Journal of Statistical Physics, Vol. 89, Nos. 1/2, 1997

The Becker–Döring Equations at Large Times and Their Connection with the LSW Theory of Coarsening

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Received January 3, 1997

A systematic procedure is given for obtaining the asymptotic late-time behavior of the Becker–Döring equations describing the time evolution of a population of clusters of particles. In lowest order of approximation, the distribution of the sizes of the largest clusters satisfies the equations of the Lifshitz–Slyozov–Wagner theory of coarsening.

KEY WORDS: Asymptotics; Becker–Döring equations; cluster kinetics; kinetics of phase transitions; Lifshitz–Slyozov theory; Ostwald ripening.

1. INTRODUCTION

The system of kinetic equations introduced by Becker and Döring in 1935(4) can be used to model a variety of phenomena in the kinetics of phase transitions, including metastability, nucleation, and coarsening. These equations are applicable when the amounts of the two phases are very unequal, so that at each moment the minority phase consists of disconnected islands in a sea of the majority phase; the equations describe the time evolution of the distribution of the sizes of these "islands."

The theory of coarsening (Ostwald ripening) in alloys, developed by Lifshitz and Slyozov(12) and by Wagner,(22) uses a similar description, but the evolution equations are different. It is the purpose of the present paper to demonstrate the connection between these two theories. We shall study the behavior of solutions of the BD equations at very late times, long after

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This paper is dedicated to Bernard Jancovici in celebration of his 65th birthday.

any possible metastable state has broken down, and show by means of a systematic approximation procedure that in lowest approximation the distribution of the large clusters at these late times obeys the equations of the LSW theory.

One result of this work is that the LSW theory is not restricted, as its original derivation might suggest, to cases where the degree of supersaturation is so small that the solute atoms do not form a significant number of dimers, trimers and other small clusters. On the other hand, our derivation does not remove the more serious restriction of the LSW theory, that the degree of superstaturation must be small enough to permit the neglect of the positional correlations of the larger clusters. Some ways of improving on the LSW theory so as to allow for these correlations are reviewed in ref. 19.

2. THE BECKER-DÖRING EQUATIONS

We begin by reviewing the derivation of the BD equations for a density-conserving phase transition, such as de-alloying, and some of the recent mathematical results about them.

The BD equations apply to a non-uniform mixture in which the atoms of one component (the *solute* atoms) are much less numerous than those of the other component (the *solvent* atoms)—at most 20–30% concentration of solute. At each instant, the configuration of the solute atoms is described by grouping them into clusters according to some well-defined criterion (in the case of lattice systems, the usual criterion is to define the clusters as maximal connected sets, with connectedness defined in terms of nearest-neighbor pairs.) By the *size* of a cluster, denoted l, we mean the number of solute atoms in the cluster, and a cluster of size l will be called an l-cluster. A 1-cluster is usually called a *monomer*. Let us define $c_l(t)$ to be the concentration of l-clusters (measured in units where the volume per atom is 1) at time t. The clusters are assumed to be distributed uniformly in space, so that c_l does not depend on a space variable.

To obtain equations for the time evolution of c_l Becker and Döring made the important assumption that only two types of process change the cluster size distribution. One of these processes is for a cluster of any size to combine with a monomer to give a single larger cluster; the other one is its inverse, where a cluster splits into two parts one of which is a monomer. The net rate at which l-clusters are being converted to $(l+1)$-clusters as a result of these two processes will be denoted by J_l (in units of clusters per unit time per unit volume). If J_l is positive, this process tends to decrease c_l, but it is counterbalanced by the interconversion of $(l-1)$-clusters and l clusters, whose net rate is J_{l-1}, and which tends to increase

c_l if this rate is positive. The total rate of change of c_l for any l other than 1 is then obtained as the algebraic sum of the two net rates:

$$\frac{dc_l}{dt} = J_{l-1} - J_l \qquad (l \geqslant 2) \tag{1}$$

For the rate of change of the monomer concentration c_1, a different equation is required because the monomers participate in every process. The interconversion of l- and $(l+1)$-clusters uses up monomers at a rate J_l, except in the case $l = 1$ where monomers are used at a rate $2J_1$ because two monomers participate in each conversion. So the total rate of change of c_1 is

$$\frac{dc_1}{dt} = -2J_1 - \sum_{l=2}^{\infty} J_l \tag{2}$$

To complete the system of equations we need a constitutive relation giving the J_l's in terms of c_l's. This takes the same form as in chemical kinetics. That is to say, we assume that the number of times an l-cluster reacts with a monomer, per unit time per unit volume, is proportional to the densities of l-clusters and of monomers; so this type of process contributes a term $a_l c_1 c_l$ to J_l, where the kinetic coefficient a_l is independent of time. Meanwhile, the process of breaking-up of a $(l+1)$-cluster into an l-cluster and a monomer is spontaneous and so the number of times it happens per unit volume per unit time is proportional to c_{l+1}; this type of process therefore contributes a term $-b_{l+1} c_{l+1}$ to J_l, where b_{l+1} is another kinetic coefficient. The complete constitutive relation is thus

$$J_l = a_l c_1 c_l - b_{l+1} c_{l+1} \qquad (l \geqslant 1) \tag{3}$$

The system of equations (1), (2), (3) is the Becker-Döring system, our main object of study in this article.

In their original paper, Becker and Döring did not use Eq. (2). Instead they made the approximation of treating c_1 as a constant. Their approximation has the disadvantage that the resulting equations do not have the density-conserving property to be proved in the next section. The full system of equations appears to be due to Burton.(6)

If the dominant mechanism for the transport of matter in the alloy is the diffusion of monomers, the coefficients a_l and b_l can be estimated for large l using the following argument (see refs. 12, 16). The argument assumes that an l-cluster is a sphere of radius R_l, related to l by

$$l = 4\pi R_l^3/3 \tag{4}$$

The steady-state probability per unit time that one of the diffusing monomers will strike a given cluster of size l can be calculated by the standard method, which is to solve a diffusion equation for the monomer density, with an absorbing boundary condition (i.e., zero monomer density) at the surface of this sphere and with monomer density at infinity equal to the overall monomer density c_1. The steady-state solution satisfying these conditions is $(1 - R_l/r)\, c_1$, where r is the distance from the centre of the sphere. From this we may calculate the rate at which monomers strike the sphere to be $4\pi D R_l c_1$ where D is the diffusivity of the monomers, and so obtain

$$a_l = 4\pi D R_l = a_1 l^{1/3} \tag{5}$$

where $a_1 = 4\pi D(3/4\pi)^{1/3}$. Similarly, the coefficient b_l is the rate at which monomers would leave the l-cluster if there were a sink of monomers at infinity and their density at the surface of the cluster were the equilibrium value. By the Gibbs–Thomson formula this equilibrium value is $z_s(1 + \Gamma/R_l)$ where z_s is the density of monomers in equilibrium with a plane surface of the high-density phase and Γ is a constant proportional to the surface tension. The solution of the steady-state diffusion problem is $z_s(1 + \Gamma/R_l)\, R_l/r$, and so the average rate of losing particles from an l-cluster is $4\pi D z_s(R_l + \Gamma)$; thus we obtain

$$b_l = 4\pi D z_s(R_l + \Gamma) = a_l(z_s + q l^{-1/3}) \tag{6}$$

where $q = (4\pi/3)^{1/3} z_s \Gamma$.

3. EXISTENCE, UNIQUENESS, DENSITY CONSERVATION

Since the BD equations (1), (2), (3) are infinite in number, it is not obvious that they have a solution at all. A theorem proved in ref. 3 (Theorem 2.2, page 663) proves that they do have a solution, for all positive t, provided that

$$\left.\begin{aligned} a_l &= O(l) \qquad (l \to \infty) \\ c_l(0) &\geqslant 0 \\ \sum_1^\infty l c_l(0) &< \infty \end{aligned}\right\} \tag{7}$$

Moreover, if $\sum l^2 c_l(0) < \infty$, this solution is unique (ref. 3 Theorem 3.6, page 674). On the other hand if a_l increases more rapidly than l as $l \to \infty$, then there is no solution (ref. 3 Theorem 2.7, page 669)).

Since the BD equations were formulated for conserving dynamics, every step of which leaves the number of particles unchanged, we would expect them to imply the conservation of density. The solute density (overall number of solute particles per unit volume) at time t is defined as

$$\rho(t) := \sum_{l=1}^{\infty} lc_l(t) \tag{8}$$

where the colon indicates a definition. Using Eqs. (1) and (2) we can calculate the time derivative of $\rho(t)$ as

$$\begin{aligned}\frac{d\rho(t)}{dt} &= \frac{dc_1}{dt} + \sum_{l=2}^{\infty} l\,\frac{dc_l}{dt} = -2J_1 - \sum_{l=2}^{\infty} J_l + \sum_{l=2}^{\infty} l(J_{l-1} - J_l)\\ &= \sum_{l=2}^{\infty} (-1 + (l+1) - l)\,J_l = 0\end{aligned} \tag{9}$$

So, if the interchange of the time differentiation with the infinite summation in the first line and the rearrangement of the infinite series in the second are justified, it follows that $\rho(t)$ is independent of time and therefore stays at its initial value:

$$\rho(t) = \rho \tag{10}$$

where ρ means the same as $\rho(0)$, i.e., the initial solute density $\sum_{l=1}^{\infty} lc_l(0)$.

Because we are dealing with an infinite system of equations, it is not obvious that the rearrangements used in (9) are justified, and indeed similar systems of equations do exist (for example in the theory of gelation[11, 13]) for which $\rho(t)$ is not constant in time but instead decreases. However, for the Becker–Döring equations Ball *et al.* show (ref. 3 Cor. 2.6, p. 668) that if the conditions (7) for the existence of a solution are satisfied then the density conservation result (10) is indeed true.

4. EQUILIBRIUM

The simplest solutions of the BD equations are the equilibrium solutions, i.e., those where all the c_l's are constant in time. For such a solution every J_l must, by (1), be equal to the next one, so that all the J_l's are equal; and by (2) the number they are all equal to must be zero. Hence by (3) we have

$$a_l c_1 c_l - b_{l+1} c_{l+1} = 0 \qquad (l = 1, 2, \ldots) \tag{11}$$

The solution of this recurrence relation is

$$c_l = Q_l c_1^l \tag{12}$$

where the Q_l's are defined by

$$Q_l = \frac{a_1 a_2 \cdots a_{l-1}}{b_2 b_2 \cdots b_l} \tag{13}$$

If the forces between the molecules are known, the equilibrium distribution can be expressed in terms of those forces using equilibrium statistical mechanics, and so the Q_l's can be found using (12). In that case Eq. (13) gives information about the ratios a_l/b_{l+1} in terms of the known Q_l's. The formula is

$$a_l Q_l = b_{l+1} Q_{l+1} \tag{14}$$

Alternatively, if we have information about the ratios a_l/b_{l+1} from another source such as the calculations leading to (5) and (6), then (14) gives information about Q_l: thus (5) and (6) give, for large l,

$$Q_l \approx l^{-1/3} \prod_{r=2}^{l} \frac{1}{z_s + q r^{-1/3}} \approx \text{const.}\, l^{-1/3} z_s^{-(l-1)} \exp\left(-\frac{3q}{z_s} l^{2/3}\right) \tag{15}$$

The equilibrium states (12) form a one-parameter family labelled by the value of c_1. The equilibrium density at a given value of c_1 is given by (12) and (8) as

$$\hat{\rho}(c_1) := \sum_{l=1}^{\infty} l Q_l c_1^l \tag{16}$$

For realistic Q_l, in particular those given by Eq. (15), the series in (16) has a finite radius of convergence z_s; moreover, the series converges even when $c_1 = z_s$, so that the corresponding density ρ_s is finite:

$$\rho_s := \hat{\rho}(z_s) = \sum_{l=1}^{\infty} l Q_l z_s^l < \infty. \tag{17}$$

Physically, we may interpret ρ_s as the saturation concentration of the solute—i.e., the concentration of solute at which the solution can be in thermodynamic equilibrium with a distinct phase containing a very high concentration of solute atoms. This phase, if it were present, could be thought of as a cluster of infinite size.

5. LONG-TIME LIMITING BEHAVIOR

Having found the equilibrium solutions, we would like to know whether a system started with an arbitrary inital distribution of cluster concentrations $\{c_l(0)\}$ will approach one of these equilibrium states, and if so which one. The first step is to find a Lyapunov function, i.e., a function of the c_l's which can be shown to change monotonically with time (like the H-function for Boltzmann's kinetic equation).

Consider the function defined by

$$L := \sum_{l=1}^{\infty} c_l[\log(c_l/Q_l) - 1]. \tag{18}$$

Its time rate of change is

$$\begin{aligned}
\frac{\partial L}{\partial t} &= \sum_1^\infty \frac{dc_l}{dt} \log\left(\frac{c_l}{Q_l}\right) && \text{by (18)}\\
&= \left(-2J_1 - \sum_2^\infty J_l\right) \log(c_1/Q_1) + \sum_2^\infty (J_{l-1} - J_l) \log(c_l/Q_l) && \text{by (2) and (1)}\\
&= J_1 \log\left(\frac{Q_1^2 c_2}{c_1^2 Q_2}\right) + \sum_2^\infty J_l \log\left(\frac{Q_1 Q_l c_{l+1}}{c_1 c_l Q_{l+1}}\right) && \text{after rearrangement}\\
&= \sum_1^\infty (a_l c_1 c_l - b_{l+1} c_{l+1}) \log \frac{b_{l+1} c_{l+1}}{a_l c_l c_1} && \text{by (3) and (14)}\\
&\leqslant 0
\end{aligned} \tag{19}$$

It is not difficult to show, using the convexity of L as a function of $c_1, c_2, \ldots$, that L has a lower bound (which happens to be $\rho \log z_s - \sum Q_l z_s^l$); therefore L must approach a limit as $t \to \infty$. Moreover, its derivative dL/dt will approach zero. Since all terms on the right side of the penultimate line in (19) are non-positive it follows that the individual terms approach zero:

$$a_l c_1 c_l - b_{l+1} c_{l+1} \to 0 \qquad \text{as} \quad t \to \infty \tag{20}$$

As in the discussion of (11), it follows that

$$c_l - Q_l c_1^l \to 0 \qquad \text{as} \quad t \to \infty \tag{21}$$

To complete the argument we need to know how c_1 behaves as $t \to \infty$. Eq. (21) tells us that if the $c_l(t)$'s approach limits for large t, then these limits satisfy

$$\sum_{l=1}^{\infty} \lim_{t \to \infty} lc_l(t) = \sum_{l=1}^{\infty} lQ_l[\lim_{t \to \infty} c_1(t)]^l$$

$$= \hat{\rho}(\lim_{t \to \infty} c_1(t)) \qquad \text{by (16)} \tag{22}$$

From the conservation of density, Eq. (9), we know that

$$\lim_{t \to \infty} \sum_{l=1}^{\infty} lc_l(t) = \rho \tag{23}$$

One may ask: can the two limit operations $t \to \infty$ and $\sum_{l=1}^{\infty}$ be interchanged, making the left sides of (23) and (22) equal so that we have

$$\hat{\rho}(\lim_{t \to \infty} c_1(t)) = \rho? \tag{24}$$

The answer to this question is given by the rigorous analysis of Ball *et al.* (ref. 3 Theorem 5.6, page 687). They prove, subject to suitable conditions on the coefficients a_l, b_l and the initial data $c_l(0)$, that

(i) if $\rho \leqslant \rho_s$, then

$$\lim_{t \to \infty} c_l(t) = Q_l z^l \qquad (l = 1, 2, ...,) \tag{25}$$

where z is the solution of

$$\hat{\rho}(z) = \rho \tag{26}$$

with $\hat{\rho}$ the function defined in (16). In this case the convergence is strong in the sense that

$$\lim_{t \to \infty} \sum_{l=1}^{\infty} l\,|c_l(t) - Q_l z^l| = 0, \tag{27}$$

and the answer to the question in (24) is "yes."

(ii) if $\rho > \rho_s$, then

$$\lim_{t \to \infty} c_l(t) = Q_l z_s^l \qquad (l = 1, 2, ...) \tag{28}$$

where z_s is the radius of convergence of the series in (16). In this case the convergence is weak; i.e., the individual terms of the series in (27) converge to zero, but their sum does not. In this case, therefore, the answer to the question in (24) is "no:" the left-hand side of (24) is equal to ρ_s whereas the right-hand side is equal to ρ. The physical interpretation of this nonuniform convergence is that the excess density $\rho - \rho_s$ is contained in a set of clusters which get larger and larger as time progresses.

6. LARGE-TIME ASYMPTOTICS

We would like to know in more detail what happens to the excess density $\rho - \rho_s$ as $t \to \infty$ in case (ii) above. To do this, let us define a new time variable $\tau := \varepsilon t$ where ε is a small parameter. The idea is that, by considering the limit $\varepsilon \to 0$ at fixed τ, we may obtain approximations which are good when t is of order $1/\varepsilon$ or greater. The same idea is used in the asymptotic analysis of phase-field equations,(18, 15) and also in the statistical mechanics derivations of hydrodynamic equations.(8) The germ of our method is contained in ref. 17, but in that paper the approximations are introduced on an *ad hoc* basis, with no small parameter ε, so that there is no systematic way to estimate the size of the errors or to proceed to a better approximation.

The BD equations (1), (2) and (3) are, because of (10), equivalent to the system

$$\varepsilon \frac{\partial c_l}{\partial \tau} = J_{l-1} - J_l \qquad (l \geqslant 2) \tag{29}$$

$$J_l = a_l(c_1 - w_l)\, c_l - (b_{l+1} c_{l+1} - b_l c_l) \tag{30}$$

$$\sum_1^\infty l c_l = \rho = \text{const} \tag{31}$$

where

$$w_l := b_l / a_l \tag{32}$$

We look for approximate solutions that are good for small ε by considering the limit $\varepsilon \to 0$. There are two ways to take this limit; we use one of them for small l and the other for large. The cut between small and large l will be made at a value $l^\dagger$ chosen to make certain error terms negligible. For the level of approximation to which we work explicitly in this paper, it is sufficient for $l^\dagger$ to satisfy the following conditions:

$$l^\dagger \to \infty, \varepsilon (l^\dagger)^2 \exp \frac{3q(l^\dagger)^{2/3}}{2z_s} \to 0 \tag{33}$$

as $\varepsilon \to 0$. (For example, the choice $l^{\dagger} = \log(1/\varepsilon)$ satisfies both conditions.) If the calculations were carried to a higher level of approximation, a more restrictive pair of conditions might be necessary.

For large l, i.e., $l \geqslant l^{\dagger}$, we make the substitution $l = \lambda/\varepsilon$ and treat λ as a continuous variable, so that part of the sum in (31) can be approximated as an integral:

$$\sum_{1}^{l^{\dagger}} lc_l + \varepsilon^{-2} \int_{\varepsilon l^{\dagger}}^{\infty} c_l \lambda \, d\lambda + O(\varepsilon) = \rho \tag{34}$$

To get a sensible limit in (34) as $\varepsilon \to 0$, define $\tilde{c}$ and $\tilde{J}$ by

$$c_l = \varepsilon^2 \tilde{c}(\lambda, \tau) \tag{35}$$

$$J_l = \varepsilon^2 \tilde{J}(\lambda, \tau), \tag{36}$$

in the expectation that $\tilde{c}$ and $\tilde{J}$ are $O(1)$. On the assumption that $\tilde{c}$ and $\tilde{J}$ are smooth functions of λ, we may approximate the differences in (29) and (30) by derivatives so that these equations, together with (34), become

$$\frac{\partial \tilde{c}}{\partial \tau} = -\frac{\partial \tilde{J}}{\partial \lambda} + O(\varepsilon) \tag{37}$$

$$\tilde{J} = v\tilde{c} + O(\varepsilon) \tag{38}$$

$$\sum_{1}^{l^{\dagger}} lc_l + \int_{\varepsilon l^{\dagger}}^{\infty} \tilde{c}\lambda \, d\lambda + O(\varepsilon) = \rho \tag{39}$$

where

$$v = a_l(c_1 - w_l) \tag{40}$$

One can think of v as the average rate at which clusters with the given value of λ (or l) increase in size.

For diffusion-controlled kinetics, Eqs. (5) and (6) bring (32) to the form

$$w_l = z_s + ql^{-1/3} \tag{41}$$

so that (40) becomes

$$v = a_1[\lambda^{1/3} u(\tau) - q] \tag{42}$$

where $u(\tau)$ is defined by

$$c_1 = z_s + \varepsilon^{1/3} u(\tau) \tag{43}$$

Turning now to the small-l régime, we expect from (36) that $J_{l^\dagger} = O(\varepsilon^2)$, and from Eq. (29) that $J_{l-1} - J_l = O(\varepsilon)$; using this information to estimate first $J_{l^\dagger - 1}$, then $J_{l^\dagger - 2}$ and so on we find that

$$J_l = O(\varepsilon l^\dagger) \qquad (l \leqslant l^\dagger) \tag{44}$$

This implies, by (33), that $J_l = o(1)$. On solving (3) explicitly for c_l in terms of the J_l's, we obtain

$$\begin{aligned} c_l &= Q_l c_1^l \left[1 - \sum_{m=1}^{l-1} \frac{J_m}{a_m Q_m c_1^{m+1}} \right] \\ &= Q_l z_s^l [1 + O(l\varepsilon^{1/3})] \left[1 + O\left((l-1)\, \varepsilon l^\dagger \exp \frac{3ql^{2/3}}{2z_s} \right) \right] \qquad (l \leqslant l^\dagger) \end{aligned} \tag{45}$$

where we have used the estimate (43) of c_1 and bounded the series by the number of terms, which is $l-1$, times a bound on the largest term which was obtained using (44), (5) and (15).

By virtue of (33), Eq. (45) implies

$$c_l = Q_l z_s^l (1 + o(1)) \qquad (l \leqslant l^\dagger) \tag{46}$$

whence (since $\sum_1^\infty l Q_l z_s^l$ converges, and $l^\dagger \to \infty$ by (33))

$$\sum_1^{l^\dagger} l c_l = \rho_s + o(1) \tag{47}$$

where ρ_s is defined in (17)). The result (47) can be inserted in (39) to give

$$\int_0^\infty \tilde{c} \lambda \, d\lambda = \rho - \rho_s + o(1) \tag{48}$$

where $\tilde{c}$ is defined in (35).

To find out more about $\tilde{c}$, we need the PDE obtained by combining Eqs. (37), (38), (35), (36) and (42), namely

$$\frac{\partial \tilde{c}}{\partial \tau} = -\frac{\partial}{\partial \lambda} [a_1 (\lambda^{1/3} u(\tau) - q)\, \tilde{c}] + o(1) \tag{49}$$

with $u(\tau)$ chosen so that (48) is satisfied. An explicit formula for $u(\tau)$ can be obtained by taking the τ-derivative of (48), obtaining after the use of (49)

$$\int_0^\infty \frac{\partial}{\partial\lambda}\left[(\lambda^{1/3}u(\tau)-q)\,\tilde{c}\right]\lambda\,d\lambda=o(1) \tag{50}$$

(assuming that the τ-derivative of the $o(1)$ term in (48) is itself $o(1)$). By partial integration, (50) is equivalent to

$$\int_0^\infty \left[\lambda^{1/3}u(\tau)-q\right]\tilde{c}\,d\lambda=o(1) \tag{51}$$

i.e., to lowest order in ε,

$$u=\frac{q\int_0^\infty \tilde{c}\,d\lambda}{\int_0^\infty \lambda^{1/3}\tilde{c}\,d\lambda} \tag{52}$$

Given sufficient time and patience, the method could be used to derive better and better approximations, by using at each stage the best available approximation to estimate the neglected terms and then re-solving the equations to obtain a better approximation. For example the next approximation for $J_l\,(l\leqslant l^\dagger)$, obtained by using (12) to estimate the left side of (29) and then solving for J_l with the help of the fact that $J_{l^\dagger}=O(\varepsilon^2)$, is

$$J_l=\varepsilon^{4/3}\frac{du}{d\tau}\sum_{l+1}^{\infty} mQ_m z_s^m+o(\varepsilon^{4/3}) \qquad (l\leqslant l^\dagger) \tag{53}$$

with $u(\tau)$ determined by solving the equations (48), (49). This could then be substituted into the first line of (45) to obtain a better approximation to $c_l\,(l\leqslant l^\dagger)$, which then gives a better approximation to $\sum_1^{l^\dagger} lc_l$ to be used in (34). The next step would be to improve the approximation for $\tilde{c}$ by solving (37), (38), using the improved (34) together with estimates of the $O(\varepsilon)$ terms obtained using the lowest-order solution.

The system of equations (48), (49) is at the heart of the LSW theory of coarsening. The analysis in this section shows that these equations can be derived in a systematic way from the BD equations, and that they are not restricted to the case where the saturation concentration ρ_s is small enough to justify neglecting the contribution of dimers, trimers, etc. to the sum (8).

7. LARGE-TIME BEHAVIOR OF THE LSW EQUATIONS

The LSW system (49), (52) has a self-similarity property: if $\tilde{c}(\lambda, \tau)$, $u(\tau)$ is a solution, so is $\tilde{c}(k\lambda, k\tau)$, $k^{-1/3}u(\tau)$ for any constant k. This suggests replacing λ by a new independent variable x proportional to λ/τ, which is invariant under this re-scaling. A convenient choice is $x = \lambda/a_1 q\tau$, in terms of which Eqs. (49) and (48) become

$$\tau \frac{\partial \tilde{c}}{\partial \tau} = -\frac{\partial}{\partial x}\left[(x^{1/3}p(\tau) - 1 - x)\,\tilde{c}\right] - \tilde{c} \tag{54}$$

$$\int_0^\infty \tilde{c}x\,dx = (\rho - \rho_s)/a_1^2 q^2 \tau^2 \tag{55}$$

where p is the re-scaled version of u, defined by

$$p(\tau) := q^{-2/3}(a_1\tau)^{1/3}\,u(\tau) \tag{56}$$

Equation (55) implies, via a derivation similar to that of (52)

$$p(\tau) = \frac{\int_0^\infty \tilde{c}\,dx}{\int_0^\infty x^{1/3}\tilde{c}\,dx} \tag{57}$$

An equivalent system of equations, using the new dependent variable

$$h(x, \tau) := \tau^2 \int_x^\infty \tilde{c}(x, \tau)\,dx \tag{58}$$

is

$$\tau \frac{\partial h}{\partial \tau} = -(x^{1/3}p(\tau) - 1 - x)\frac{\partial h}{\partial x} + h \tag{59}$$

$$\int_0^\infty h\,dx = (\rho - \rho_s)/a_1^2 q^2 \tag{60}$$

implying

$$p(\tau) = \frac{h(0, \tau)}{\int_{x=0}^\infty x^{1/3}[-dh(x, \tau)]} \tag{61}$$

From this version it follows that h/τ is constant on the characteristic curves in the (x, t) plane, whose equations are

$$\tau \frac{dx}{d\tau} = x^{1/3}p(\tau) - 1 - x \tag{62}$$

Equation (59) has a family of time-independent solutions, in which p has a constant value, call it p_0. They are

$$h \propto \exp - \int_0^x \frac{d\xi}{1+\xi-\xi^{1/3}p_0} \tag{63}$$

The normalization constant is determined by (60), and $\tilde{c}$ can then be found by differentiation, in accordance with (58).

The behavior of the integral in (63) depends on the value of p_0. If $p_0 < (27/4)^{1/3}$, the denominator is positive for all positive ξ; in this case h and $\tilde{c}$ are positive for all positive ξ, and h decays like const.x^{-1} for large x, so that the integral in (60) just diverges at infinity. If $p_0 = (27/4)^{1/3}$, the denominator has a double zero at $\xi = 1/2$; the integral in (63) then diverges for $x \geqslant 1/2$, so that the functions h and $\tilde{c}$ are positive for $x < 1/2$ and zero thereafter, and the integral in (60) converges. If $p_0 > (27/4)^{1/3}$, the denominator has two zeros, and the integral diverges for all x exceeding the smaller of these two zeros; in this case h and $\tilde{c}$ are positive up to this value of x (which is less than 1/2) and zero thereafter.

8. DISCUSSION OF THE LSW THEORY

The LSW theory hinges on the asymptotic behavior of $p(\tau)$ and $\tilde{c}(x, \tau)$ for large τ. It is argued in the theory that $p(\tau)$ must approach a limit, and that this limit must be $(27/4)^{1/3}$; indeed, if the limit were less than $(27/4)^{1/3}$ then the integral in (60) would diverge for the limiting distribution of cluster sizes, and if it were greater then (as noted by Velazquez$^{(21)}$) a large family of characteristics would converge on the larger zero of the right side of (62), which is only compatible with the existence of a limiting cluster distribution h in the special (and probably inadmissible) case where $h = 0$ on all these characteristics.

The LSW theory makes two definite predictions about the results of possible experiments. One is that that after a long time the distribution of the scaled cluster size variable x, which is proportional to l/t, becomes independent of time, so that the average cluster radius (proportional to the average cube root of l) grows in proportion to $t^{1/3}$. The other prediction is that the actual distribution of scaled cluster sizes should be given by (63) with p_0 set equal to $(27/4)^{1/3}$, and in particular that there will be no clusters at all larger than the size corresponding to $x = 1/2$. This maximum size corresponds to a radius which is $(1/2 \div 4/27)^{1/3} = 1.5$ times the mean cluster radius.

Experiment confirms the prediction of $t^{1/3}$ growth in many cases: see, for example ref. 10, 14; when it is not confirmed one may reasonably infer either that the steady state has not yet been reached(24) or that that other mechanisms such as cluster coagulation, not allowed for in the BD picture, are at work.(9) On the other hand the predicted coefficient of $t^{1/3}$ in the growth law for mean cluster radius does not agree well with experiment if the density of solute is more than about 10%;(14) the discrepancy is believed to be due to the approximations used in deriving (5) and (6), particularly the approximation of neglecting the effect of nearby large clusters on the density of monomers near a given cluster. Some of the proposed ways of improving on this approximation are discussed in the excellent review articles(19, 20).

The other main prediction of the LSW theory concerns the distribution of cluster sizes, in particular the prediction that there will be no clusters with radii larger than about 1.5 of the average radius. Measuring such distributions is not an easy experiment, but the actual ratio of cut-off to average radius tends to be larger than 1.5,(2, 1, 5) and the distribution is generally somewhat broader than the LSW prediction.(24, 23) The same is true of a distribution obtained by direct integration of the BD equations.(17, 16) The reason for the broadening may be that the asymptotic state predicted in the LSW theory has not yet been reached—the theory does predict that it will be reached very slowly (see ref. 21 and the Appendix to ref. 12), and that on the way to this steady state p will be less than its final value $(27/4)^{1/3}$.

From the rigorous mathematical point of view, very little is known about the asymptotic behavior of the LSW equations. It is not even clear whether one can prove that $p(\tau)$ approaches a limit at all. For the simpler equation obtained by replacing $x^{1/3}$ by x in (54) and (57) it is possible(7) to invent initial data for which $p(\tau)$ oscillates for ever, and the same may be true of the real LSW equations. If so, one would have to restrict the initial data in some way if one wished to ensure that the equations really did behave as in the LSW theory. The structure of the LSW equations is unusual and interesting, and they are well worth further mathematical study.

ACKNOWLEDGMENTS

I am grateful to many colleagues, particularly John Cahn, Jack Carr, Peter Fratzl, Miguel Herrero and Juanjo Velazquez, for valuable information and enjoyable discussions.

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