r and x_{r+1}. From (6.7), (6.8) and (6.11) we have

$$c_l(t) \leqq l^{-1}\rho\exp(2Ac_1(0)t), \tag{6.25}$$

so that

$$|x_N| \leqq 2N^{-1}\rho\exp(2Ac_1(0)t), \quad |x_{N+1}| \leqq 2(N+1)^{-1}\rho\exp(2Ac_1(0)t). \tag{6.26}$$

Substituting this into (6.24), integrating from 0 to t with the initial conditions $x_r(0) = 0$ $(r = 1, 2, \dots)$, and then taking the limit $N \to \infty$, we obtain

$$\sum_{r=2}^{\infty} |x_r(t)| \leqq 0. \tag{6.27}$$

From this it follows that all the $x_r(t)$ are 0 for all t. So the two solutions c_l and c_l' are in the fact identical, and uniqueness is proved.

7. The Becker–Döring Steady State as an Upper Bound

Now we can prove the first result in Theorem 1: Eq. (4.6). We prove that if Eq. (4.6) (repeated here for convenience)

$$0 \leqq c_l(t) \leqq f_l(z) \quad (l = 1, 2, \dots) \tag{7.1}$$

holds for $t = 0$, then it holds for all $t \geqq 0$.

Proof. We first prove the inequalities (7.1) for the auxiliary n-dimensional system of equations considered in Lemma 2 (Eqns. 6.1–4) and then take the limit $n \to \infty$ using (6.11). The first step is to show that (7.1) is true of the modified version of these equations obtained by subtracting a term $\varepsilon c_l^{(n)}(t)$, where ε is a small positive constant, from the right side of (6.1). This modification does not affect the proofs and results in Lemma 2. In particular, (6.7) still holds, and so the left-hand part of (7.1) is proved for the modified system. To prove the right-hand part of (7.1), choose any positive integer n, let $c_l^{(n)}(t)$ be the solution of the modified version of the equations, and suppose the right-hand inequality in (7.1) to be untrue for some particular positive value or values of l and t. We shall show that this hypothesis leads to a contradiction.

Supposing the hypothesis to be true, let T be the infimum of the values of t for which the right side of (7.1) fails, so that $T \geqq 0$ and (by continuity of the functions c_l)

$$0 \leqq c_l^{(n)}(T) \leqq f_l(z) \quad (l=1,\ldots,n), \tag{7.2}$$

but there is at least one value of l, call it L, and a T^+ greater than T such that

$$\left.\begin{array}{l} c_L^{(n)}(T) = f_L(z) \\ c_L^{(n)}(t) > f_L(z) \quad (T < t < T^+) \end{array}\right\}. \tag{7.3}$$

It is clear from the definition of a derivative that (7.3) implies

$$\frac{d}{dt} c_L^{(n)}(T) \geqq 0. \tag{7.4}$$

Consider first the case $L=1$. For version A of the equations, $c_1^{(n)}(t)$ does not change in time, so that (7.3) contradicts (7.1). For version B (again omitting the superscripts (n) for easier reading), we have from (6.4B and 6.3)

$$\begin{aligned} \frac{dc_1}{dt}(T) &= -a_1 c_1(T)^2 + b_2 c_2(T) - \sum_{l=1}^{n} [a_l c_1(T) c_l(T) - b_{l+1} c_{l+1}(T)] \\ &= -a_1 z^2 + b_2 c_2(T) - a_1 z^2 + \sum_{l=2}^{n} (b_l - a_l z) c_l(T), \end{aligned} \tag{7.5}$$

since $c_1(T) = f_1(z) = z$ by (7.3a) and (4.4), and $c_{n+1}(T) = 0$ by (6.2). Now the coefficient of c_l is, by (2.9) and (4.13), non-negative for $l \leqq l^*$ but negative for larger l, and so we obtain, using (7.2),

$$\frac{dc_1}{dt}(T) \leqq -a_1 z^2 + b_2 f_2 - a_1 z^2 + \sum_{l=2}^{l^{**}} (b_l - a_l z) f_l, \tag{7.6}$$

where l^{**} means the smaller of l^* and n. Rearranging, we obtain

$$\begin{aligned} \frac{dc_1}{dt}(T) &\leqq -a_1 z^2 + b_2 f_2 - \sum_{l=1}^{l^{**}-1} (a_l z f_l - b_{l+1} f_{l+1}) - a_{l^{**}} z f_{l^{**}} \\ &= -l^{**} J(z) - a_{l^{**}} z f_{l^{**}} \end{aligned} \tag{7.7}$$

by (4.4) and (5.6). Since both $J(z)$ and $f_{l^{**}}$ are positive (by (5.8) and (5.9)), we have a contradiction with (7.4).

Now consider the case $L > 1$. The modified version of (6.1), with (6.3), gives

$$\begin{aligned} \frac{dc_L}{dt}(T) &= a_{L-1} c_1(T) c_{L-1}(T) - [b_L + a_L c_1(T)] c_L(T) + b_{L+1} c_{L+1}(T) - \varepsilon c_L(T) \\ &\leqq a_{L-1} c_1(T) f_{L-1}(z) - [b_L + a_L c_1(T)] f_L(z) + b_{L+1} f_{L+1}(z) - \varepsilon c_L(T) \end{aligned} \tag{7.8}$$

by (7.2 and 3); for the case where $L=n$ we have also used (6.2) in the form $c_{n+1}^{(n)}(T) = 0$. Subtracting the left side of (4.3) (with $l=L$) from the right side of

(7.8), we obtain

$$\frac{dc_L}{dt}(T) \leqq (a_{L-1} f_{L-1} - a_L f_L)(c_1(T) - z) - \varepsilon c_L(T). \tag{7.9}$$

By Lemma 1 (Eq. (5.1)), the first quantity in brackets on the right is positive, and by (7.2) and (4.4) the second is non-positive; so we have a contradiction with (7.4). Thus, for the system of equations obtained by subtracting $\varepsilon c_l^{(n)}(T)$ from each equation in (6.1), our hypothesis that the condition (7.1) is violated for some positive t leads to a contradiction in all the possible cases, and we conclude that (7.1) is true for this system of equations.

To complete the proof that (7.1) is true of the finite system of equations (6.1–5) we take the limit $\varepsilon \to 0$ and use the fact that the solutions of a differential equation depend continuously on parameters in the equation (Hartman 1964, pp. 93–94). Finally we extend the result to the infinite system of equations (2.1–3) by applying Eq. (6.11).

8. Proof of Theorem 1: A Bound on the Number of Large Clusters

Now we can complete the proof of Theorem 1. To prove the upper bound (4.7) on $M_0(t)$, the number of super-critical clusters, as defined in (4.9), we use (2.1) to obtain

$$\begin{aligned} M_0(t) - M_0(0) &= \lim_{L\to\infty} \sum_{l^*+1}^{L} \int_0^t (J_{l-1}(u) - J_l(u))\,du \\ &= \lim_{L\to\infty} \int_0^t (J_{l^*}(u) - J_L(u))\,du \\ &= \int_0^t J_{l^*}(u)\,du \end{aligned} \tag{8.1}$$

because of the uniform upper bound on J_L implied by (6.19). Using (2.2) to evaluate J_{l^*} we obtain

$$\begin{aligned} J_{l^*} &= a_{l^*} c_1 c_{l^*} - b_{l^*+1} c_{l^*+1} \\ &\leqq z a_{l^*} f_{l^*} \quad \text{by (4.6) and (4.4)} \\ &\leqq J^* \quad\quad\ \ \text{by (5.3) and (4.12).} \end{aligned} \tag{8.2}$$

Substituting from (8.2) into (8.1), we complete the proof of (4.7).

The proof of (4.8) is analogous. From (4.9) and (2.1) we have

$$\begin{aligned} M_1(t) - M_1(0) &= \lim_{L\to\infty} \sum_{l^*+1}^{L} \int_0^t l(J_{l-1}(u) - J_l(u))\,du \\ &= \lim_{L\to\infty} \int_0^t \left[(l^*+1) J_{l^*}(u) + \sum_{l^*+1}^{L-1} J_l(u) - L J_L(u) \right] du \\ &= \int_0^t \left[(l^*+1) J_{l^*}(u) + \sum_{l^*+1}^{\infty} J_l(u) \right] du, \end{aligned} \tag{8.3}$$

the last line following, by dominated convergence, from the uniform upper bound on $J_l(u)$ implied by (6.19). Differentiating both sides of (8.3), we obtain, since the integrand is continuous (being, because of (6.19), the sum of a uniformly convergent series of continuous functions),

$$\begin{aligned}\frac{dM_1}{dt}(t) &= (l^*+1)J_{l^*}(t) + \sum_{l=l^*+1}^{\infty} J_l(t)\\ &\leqq (l^*+1)za_{l^*}f_{l^*} + \sum_{l=l^*+1}^{\infty} za_l c_l(t) \quad \text{by (4.6) and (4.4)}\\ &\leqq (l^*+1)J^* + zAM_0^{1-\alpha}(t)M_1^{\alpha}(t) \qquad (8.4)\end{aligned}$$

by (2.7) and Hölder's inequality (Hardy et al 1959).

To solve the differential inequality (8.4) it is convenient to introduce the scaled variables

$$\mu_r(t) := M_r(t)/t_0 J^* \quad (r = 0, 1), \qquad (8.5)$$

$$\tau := t/t_0, \qquad (8.6)$$

where t_0 is defined in (4.11). In this notation, (8.4) becomes

$$\begin{aligned} d\mu_1/d\tau &\leqq (l^*+1)(1+\mu_0{}^{1-\alpha}\mu_1{}^{\alpha})\\ &\leqq (l^*+1)(1+\mu_0)^{1-\alpha}(1+\mu_1)^{\alpha} \qquad (8.7)\end{aligned}$$

by Hölder's inequality. Using the integrating factor $(1+\mu_1)^{-\alpha}$, we obtain

$$\frac{d}{d\tau}(1+\mu_1)^{1-\alpha} \leqq (l^*+1)(1-\alpha)(1+\mu_0)^{1-\alpha}, \qquad (8.8)$$

and hence

$$(1+\mu_1(\tau))^{1-\alpha} \leqq (1+\mu_1(0))^{1-\alpha} + (l^*+1)(1-\alpha)\int_0^{\tau}(1+\mu_0(\tau'))^{1-\alpha}d\tau'. \qquad (8.9)$$

Substituting from (4.7), which in the present notation takes the form $\mu_0(\tau) \leqq \mu_0(0) + \tau$, and carrying out the integration, we obtain

$$(1+\mu_1(\tau))^{1-\alpha} \leqq (1+\mu_1(0))^{1-\alpha} + [(l^*+1)/\beta][(1+\mu_0(0)+\tau)^{2-\alpha} - (1+\mu_0(0))^{2-\alpha}] \qquad (8.10)$$

where $\beta = (2-\alpha)/(1-\alpha)$ as defined in (4.10). It follows, by omitting the negative term on the right-hand side and then applying Hölder's inequality once again, that

$$(1+\mu_1(\tau))^{1-\alpha} < 2^{\alpha}[1+\mu_1(0) + [(l^*+1)/\beta]^{1/(1-\alpha)}(1+\mu_0(0)+\tau)^{\beta}]^{1-\alpha}. \qquad (8.11)$$

Solving for $\mu_1(\tau)$ and returning to the original notation with the help of (8.5) and (8.6) we obtain (4.8), completing the proof of Theorem 1.

9. Proof of Theorem 2

For part (i), that l^* is not exponentially large, we use (4.13) and the right side of (2.12) to show that

$$z \leqq b_{l^*}/a_{l^*} < z_s \exp(G' l^{*-\gamma'}). \qquad (9.1)$$

Rearranging, we obtain

$$l^* < [G'^{-1}\log(z/z_s)]^{-1/\gamma'}. \tag{9.2}$$

So l^* grows no faster than $[\log(z/z_s)]^{-1/\gamma'}$ as $z \searrow z_s$ and is therefore at most algebraically large.

For the other three parts of the theorem, the following lemma will be useful. *Let n, m be any integers with $1 \leqq m \leqq n$. Then we have*

$$\begin{aligned}
Q_n/Q_m &= (a_m/a_n) \prod_{r=m+1}^{n} (a_r/b_r) && \text{by (2.6)}\\
&\leqq (a_m/a_n) z_s^{m-n} \exp\left[-\sum_{r=m+1}^{n} Gr^{-\gamma}\right] && \text{by (2.12)}\\
&\leqq (a_m/a_n) z_s^{m-n} \exp\left[-\int_m^n Gr^{-\gamma} dr\right], && \text{since } \gamma < 1 \text{ by (2.11)}\\
&= (a_m/a_n) z_s^{m-n} \exp[-G(n^{1-\gamma} - m^{1-\gamma})/(1-\gamma)]. && (9.3)
\end{aligned}$$

We first use this lemma to prove part (ii) of the theorem, that all moments of the equilibrium cluster size distribution converge when $z = z_s$. Setting $m = 1$ in (9.3), and remembering that $Q_1 = 1$ by (2.5), we can use the lemma to estimate the large-N behaviour of the sum

$$\begin{aligned}
\sum_{l=1}^{N} l^n Q_l z_s^l &\leqq \sum_{l=1}^{N} l^n z_s (a_1/a_l) \exp[-G(l^{1-\gamma} - 1)/(1-\gamma)] \quad \text{by (9.3)}\\
&< 2z_s(a_1/A') \int_1^N l^n \exp[-G(l^{1-\gamma} - 1)/(1-\gamma)]\,dl, \qquad (9.4)
\end{aligned}$$

since $1/a_l \leqq 1/A'$ by (2.7), $\gamma < 1$ by (2.11), and the integrand comprises at most 2 monotonic sections. The integral converges as $N \to \infty$, and hence the sum does so too, which proves part (ii) of the theorem.

For part (iii) it is enough to show that $J^*(z)$ is exponentially small; for $J(z)$ is even smaller, the sum for $1/J(z)$ in Eq. (4.16) being larger than its largest term $1/J^*(z)$. Setting $m = 1$, $n = l$ in (9.3) and again using $Q_1 = 1$, we have

$$\begin{aligned}
a_l Q_l z^l &< a_1 z_s (z/z_s)^l \exp[-G(l^{1-\gamma} - 1)/(1-\gamma)]\\
&= a_1 z_s \exp[l \log(z/z_s) - G(l^{1-\gamma} - 1)/(1-\gamma)]. \qquad (9.5)
\end{aligned}$$

The minimum value of the right-hand side, achieved when $l = [G/\log(z/z_s)]^{1/\gamma}$, is

$$a_1 z_s \exp\left[G/(1-\gamma) - \frac{\gamma}{1-\gamma} G^{1/\gamma} [\log(z/z_s)]^{-(1-\gamma)/\gamma}\right].$$

Since we are considering the limit $z \searrow z_s$, we may take z close enough to z_s to ensure that $[G/\log(z/z_s)]^{1/\gamma} \geqq 1\frac{1}{2}$. Then the second derivative of the exponent in (9.5), $G\gamma l^{-\gamma-1}$, is bounded above by $G\gamma$ for all l in the interval defined by

$$[G/\log(z/z_s)]^{1/\gamma} - \tfrac{1}{2} \leqq l \leqq [G/\log(z/z_s)]^{1/\gamma} + \tfrac{1}{2},$$

and so (by Taylor's theorem) the exponent itself exceeds its minimum value by at most $\frac{1}{2}G\gamma(\frac{1}{2})^2$ for all l in this interval. There is an integer value of l within this interval, and for this value of l the inequality (9.5) therefore implies

$$a_l Q_l z^l < a_1 z_s \exp\left[G/(1-\gamma) - \frac{\gamma}{1-\gamma} G^{1/\gamma}[\log(z/z_s)]^{-(1-\gamma)/\gamma} + \tfrac{1}{2}G\gamma(\tfrac{1}{2})^2 \right]. \tag{9.6}$$

Since l^* is by definition the value of l minimizing the left side of (9.6), it follows that (9.6) is also true with l replaced by l^*, that is when the left-hand side is (by the definition (4.15)) equal to $J^*(z)$. Since $\gamma < 1$ by (2.11) and $\log(z/z_s) \leqq (z - z_s)/z_s$, the right-hand side is exponentially small and so part (iii) of the theorem is proved.

For part (iv) we use the definitions (4.15) and (4.17), and then (9.3) with $m = l^*$, to write

$$\begin{aligned} z\rho^*(z)/J^*(z) &= \sum_{n=l^*+1}^{\infty} nQ_n z_s^{\,n}/a_{l^*}Q_{l^*}z^{l^*} \\ &\leqq (z_s/z)^{l^*} \sum_{n=l^*+1}^{\infty} (n/a_n)\exp[-G(n^{1-\gamma} - (l^*)^{1-\gamma})/(1-\gamma)] \\ &< (2/A') \int_{l^*}^{\infty} n\exp[-G(n^{1-\gamma} - (l^*)^{1-\gamma})/(1-\gamma)]\,dn, \end{aligned} \tag{9.7}$$

since $z > z_s$ is a condition of the theorem, $a_n \geqq A'$ by (2.7), and the integrand comprises at most 2 monotonic sections. Changing the variable of integration to

$$x := G(n^{1-\gamma} - (l^*)^{1-\gamma})/(1-\gamma),$$

we obtain

$$\begin{aligned} \rho^*(z)/J^*(z) &< (2/A'G) \int_0^{\infty} [(l^*)^{1-\gamma} + (1-\gamma)x/G]^{(1+\gamma)/(1-\gamma)} e^{-x}\,dx \\ &< (2/A'G)\,\mathrm{Max}\,\{l^{*1+\gamma}, [(1-\gamma)/G]^{(1+\gamma)/(1-\gamma)}\} \int_0^{\infty} [1+x]^{(1+\gamma)/(1-\gamma)} e^{-x}\,dx. \end{aligned} \tag{9.8}$$

So, as $z \searrow z_s$, the ratio $\rho^*(z)/J^*(z)$ grows no faster than a power of l^*, and therefore, by part (i) of the theorem, it is at most algebraically large. This completes the proof of Theorem 2.

10. Proof of Theorem 3

For part (i), that $M_1(t)$ is exponentially small if t is at most algebraically large, we use the bound on $M_1(t)$ given in (4.8). On the right there are various quantities to be bounded. The first is $M_1(0)$; this is exponentially small because it is equal (by (4.17 and 18)) to $\rho^*(z)$ which is exponentially small by part (iv) of Theorem 2. By part (iii) of Theorem 2, the factor J^* is exponentially small, and by part (i) the factor involving l^* is at most algebraically large. By (4.17 and 18) we have here $M_0(0) < \rho^*(z)$, and hence by part (iv) of Theorem 2 the factor in (4.8) involving $M_0(0)$ is at most algebraically large. So part (i) is proved.

For part (ii) of the theorem, that $M_1(t) \to \infty$ for large t, the proof is longer. Let m, n be any integers satisfying $l^* < m \leqq n$. We shall first prove the following preliminary results:

(a) $$M_1(t) \geqq \sum_{l^*+1}^{m} l c_l(t); \tag{10.1}$$

(b) $$c_l(t) \geqq c_l^{(n)}(t), \tag{10.2}$$

with $c_l^{(n)}(t)$ the solution of the finite approximating system used in Lemma 2;

(c) $$\lim_{t\to\infty} c_l^{(n)}(t) = f_l^{(n)}(c_1), \tag{10.3}$$

where $f_l^{(n)}(z)$ is defined as in (5.8–9) but with the sums going from 1 to n instead of 1 to ∞ (see Eq. (10.18) below);

(d) $$\lim_{n\to\infty} f_l^{(n)}(z) = f_l(z); \tag{10.4}$$

(e) $$f_l(z) \geqq J(z)/Al^\alpha z. \tag{10.5}$$

By combining the results (10.1–3) we find that

$$\liminf_{t\to\infty} M_1(t) \geqq \sum_{l^*+1}^{m} f_l^{(n)}(c_1). \tag{10.6}$$

Taking the limit $n \to \infty$ on both sides, and using (10.4 and 5) with z replaced by c_1, we find that

$$\liminf_{t\to\infty} M_1(t) \geqq \sum_{l^*+1}^{m} J(c_1)/Al^\alpha c_1, \tag{10.7}$$

and since the right side increases without bound as $m \to \infty$, part (ii) of Theorem 3 follows.

It remains to prove the results (10.1 to 5). Equation (10.1) comes from the definition (4.9) of $M_1(t)$ and the non-negativity of solutions. For (10.2), we define

$$y_l(t) := c_l^{(n+1)}(t) - c_l^{(n)}(t) \quad (l = 1, 2, \ldots, n+1) \tag{10.8}$$

with the aim of showing that $y_l(t)$ is non-negative for all $l \leqq n+1$. By (6.1–3) the quantities $y_l(t)$ satisfy the equations

$$dy_l/dt = a_{l-1}c_1 y_{l-1} - (a_l c_1 + b_l)y_l + b_{l+1}y_{l+1} \quad (l = 2, 3, \ldots, n), \tag{10.9}$$

but

$$\begin{aligned} dy_{n+1}/dt &= a_n c_1 c_n^{(n+1)} - (a_n c_1 + b_n)y_{n+1} \quad \text{since} \quad c_{n+1}^{(n)} = 0 \\ &\geqq a_n c_1 y_n - (a_n c_1 + b_n) y_{n+1} \quad \text{by (10.8).} \end{aligned} \tag{10.10}$$

The end condition is

$$y_1(t) = 0 \quad (\text{all } t \geqq 0), \tag{10.11}$$

and the initial conditions satisfy

$$y_l(0) = 0 \quad (l = 1, 2, \ldots, n), \tag{10.12}$$

$$y_{n+1}(0) = c_n^{(n+1)}(0) \geqq 0. \tag{10.13}$$

By an argument similar to the one used in proving the right side of (7.1), we can now show that

$$y_l(t) \geqq 0 \quad (l = 2, 3, \ldots, n+1 \text{ and all } t \geqq 0), \tag{10.14}$$

and hence (by (10.8)) that $c_l^{(n)}(t)$ increases monotonically with n at fixed l and t. Using the formula (6.11) for $c_l(t)$ we deduce (10.2).

To prove (10.3) we again start from the finite approximating system (6.1–4). We define the Lyapunov function

$$V(t) = \sum_{l=1}^{n} [J_l^{(n)}]^2 / 2a_l Q_l c_1^{\,l+1} \tag{10.15}$$

which, by (6.2–4) satisfies

$$\begin{aligned} dV/dt &= \sum_1^n (J_l^{(n)}/a_l Q_l c_1^{\,l+1})[a_l c_1 dc_l^{(n)}/dt - b_{l+1} dc_{l+1}^{(n)}/dt] \\ &= \sum_2^n [(J_l^{(n)}/a_l Q_l c_1^{\,l+1}) a_l c_1 - (J_{l-1}^{(n)}/a_{l-1} Q_{l-1} c_1^{\,l}) b_l] dc_l^{(n)}/dt \\ &= -\sum_2^n (1/Q_l c_1^{\,l})(J_{l-1}^{(n)} - J_l^{(n)})^2 \quad \text{by (2.6) and (6.1).} \end{aligned} \tag{10.16}$$

This shows that $V(t)$ is non-increasing, and since it is also non-negative it tends, as $t \to \infty$, to a limit at which $J_{l-1} = J_l$ $(l = 2, \ldots, n)$. Proceeding as in the argument based on (5.6) we obtain (10.3), with

$$f_l^{(n)}(z) = Q_l z^l \sum_{r=l}^{n} \frac{1}{a_r Q_r z^{r+1}} \left[\sum_{l=1}^{n} \frac{1}{a_l Q_l z^{l+1}} \right]^{-1}. \tag{10.17}$$

To prove (10.4), we need only take the limit $n \to \infty$ in the formula (10.17) and compare with the formulas (5.8 and 9) for $f_l(z)$.

Finally, to prove (10.5) we use (5.6) and (2.7), obtaining

$$J(z) \leqq A l^\alpha f_l(z) z, \tag{10.18}$$

which is equivalent to (10.5).

11. Proof of Theorem 4

For part (i) we use Theorem 1 to obtain upper and lower bounds on $c_l(t)$. Condition (4.1) for the validity of Theorem 1 is satisfied because of (4.18) and (5.5), and condition (4.2) because of (4.14). Some of the bounds we need are given by (4.6):

$$0 \leqq c_l(t) \leqq f_l(z) \quad (l = 1, 2, \ldots). \tag{11.1}$$

To obtain the rest of them we use the fact, proved in Ball et al. (1986), that $\sum_1^\infty l c_l(t)$ is independent of t. By (4.9) this gives

$$\sum_{l=1}^{l^*} l[c_l(0) - c_l(t)] = M_1(t) - M_1(0). \tag{11.2}$$

Given any fixed value of l, the summation in (11.2) will eventually include a term $l[c_l(0)-c_l(t)]$, since l^* increases without bound as $z \searrow z_s$. By (4.18) and (4.6), every term of the sum in (11.2) is non-negative; so the term corresponding to the given value of l cannot exceed the right-hand side. But we have already seen, in the proof of part (i) of Theorem 3, that the right-hand side is exponentially small; so we conclude, for every fixed value of l, that $c_l(0)-c_l(t)$ is non-negative and exponentially small. This completes the proof of part (i) of Theorem 4.

For part (ii) we use the result of Ball and Carr (1988) that

$$\lim_{t\to\infty} c_l(t) = Q_l z_s{}^l, \tag{11.3}$$

so that, by (4.18),

$$\lim_{t\to\infty} [c_l(0)-c_l(t)] = f_l(z) - Q_l z_s{}^l \quad (l \leqq l^*). \tag{11.4}$$

Now, we know from parts (iii) and (v) of Lemma 1 that $f_l(z)/z$ increases monotonically with z at fixed l and has the limit $Q_l z_s{}^l/z_s$ when $z \searrow z_s$. So we have (since $z > z_s$)

$$f_l(z) - Q_l z_s{}^l \geqq z Q_l z_s{}^l/z_s - Q_l z_s{}^l = (z-z_s) Q_l z_s{}^l/z_s, \tag{11.5}$$

which is not exponentially small. For any fixed l, we can always make $l^* \geqq l$ by choosing z close enough to z_s; so Eq. (11.4) will apply as we approach the limit $z \searrow z_s$ and hence, by (11.5), the left side of (11.4) is not exponentially small. This completes the proof of Theorem 3.

12. Discussion

The discussion given so far refers to the case of a phase transition in a system of particles, even though the equations of case A do not in fact conserve the total concentration of particles. However, we would also like to have corresponding results for a system such as a ferromagnet in which the order parameter is not conserved. A version of the Becker–Döring equations suitable for the Ising ferromagnet is

$$\frac{dc_l(t)}{dt} = J_{l-1}(t) - J_l(t) \qquad (l = 1, 2, 3, \ldots), \tag{12.1}$$

$$J_l(t) = a_l z_0 c_l(t) - b_{l+1} c_{l+1}(t) \quad (l = 1, 2, 3, \ldots), \tag{12.2}$$

$$J_0(t) = a_0 z_0 - b_1 c_1(t), \tag{12.3}$$

where c_l represents the concentration of clusters of "wrong" spins—i.e. ones that are magnetized in the opposite direction to the majority—and z_0 is a parameter related to the strength of the applied magnetic field. In the equation for J_0 the term $a_0 z_0$ represents the spontaneous appearance of isolated "wrong" spins and the other term represents their spontaneous disappearance.

The system of equations (12.1–3) is equivalent to case A of the original system (2.1–3), under the following change of notation:

Eqs. (12.1–3)	Eqs. (2.1–3)	
c_l	c_{l+1}	$(l=1,2,\dots)$
J_l	J_{l+1}	$(l=0,1,\dots)$
a_l	a_{l+1}	$(l=1,2,\dots)$
b_l	b_{l+1}	$(l=1,2,\dots)$
z_0	c_1	
a_0	$a_1 c_1$	

Thus, all the theorems proved in this paper can be carried over to the system (12.3). The only change of any moment is the factor c_1 in the last line above, which has the effect of introducing a factor c_1 or c_1^{-1} into some of the formulas. This change does not, however, affect the conclusions about metastability drawn in Theorem 3.

To conclude, let us see how far the picture developed in this paper agress with one's usual ideas about the nature of metastability. First, we test it against the three criteria for a metastable state mentioned in the Introduction. (By a metastable state we mean here a set of values for the c_l variables differing by at most an exponentially small amount from the initial values (4.18) used in Theorems 3 and 4.) The three criteria are:

(i) A single thermodynamic phase is present.
(ii) The lifetime of the metastable state is very long.
(iii) The probability of return, once the system has left the metastable state, is very small.

For criterion (i) we need an interpretation of the phrase "a single thermodynamic phase." It is natural to interpret small clusters as belonging to the vapour phase and large ones to the liquid phase. If we draw the line between small and large clusters at the critical size l^* then we can interpret M_1, defined in (5.9), as the density of the liquid phase. According to Theorems 3 and 4, M_1 is exponentially small for the metastable state; thus there is virtually no liquid present and so criterion (i) is satisfied. Moreover, to a very good approximation, the vapour phase can be regarded as being in thermodynamic equilibrium in the sense that the distribution of cluster sizes in the vapour is very close to the equilibrium distribution (2.4), albeit with too large a value of c_1; this follows from the fact that when z is only a little greater than z_s most of the contribution to the sums in (5.8) and (5.9) comes from terms with l not far from l^*, so that Eq. (5.9) implies $f_l(z) \approx Q_l z^l$ for $l \ll l^*$.

The second criterion is taken care of in Theorems 3 and 4, where it is shown that the lifetime is very long.

For the third criterion we can use an argument based on a Lyapunov function. For case A, the Lyapunov function given in (10.15) is appropriate; for case B a suitable Lyapunov function (in physicist's language, the free energy density) is

$$F(c_1, c_2, \dots) := \sum_{r=1}^{\infty} c_r[\log(c_r/Q_r z_s^r) - 1], \tag{12.4}$$

which is shown in Theorem 4.7 of Ball et al. (1986) to be a non-increasing function of time if $c_1(t), c_2(t), \dots$ satisfy the Becker–Döring equations (2.1–3B). For brevity, we give the rest of the argument only for case B. By (11.13) the value of F in the final equilibrium is

$$-\sum_{r=1}^{\infty} Q_r z_s^r, \tag{12.5}$$

whereas its value for the metastable state with cluster concentrations given by (4.18) is

$$\sum_{r=1}^{l^*} f_r[\log(f_r/Q_r z_s^r) - 1], \tag{12.6}$$

which exceeds the final equilibrium value by

$$\sum_{r=1}^{l^*} f_r[-\log(u_r) - 1 + u_r], \tag{12.7}$$

where u_r stands for $Q_r z_s^r / f_r$. Since the summand is non-negative, the sum is bounded below by its first term, which is $z[-\log(z_s/z) - 1 + z_s/z]$ and is not exponentially small, being positive and $O(z - z_s)^2$ as $z \searrow z_s$. This indicates that no return from the final equilibrium to the metastable state is possible, no matter how small we make $z - z_s$. This argument provides a partial verification that criterion (iii) is satisfied. A complete verification is hardly to be expected without going outside the framework provide by the Becker–Döring equations; for it would demand a discussion of the role of fluctuations in the distribution of cluster sizes, while the Becker–Döring approximation is concerned only with the average behaviour of that distribution.

In addition to satisfying these three criteria, we would also like the metastable state to have, in keeping with its name, some stability against perturbations of the cluster size distribution c_l which are not too large. Provided the perturbation does not seriously affect M_1, the number of particles in super-critical clusters, it is plausible that the metastable state will exhibit some form of asymptotic stability—i.e that the perturbed system will return close to its original metastable state in a time which is not exponentially long, and then remain close for a time which is exponentially long—but the results given here are not sufficient to prove it. This insufficiency may be connected with the fact that our results do not say anything about the uniqueness of the metastable state. Our results are, however, sufficient to prove a weaker kind of stability: that for a particular class of perturbations—namely those which do not violate (4.1) and (4.2) and which lead to only exponentially small changes in M_0 and M_1–the perturbed state will also be metastable, in the sense that, despite the perturbation, M_0 and M_1 will remain small for an exponentially long time. It may be possible to improve on this last result, using the method Lyapunov functions as in Theorem 5.7 of Ball et al. (1986), but we shall not enter into such a discussion here.

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