

Kinetics of Nucleation in a Lattice Gas Model: Microscopic Theory and Simulation Compared

O. Penrose and A. Buhagiar¹

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A method is described for calculating from first principles the coefficients in the Becker–Döring equations for the rate of change of the distribution of cluster sizes in a low-density lattice gas with Kawasaki dynamics. The method depends on solving a diffusion problem for the concentration of particles near a given cluster. The coefficients are calculated for cluster sizes up to 6, on a simple cubic lattice at a temperature 0.59 times the critical temperatures, and extrapolated to larger sizes. The resulting version of the Becker–Döring equations is then solved numerically. Comparison with the results of a computer simulation (at overall concentration 0.075) carried out by Kalos and others indicates that the method gives quite good predictions of the dependence of the cluster distribution on the critical cluster size (usually denoted by l^*) but that the predicted rate of change of critical cluster size with time is too small, at this overall concentration, by a factor of about 0.3.

KEY WORDS: Kinetics; phase transitions; nucleation; lattice gas; Becker–Döring equations; clusters.

1. INTRODUCTION

The system of kinetic equations put forward by Becker and Döring⁽¹⁾ in 1935 is well established as the basis for successful treatments of some topics in phase transition kinetics, such as metastability and Ostwald ripening. The physical basis of these equations is that droplets of the new phase grow or shrink by absorbing or emitting particles one at a time. For each size of droplet, the equations contain two kinetic coefficients, one giving the

¹Faculty of Mathematics, the Open University, Milton Keynes MK76AA, England.

probability per unit time that the droplet will emit a particle, the other giving the probability that it will absorb a particle. The normal methods for calculating these coefficients⁽²⁾ depend on treating the droplets as if they were spheres of the new phase; this assumption is, however, obviously invalid for "droplets" consisting of only a few particles and is in any case difficult to relate quantitatively to the basic microscopic model. The difficulty of establishing such a relationship has already led to much controversy in the treatment of metastability.⁽³⁾

It is the purpose of this paper to describe, for a particular microscopic model, how the kinetic coefficients can be calculated directly from microscopic quantities. These kinetic coefficients, when used in the Becker–Döring theory, give a system of differential equations which can be integrated numerically to predict how the distribution of cluster sizes varies with time. At the end of the paper these predictions are compared with the results of computer simulations of the same microscopic model carried out by Kalos *et al.*⁽⁴⁾ and also with some experimental results due to Ardell *et al.*⁽⁵⁾

The model to which our results apply is the Ising model on a cubic lattice, with Kawasaki dynamics.⁽⁶⁾ This is a model of a binary alloy in which each lattice site is occupied by one atom and the state changes with time according to a Markov process where the allowed transitions are interchanges of the atoms on two neighboring sites. The model is mathematically equivalent to a lattice gas, with each site either empty or occupied by a particle, in which case the allowed transitions are jumps of any particle to any neighboring empty site. In either case, a nearest-neighbor attractive interaction law is assumed, and the transition probabilities are chosen in accordance with a detailed balancing condition which includes a specification of the temperature.

The Becker–Döring theory assumes that the new phase consists of widely separated droplets or nuclei immersed in the old phase. This requires one of the components of the alloy (the one which predominates in the new phase) to have a relatively small overall concentration. At such concentrations it is convenient to use a lattice gas picture, regarding the minority atoms as "particles" and the majority atoms as "empty sites." We can then describe the configuration in terms of clusters, a cluster being defined as a maximal connected set of particles (i.e., of minority atoms), and to identify the clusters with the "droplets" in the Becker–Döring theory. It was pointed out by Lifshitz and Slyozov,⁽⁷⁾ and by Wagner,⁽⁸⁾ that the rate of change of the average number of particles in a large spherical cluster can be found by treating the motion of the other particles near by as a diffusion problem. What we have done in this paper is to apply a similar idea to the motion of the particles near a cluster of any size: we express the Becker–Döring

kinetic coefficient in terms of the solution of a lattice diffusion problem describing the motion of the other particles near a specified cluster, with suitable boundary conditions at infinity and at the surface of the cluster.

2. THE KINETIC EQUATIONS

To describe the distribution of cluster sizes we define c_l to be the concentration of l -particle clusters (i.e., the number of such clusters per lattice site). The Becker–Döring equations give the time rate of change of c_l as

$$\frac{dc_l}{dt} = J_{l-1} - J_l \quad (l = 2, 3, \dots) \quad (2.1)$$

where J_l is the net rate of conversion, per unit volume, of l -particle to $(l + 1)$ -particle clusters. It is given in this theory by

$$J_l = a_l c_1 c_l - b_{l+1} c_{l+1} \quad (l = 1, 2, \dots) \quad (2.2)$$

The kinetic coefficients a_l and b_{l+1} are independent of the individual cluster concentrations c_1, c_2, \dots though they may depend on more general properties of the system such as the overall concentration of particles,

$$\rho = \sum_{l=1}^{\infty} l c_l \quad (2.3)$$

The concentration of monomers (one-particle clusters) does not satisfy an equation of the form (2.1) but can instead be determined from the conservation law

$$\frac{d}{dt} \sum_{l=1}^{\infty} l c_l = 0 \quad (2.4)$$

Further details about the derivation of these equations can be found elsewhere.⁽⁹⁾

Before embarking upon the analysis of diffusion near a cluster, we note a simple relation between a_l and b_{l+1} , which follows from the fact that (by detailed balancing), $J_l = 0$ at equilibrium. The equilibrium cluster concentrations $c_l^{(\text{eq})}$ are given approximately⁽¹⁰⁾ by the empirical formula

$$c_l^{(\text{eq})} = \begin{cases} (1 - \rho)^3 w & (l = 1) \\ (1 - \rho)^4 Q_l w^l & (l \geq 2) \end{cases} \quad (2.5)$$

where w is a parameter and Q_l is the “cluster partition function” at the relevant temperature. The definition of Q_l is⁽¹⁰⁾

$$Q_l = \sum_K e^{U_b(K)/kT} \quad (2.6)$$

where the sum is over all translationally inequivalent l -particle clusters, $b(K)$ is the number of nearest-neighbor pairs of particles in the cluster K , and U is the binding energy per pair (i.e., U is the energy required to separate a pair of neighboring minority atoms).

Substituting (2.5) into (2.2) and using the detailed balance condition $J_l = 0$ we obtain⁽¹¹⁾

$$\frac{b_{l+1}}{a_l} = \begin{cases} (1 - \rho)^2 w_l & (l = 1) \\ (1 - \rho)^3 w_l & (l \geq 2) \end{cases} \quad (2.7)$$

where

$$w_l = \frac{Q_l}{Q_{l+1}} \quad (l \geq 1) \quad (2.8)$$

At the temperature where the simulations were carried out, $T = 0.59 T_c$ with T_c the critical temperature, the ratio w_l satisfies⁽¹²⁾ an approximate empirical relation of the form

$$w_l \simeq w_s \left[1 + \frac{C}{(l-2)^{1/3}} \right] \quad (3 \leq l \leq 9) \quad (2.9)$$

with $w_s = 0.010526$ and $C = 2.415$. A similar empirical relation, with different values for w_s and C , holds at other temperatures.

To calculate the absolute, as opposed to the relative, values of a_l and b_{l+1} we need more specific assumptions about the dynamical model. It is usual to assume that the probability per unit time of a transition from configuration X to a configuration Y , obtained from X by moving just one particle to a vacant neighboring site, depends only on the energy change

$$\Delta E = E(Y) - E(X) \quad (2.10)$$

where $E(X)$ is the energy of configuration X . For each integer n , we shall denote by p_n the probability per unit time of any given transition which increases the energy by nU ; then the detailed balance condition gives

$$p_{-n}/p_n = \theta^n \quad (2.11)$$

where $\theta = e^{U/kT}$. The actual choice of p_n used in the simulation was

$$p_n = \frac{1/3}{1 + \theta^n} \quad (2.12)$$

where the unit of time is one attempted interchange per site. In the limit of low densities, the diffusion constant for this model is equal to $p_0 = 1/6$, where the unit of distance is one lattice spacing.

3. A METHOD FOR CALCULATING THE KINETIC COEFFICIENTS

One thing that can be seen at once from the ratio formula (2.7) is that at least one of a_l and b_{l+1} must depend on the overall concentration ρ . To begin with, however, we shall consider their values in the limit of very small ρ , which we shall denote by $a_l(0)$ and $b_{l+1}(0)$. To illustrate the method, let us consider the calculation of the particular coefficients $a_2(0)$ and $b_3(0)$. The equation in which they appear is (2.2) with $l = 2$,

$$J_2 = a_2(0)c_1c_2 - b_3(0)c_3 \quad (3.1)$$

in which the first term on the right gives the mean number of two-particle clusters per site per unit time which become three-particle clusters, and the second term gives the mean number of three-particle clusters per site per unit time which become two-particle clusters. Dividing on both sides by c_2 gives

$$\frac{J_2}{c_2} = a_2(0)c_1 - b_3(0)\frac{c_3}{c_2} \quad (3.2)$$

where the first term on the right now gives the probability per unit time that a given two-particle cluster becomes a three-particle cluster.

In Fig. 1 the two-particle cluster is indicated by black dots, and sites at which a third particle may arrive to add itself to the cluster are indicated by circles. For the two-dimensional square lattice there are 6 such sites, as shown in Fig. 1, but for the cubic lattice there are 10. We want to calculate

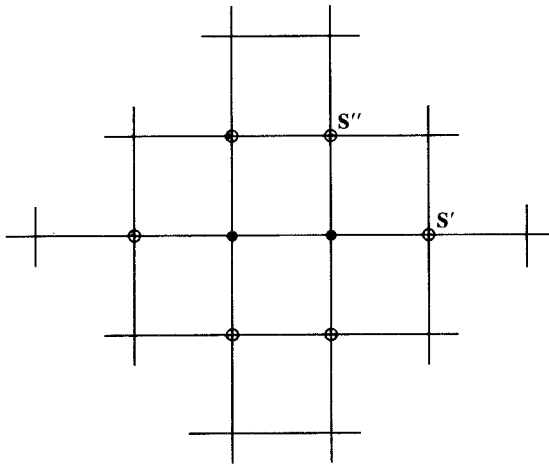


Fig. 1. A two-particle cluster and the sites at which a third particle can attach itself to the cluster.

J_2/c_2 by calculating the probability per unit time that a particle will arrive at one of the encircled sites, less the probability per unit time that a particle will leave one of these sites.

Let $f(\mathbf{x})$ denote the conditional probability of finding a particle at the lattice site \mathbf{x} , given that the two sites marked in black are occupied. If \mathbf{x} is one of the sites marked with a circle, then $f(\mathbf{x})$ is related to the probability that a three-body cluster is present; otherwise it is related to the probability that there is a one-body cluster near the two-body cluster shown in Fig. 1. In the low-density limit we may assume that no other particles, apart from the one which may be at \mathbf{x} and the ones in the two-body cluster, are near by; if we also neglect the possibility of the two-body cluster breaking up, we obtain from the Kawasaki dynamical assumption the condition

$$\frac{df(\mathbf{x})}{dt} = \sum_{\mathbf{y}} [f(\mathbf{y})p(\mathbf{y}, \mathbf{x}) - f(\mathbf{x})p(\mathbf{x}, \mathbf{y})] \quad (\mathbf{x} \notin S) \quad (3.3)$$

where $p(\mathbf{x}, \mathbf{y})$ is the probability per unit time [as given by (2.12)] that a particle initially at lattice site \mathbf{x} will jump to \mathbf{y} , and S denotes the set of all sites that are adjacent to the given cluster.

Provided that the cluster distribution changes slowly enough with time (an assumption which will be looked at in Section 8) we can replace (3.3) approximately by the steady-state condition

$$\sum_{\mathbf{y}} [f(\mathbf{y})p(\mathbf{y}, \mathbf{x}) - f(\mathbf{x})p(\mathbf{x}, \mathbf{y})] = 0 \quad (\mathbf{x} \notin S) \quad (3.4)$$

For all sites \mathbf{x} which are not nearest or second nearest neighbors of the two-body cluster shown, Eq. (3.4) reduces to the finite-difference analog of Laplace's equation,

$$\sum'_{\mathbf{y}} [f(\mathbf{y}) - f(\mathbf{x})] = 0 \quad (3.5)$$

where the sum is over all nearest neighbors of \mathbf{x} . For the second-nearest-neighbor sites, however, the more general equation (3.4) must be used, since some of the possible transitions change the energy.

The boundary conditions for the difference equation describe what happens at infinity and at the sites adjacent to the two-body cluster. At infinity we have, assuming widely separated parts of the system to be statistically independent,

$$f(\mathbf{x}) \rightarrow c_1 \quad \text{as } |\mathbf{x}| \rightarrow \infty \quad (3.6)$$

For adjacent sites, the relevant condition describes the fact that if the third particle is at one of the sites marked by circles in Fig. 1 then we have a three-body cluster. The probability per unit volume of finding the particular three-body cluster, for which the third particle is at a particular

nearest-neighbor site \mathbf{x} , is (in three dimensions) $\frac{1}{3} c_2 f(\mathbf{x})$; the factor $\frac{1}{3}$ arises because there are three possible orientations for two-body clusters, so that the orientation shown has probability $\frac{1}{3} c_2$ per unit volume. To relate this to c_3 , the concentration of three-body clusters, we write

$$c_3 = c'_3 + c''_3 \quad (3.7)$$

where c'_3 is the concentration of straight three-body clusters and c''_3 that of bent ones. Since there are three different orientations for straight clusters, the probability of any one such cluster is $\frac{1}{3} c'_3$. Hence we have (using the notation defined in Fig. 1)

$$\frac{1}{3} c_2 f(\mathbf{s}') = \frac{1}{3} c'_3, \quad \text{i.e., } f(\mathbf{s}') = c'_3 / c_2 \quad (3.8)$$

Similarly, since there are 12 different orientations for the bent three-body clusters, we have

$$\frac{1}{3} c_2 f(\mathbf{s}'') = \frac{1}{12} c''_3, \quad \text{i.e., } f(\mathbf{s}'') = c''_3 / 4c_2 \quad (3.9)$$

Combining (3.8) and (3.9) with (3.7) we obtain

$$f(\mathbf{s}') + 4f(\mathbf{s}'') = c_3 / c_2 \quad (3.10)$$

To complete the specification of the difference equation we need to specify $f(\mathbf{s}')$ and $f(\mathbf{s}'')$ individually as well as the weighted average (3.10). The most logical way of taking this into account would be to go over to a more complicated system of kinetic equations which included information about the shapes of the various clusters as well as their sizes; for example it would include separate equations for c'_3 and c''_3 . For simplicity, however, we used instead the approximation of assuming that c'_3 and c''_3 always have the same ratio as at equilibrium, which is

$$\frac{c''_3}{c'_3} = \frac{12}{3} = 4 \quad (3.11)$$

Some measure of justification for this assumption is provided by the observation that in the simulation the nonequilibrium distribution of the sizes of the small clusters was found to be very close to an equilibrium distribution; this gives some grounds for hoping that, at least for small clusters, the same may be true of their shapes. The effect of the assumption (3.11) is, by (3.8) and (3.9), to supplement (3.10) with the condition

$$f(\mathbf{s}') = f(\mathbf{s}'') \quad (3.12)$$

The difference equation (3.4), together with the boundary conditions (3.6), (3.10), and (3.12) gives a system of linear equations which can be shown to have a unique solution. By the superposition principle, this solution depends linearly on the parameters c_1 and c_3/c_2 in the boundary

conditions:

$$f(\mathbf{x}) = c_1 f_1(\mathbf{x}) + (c_3/c_2) f_2(\mathbf{x})$$

The function f_1 can be found by solving the difference equation (3.4) under the conditions

$$\begin{aligned} f_1(\mathbf{x}) &\rightarrow 1 & \text{as } \mathbf{x} &\rightarrow \infty \\ f_1(\mathbf{x}) &= 0 & \text{for } \mathbf{x} &\in S \end{aligned} \quad (3.13)$$

The function f_2 can be found [provided condition (3.12) is valid] by solving the difference equation (3.4) under the conditions

$$\begin{aligned} f_2(\mathbf{x}) &\rightarrow 0 & \text{as } \mathbf{x} &\rightarrow \infty \\ f_2(\mathbf{x}) &= \frac{1}{5} & \text{for } \mathbf{x} &\in S \end{aligned} \quad (3.14)$$

Once the solution of the difference equation with the boundary conditions (3.6) and (3.12) is known, we can calculate J_2/c_2 , as the probability per unit time that the two-body cluster we are considering will be converted to some three-body cluster. This rate is equal to the sum, over any closed surface which encloses the two-body cluster and does not pass through any lattice sites, of all the "probability flows"

$$f(\mathbf{y})p(\mathbf{y}, \mathbf{x}) - f(\mathbf{x})p(\mathbf{x}, \mathbf{y}) \quad (3.15)$$

along bonds which cross the surface, using a sign convention in which an inward flow counts as positive. By (3.4) and the finite difference analog of the divergence theorem, the quantity so defined is the same for all such surfaces, so we may calculate it using a large sphere. At large distances our difference equation (3.5) may be approximated by the Laplace equation, and the probability flow along a bond in the x direction by $-p_0 \partial f / \partial x$. In this approximation the total inward flow across a surface S is given by a surface integral

$$\frac{J_2}{c_2} = p_0 \int \frac{\partial f}{\partial n} dS \quad (3.16)$$

where $\partial/\partial n$ denotes the outward normal derivative. At large distances the solution of the difference equation (3.5), with the boundary condition (3.6), has the same asymptotic form as that of Laplace's equation, namely,

$$f(\mathbf{x}) \sim c_1 - A/r + O(1/r^2) \quad (3.17)$$

where r is the Euclidean length of the position vector \mathbf{x} , and A is independent of \mathbf{x} . The vector \mathbf{x} may be measured from any origin, but the correction terms are smallest if the origin is at the center of the two-body cluster. Putting (3.17) into (3.16) we obtain

$$J_2/c_2 = 4\pi p_0 A \quad (3.18)$$

By the superposition principle, the number A must depend linearly on the boundary conditions for the difference equation; that is, it has the form

$$A = A_1 c_1 + A_2 c_3 / c_2 \quad (3.19)$$

Substituting (3.18) and (3.29) into (3.2) we see that

$$a_2(0) = 4\pi p_0 A_1, \quad b_3(0) = -4\pi p_0 A_2 \quad (3.20)$$

However, since $a_2(0)$ and $b_3(0)$ are related by the detailed balance condition (2.7) (with $\rho = 0$) one need only calculate one of A_1 and A_2 . We chose to calculate A_1 . This was done by solving the difference equation (3.4) with the boundary condition (3.13); for this solution the coefficient A in (3.17) is, by (3.19), equal to A_1 , since the boundary condition is equivalent to taking $c_1 = 1$ and $c_3/c_2 = 0$.

The method we have described can in principle be used for any pair of kinetic coefficients ($a_l(0), b_{l+1}(0)$). The only new features are as follows:

i. For $l = 1$ the values of a_1 and b_2 are twice as big as the formula (3.21) would suggest, because in this case both the clusters being considered can move.

ii. For $l \geq 3$, Eq. (3.12) has to be generalized since not all sites of S have the same number of neighbors in the fixed cluster. The appropriate generalization is a Gibbs distribution over S :

$$f(\mathbf{s}) = \text{const} \times \theta^{n(\mathbf{s})} \quad (\mathbf{s} \in S) \quad (3.21)$$

where $n(\mathbf{s})$ is the number of sites in the l -particle cluster that are adjacent to \mathbf{s} . Our method of calculation based on the boundary conditions (3.13) allows for the new feature (ii) automatically.

iii. For $l \geq 3$ it is necessary to solve more than one difference equation problem, because the central cluster can take different shapes (e.g., straight and bent in the case $l = 3$). In accordance with the principle used to obtain (3.11), these were aggregated by assuming that the different shapes for the central cluster were present in the same proportions as they would be at equilibrium.

At the temperature for which we did our calculations, the kinetic coefficients for differently shaped clusters of the same size were found to differ by at most 10%, and so the effect of deviations from the assumed proportions is unlikely to be important.

4. RESULTS OF THE CALCULATION OF KINETIC COEFFICIENTS

Since the function $f(\mathbf{x})$ satisfies the finite-difference analog of Laplace's equation at all sites of the lattice except for a finite set on and near the central fixed cluster, the appropriate solution of the difference equa-

tions can be expressed in the form

$$f(\mathbf{x}) = c_1 + \sum_{\mathbf{y}} G(\mathbf{x}, \mathbf{y})q(\mathbf{y}) \quad (4.1)$$

where $G(\mathbf{x}, \mathbf{y})$ is the Green's function for the finite-difference Laplacian and q is a function with finite support on the lattice. The conditions which $f(x)$ must satisfy then reduce to a finite system of linear equations for the values taken by $q(\mathbf{y})$ at different lattice sites \mathbf{y} . Solving this system of equations for the cases $l = 1$ and $l = 2$ we found that

$$a_1(0) = \frac{11.62p_{-1}(1 + 0.233\gamma)}{1 + 0.833\gamma + 0.1347\gamma^2} \simeq \frac{11.62p_{-1}}{1 + 0.6\gamma} \quad (4.2)$$

$$a_2(0) = \frac{14.474p_{-1}(1 + 0.901\gamma + 0.260\gamma^2 + 0.024\gamma^3)}{1 + 1.547\gamma + 0.836\gamma^2 + 0.187\gamma^3 + 0.015\gamma^4} \simeq \frac{14.47p_{-1}}{1 + 0.64\gamma} \quad (4.3)$$

where

$$\gamma = p_{-1}/p_0 - 1 \quad (4.4)$$

For l larger than 2 we found it more convenient to use a direct numerical solution of the difference equation. This was done by the S.O.R. method, replacing the boundary condition at infinity by an approximate condition of the form

$$f(\mathbf{x}) = c_1 - K/r \quad (4.5)$$

on the surface of a large box containing the cluster. The unknown K was related to the other unknowns by a condition based on the finite difference analog of the divergence theorem. To check that the approximation (4.5) was not affecting the accuracy we repeated the calculation for boxes of different sizes, obtaining results that were the same to three decimal places for a_l ($1 \leq l \leq 3$) for boxes of sizes 9, 10, and 11, and for a wide range of parameters γ . Some results of these calculations are shown in Table I. As l increases the calculations rapidly become more complicated; for this reason we only did them for $l \leq 6$.

As a check on the calculation as a whole, we solved (3.4) by the S.O.R. method for $l = 1$ and $l = 2$. The results (also shown in Table I) agreed well with Eqs. (4.2) and (4.3).

In order to solve the Becker-Döring equations we need values of $a_l(0)$ for values of l beyond 6. These were obtained by extrapolation. If we assume that a large l -body cluster behaves like a sphere of radius proportional to $l^{1/3}$, then it follows⁽¹²⁾ that a_l is asymptotically proportional to $l^{1/3}$ for large l . A formula satisfying this condition which also fits the calculated values of a_l quite well for $l \leq 6$ is

$$a_l(0) = \frac{1}{6} [M + Nl]^{1/3} \quad (4.6)$$

Table I. Zero-Density Kinetic Coefficients $a_l(0)$ for a Cubic Lattice at Temperature $0.59T_c$ ($T_c = \text{Critical Temperature}$) which Corresponds to $U/kT = 1.5$. The Values of M and N for Eq. (4.6) were $M = 874, N = 1888$

l	$a_l(0)$		
	Eqs. (4.2) and (4.3)	S.O.R.	Eq. (4.6)
1	2.30	2.29	2.34
2	2.80	2.81	2.78
3		3.17	3.12
4		3.34	3.39
5		3.63	3.63
6		3.78	3.84

where M, N are constants depending on temperature. Table I shows that at the temperature $0.59T_c$ the accuracy of formula (4.6) is about $1\frac{1}{2}\%$ for $l \leq 6$. The formula (4.6) also gives⁽¹³⁾ a good representation (for $l \leq 6$) at other temperatures; see Table II for some details.

As a working hypothesis, then, let us assume that Eq. (4.6) gives a satisfactory approximation to $a_l(0)$ for all values of l , at the temperatures we are interested in. The corresponding approximation to $b_{l+1}(0)$ can be deduced from (2.7) and (2.9); it is

$$b_{l+1}(0) = \frac{1}{6} w_s \left[1 + \frac{C}{(l-2)^{1/3}} \right] (M + Nl)^{1/3} \tag{4.7}$$

In order to make useful predictions from the Becker–Döring equations, however, we need values for a_l and b_{l+1} at nonzero values of the overall concentration ρ ; and Eq. (2.7) implies that at least one of them varies by a factor of order $(1 - \rho)^3$ when ρ is varied. One might expect $a_l(\rho)$ to be larger than $a_l(0)$; for $a_l(0)$ is a measure of the rate at which fresh particles arrive

Table II. Values of the Kinetic Coefficients $a_l(0)$ and also of the Numbers M, N in Eq. (4.6) at Various Temperatures

$\frac{T}{T_c}$	$\frac{p-1}{p_0} - 1$	$a_l(0)$						M	N
		$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$	$l = 6$		
∞	0.0	1.937	2.415	2.750	2.924	3.208	3.360	341	1324
2.18	0.2	2.077	2.567	2.922	3.086	3.383	3.533	558	1519
1.04	0.4	2.187	2.691	3.046	3.223	3.509	3.663	799	1663
0.64	0.6	2.279	2.792	3.149	3.325	3.609	3.761	1040	1776
0.40	0.8	2.359	2.876	3.233	3.405	3.671	3.826	1341	1837

at the surface of an l -particle cluster given a standard density of monomers at infinity, and at larger densities we may expect more particles to arrive, since more of the arriving particles may have traveled as members of dimers or other small clusters, rather than as monomers.

Rather than attempt a detailed theory of these effects we shall simply allow for them crudely by multiplying all of the kinetic coefficients a_l by an empirical factor which, for generality, we may assume for the present to depend not only on the total concentration ρ but also on the concentration of small clusters as measured, for example, by the value of c_1 . Thus we shall assume

$$a_l(\rho) = \mu a_l(0) \quad (4.8)$$

where $\mu = \mu(\rho, c_1)$. When (4.8) is substituted into (2.2) and then (2.1) we obtain a system of equations which can be written

$$\frac{dc_l}{d\tau} = J_{l-1}^{(0)} - J_l^{(0)} \quad (l = 2, 3, \dots) \quad (4.9)$$

where

$$\tau = \int_0^t \mu dt \quad (4.10)$$

$$\begin{aligned} J_1^{(0)} &= a_1(0) [c_1^2 - (1 - \rho)^2 w_1 c_2] \\ J_l^{(0)} &= a_l(0) [c_1 c_l - (1 - \rho)^3 w_l c_{l+1}] \quad (l = 2, 3, \dots) \end{aligned} \quad (4.11)$$

These equations have a form very similar to that which applies to zero density, but the time variable is rescaled by a factor μ which may itself change with time, and whose value is not given by the theory as it stands at present. This rescaling permits us to solve the Becker–Döring equations for nonzero ρ without knowing anything about the value of μ . This value, and the way it depends on time, can be found empirically afterwards by comparing the calculated solution with the results of computer simulations.

5. SOLVING THE BECKER–DÖRING EQUATIONS NUMERICALLY

In order to construct a numerical solution of the system of equations (4.9) and (4.11) we must choose a temperature T , a density ρ , and a set of initial values for c_1, c_2, c_3, \dots compatible with the sum rule (2.3). In our calculations we used a temperature T such that $U/kT = 1.5$ (i.e., $T = 0.59T_c$, where T_c is the critical temperature) and various values for the total concentration ρ , most notably $\rho = 0.075$ (i.e., 7.5% of the sites are occupied). The temperature $0.59T_c$ is one for which a number of simulation runs have been done⁽¹⁰⁾ and for which the values of w_s, C, M , and N are known. The concentration 0.075 is the one for which the longest of the simulation

Table III. Comparison of Values for the Number of Clusters Observed in the Simulation on a $50 \times 50 \times 50$ Cubic Lattice with Values Implied by the Formula (2.5) for $\rho = 0.075$ and $T = \infty$ (i.e., $\theta = 1$).

Number of Clusters = $125000c_l$		
l	Simulation	Formula
1	5790	5866
2	965	965
3	310	286
4	88	97
5	35	36
6	11	14
7	11	6
8	4	2
9	1	1
10	0	0
> 10	1	0

runs was carried out, and for which a detailed analysis of the long-term behavior is available.⁽¹²⁾

In the simulations, the initial positions of the particles were chosen randomly and independently; that is, the initial configuration corresponded to equilibrium at infinite temperature. To reproduce this initial condition in our numerical integration of the Becker–Döring equations, we used as initial values c_1, c_2, \dots for $t = 0$ the equilibrium values predicted by the theory of Section 2 for infinite temperature. That is to say we used the formulas (2.5) and (2.6) with $\rho = 0.075$ and $U/kT = 0$, the value of w in (2.5) being chosen so that (2.3) was satisfied with $\rho = 0.075$.

These theoretical values of c_l are shown in Table III, together with the values obtained in the simulation run. There is no significant deviation between them: the simulation results are consistent with the empirical formula (2.5).

To integrate the Becker–Döring equations numerically it was necessary to truncate the system at some large value, say L , of the subscript l . This can be done either by requiring $J_L = 0$ for all times t or $c_L = 0$ for all times t , in place of the value given by Eq. (2.1) or (2.2) for $l = L$. We chose the condition $J_L = 0$, with $L = 800$. Our reason for choosing $L = 800$ was that in the simulation no cluster larger than 800 was ever observed. Moreover, no more than one cluster larger than 600 was ever observed, so that the simulation data concerning values of c_l with $l > 600$ are subject to large fluctuations and there is little point in trying to compute very accurate values of c_l from the Becker–Döring equations to compare them with. We

believe that the accuracy of our values of c_l , over the entire time interval considered, is no worse than 10% for $l = 600$, and is correspondingly better than this for smaller values of l ; this estimate was obtained by comparing the solution for $L = 800$ and a similar solution for $L = 1600$.

A convenient way of estimating the value of the empirical factor μ is to study the evolution of the distribution of small clusters. We take advantage of the fact that for any but the very earliest times the instantaneous distribution of small clusters ($l \leq 10$) can be fitted quite well by the equilibrium formula (2.5), with a value of w which decreases as time progresses. When solving the Becker–Döring equations, w is conveniently calculated from c_1 using the formula [based on (2.5)]

$$c_1 = (1 - \rho)^3 w \quad (5.1)$$

For the simulations, the effect of fluctuations can be reduced by considering instead clusters of sizes up to (say) 10 and calculating w from the formula

$$\sum_{l=1}^{10} l c_l = (1 - \rho)^3 w + (1 - \rho)^4 \sum_{l=2}^{10} l Q_l w^l \quad (5.2)$$

where the numbers c_l are observed cluster concentrations. In practice the effect of fluctuations was further reduced by replacing c_l in the above formula by an average of (say) 10 successive observations.

From the time-varying values of w obtained in the ways just described, we can calculate a time-varying quantity l^* defined⁽¹²⁾ by

$$w = w_s \left[1 + \frac{C}{(l^* - 2)^{1/3}} \right] \quad (5.3)$$

with w_s and C as in Eq. (2.9); the interpretation of l^* is that clusters larger than l^* tend to grow and clusters smaller than l^* to shrink. It turns out that l^* increases monotonically with time and so it provides a convenient link between the time variables in the simulation and the Becker–Döring solution, enabling us to determine μ .

Figure 2 shows a graph of pairs of values of τ and t which correspond to the same value of l^* . According to Eq. (4.10) the slope of the graph gives the value of μ . We see that over most of the time range considered ($1000 < t < 7000$, corresponding to $20 < l^* < 200$) the value of μ is constant at about 3.3; but for earlier times it is larger than 3.3. Thus μ cannot be a function of ρ alone; it seems also to depend on the density of small clusters, of which l^* is a convenient measure. Further information can be obtained by making similar comparisons at other values of the total concentration ρ ; for $\rho = 0.05$ and 0.1 this was done by Buhagiar.⁽¹³⁾ He found similar behavior, the value of μ again being not far from 3 as long as

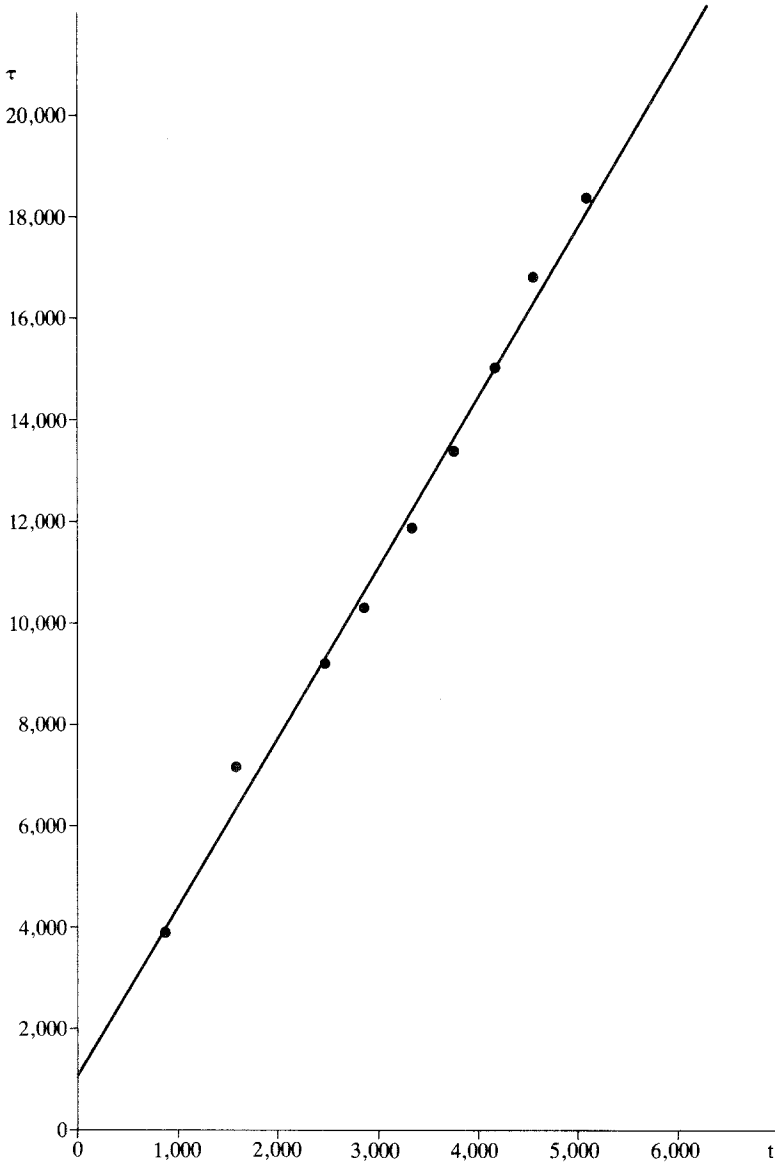


Fig. 2. Pairs of values of t , the time variable in the simulation, and τ , the time variable in the Becker-Döring equations, which correspond to the same critical cluster size l^* . The equation of the straight line shown is $\tau = 3.3(t + 400)$. The temperature is $0.59 T_c$ and the overall concentration is 0.075.

l^* was greater than 20 or 30. Thus it appears that the value of μ is determined mainly by l^* rather than by ρ , that for values of l^* between about 20 and 200 it takes values not far from 3.3, regardless of the overall concentration ρ , and that for smaller values of l^* the value of μ is greater than 3.3. We hope to return to the question of a theoretical explanation of these results in a separate paper, but for the present paper we treat them as purely empirical.

6. THE DISTRIBUTION OF CLUSTER SIZES

Having established the relationship between the time scales of the simulation and of the Becker–Döring equations we can now test the values of c_l predicted by the equations against those observed in the simulation. For small clusters ($l \leq 10$ or 20), we have already noted that the distributions for both the simulation and the differential equation agree well with the equilibrium distribution (2.5) for suitable (time-dependent) values of w . Our method of relating the time variables t and τ ensures automatically that the “predicted” value of w is always equal to the observed value, and so the agreement of observed and predicted distributions for small clusters is also ensured automatically.

For larger clusters ($l \geq 10$ or 20), our test is illustrated in Fig. 3. Each curve is the distribution predicted by the Becker–Döring equations for some value of τ , and hence of l^* ; the corresponding histogram shows values of c_l observed in the simulation at the same value of l^* , averaged over blocks of consecutive values of l large enough to smooth out most of the fluctuations. (It turned out that a good choice for the number of values of l in each block was about $\frac{1}{2}l^*$.)

Comparison of the graphs and histograms indicates that the agreement between prediction and observation is good if $l^* \leq 67$. For a value of l^* somewhere between 67 and 98 a local maximum and minimum appear in the distribution; this phenomenon is correctly predicted by the Becker–Döring equations. For larger values of l^* the agreement is still quite good for values of l larger than the position of the maximum (a more detailed discussion of the large clusters is given by Buhagiar⁽¹³⁾), but the Becker–Döring equations underestimate the values of l at which these maxima and minima occur.

7. COMPARISON WITH EXPERIMENT

It was pointed out by Lifshitz and Slyozov⁽⁷⁾ that for very large values of l^* the distribution of large clusters may be expected to exhibit a simple

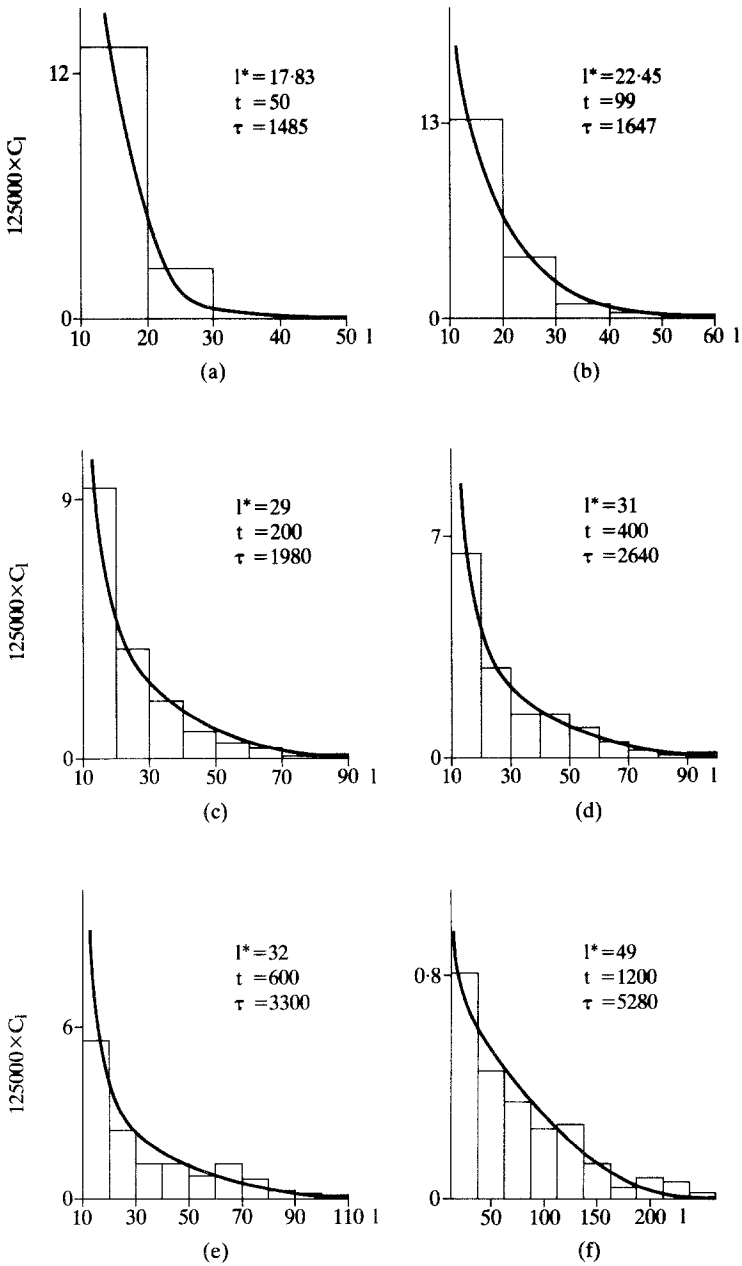


Fig. 3. Comparison of cluster size distributions c_l , for $l \geq 20$, given by computer simulation (histograms) and by the Becker-Döring system of differential equations (continuous curves). The temperature is $0.59T_c$ and the overall concentration is 0.075.

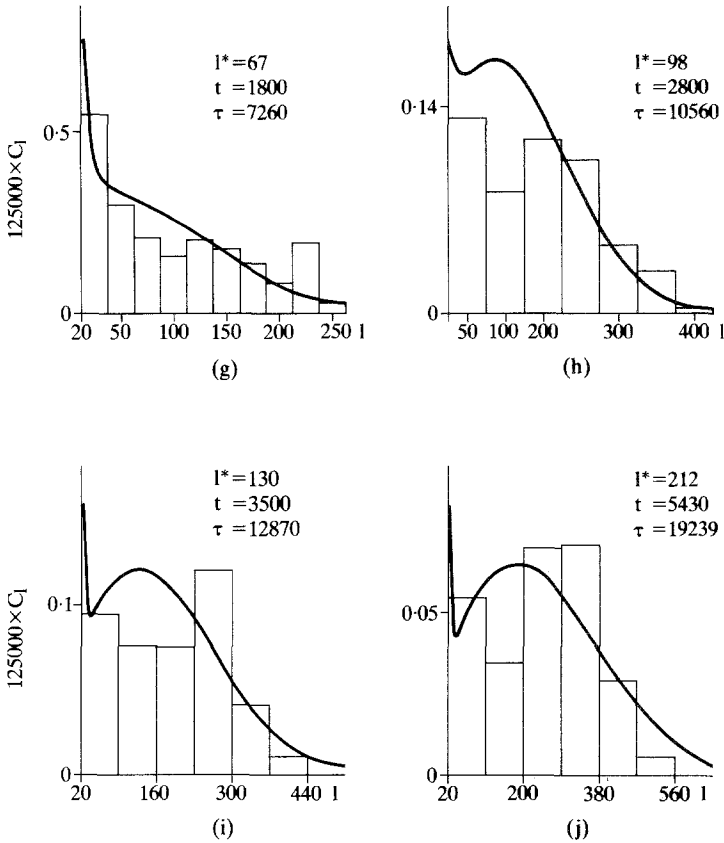


Fig. 3. Continued.

scaling property: that the number of particles in clusters larger than l is a function of l/l^* alone so that c_l is equal to l^{*-2} times a function of l/l^* .

Experimentally we measure not the number of particles in a cluster but its radius, which may be assumed proportional to $l^{1/3}$ where l is the number of particles. The observed distribution of cluster sizes can be described by giving the number of clusters per unit radius increment, which is proportional to $l^{2/3}c_l$. According to the scaling property, this quantity should be equal to $l^{2/3}l^{*-2}$ times a function of l/l^* , and consequently $l^{*4/3}$ times this quantity should be a function of l/l^* —and hence, also, a function of $(l/l^*)^{1/3}$. Figure 4 shows $l^{*4/3}l^{2/3}c_l$ plotted against $(l/l^*)^{1/3}$, both for theory and experiment.

The predictions given by the Becker–Döring equation confirm the scaling hypothesis and fit the experimental results somewhat better than the

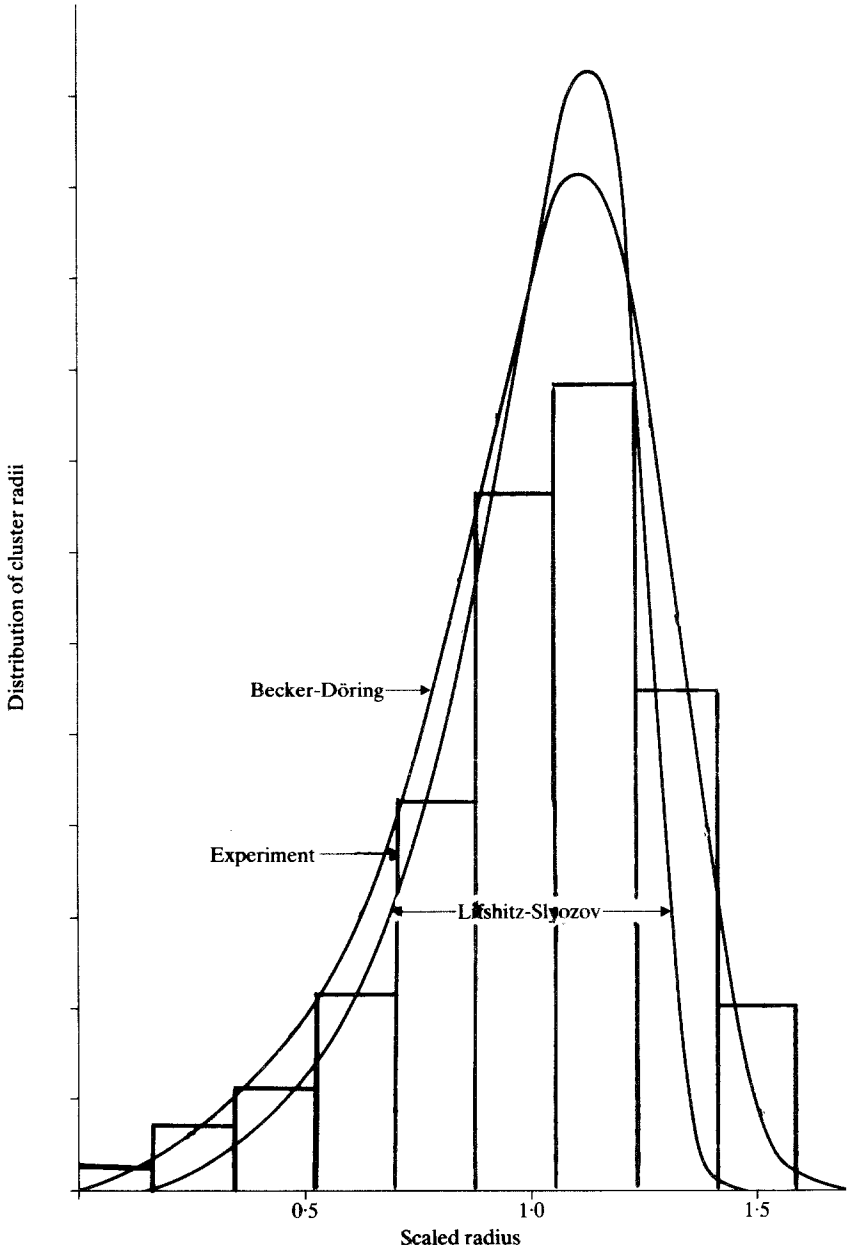


Fig. 4. Plot of a quantity proportional to $l^{2/3}c_l$, which in turn is proportional to the distribution of cluster radii, against $(l/l^*)^{1/3}$, the ratio of cluster radius to critical cluster radius. One curve is the prediction of the Becker-Döring equations; the other that of the Lifshitz-Slyozov theory. Experimental results for a 6.35% Al-Ni alloy 72 hr after quenching to 625°C, taken from a paper by Ardell and Nicholson (Ref. 5), are also shown.

scaling function predicted by Lifshitz and Slyozov, which is

$$x^2 \left(\frac{3}{3+x} \right)^{7/3} \left(\frac{3}{3-2x} \right)^{11/3} \exp\left(\frac{-2x}{3-2x} \right) \quad \text{if } x < \frac{3}{2}$$

$$0 \quad \text{if } x \geq \frac{3}{2}$$

where $x = (l/l^*)^{1/3}$. In particular the incorrect prediction that there are no clusters at all with $l/l^* > 3/2$ is avoided. Further details of this comparison are given by Buhagiar.⁽¹³⁾

8. DISCUSSION

The comparisons made in the previous section give some confirmation of the method used in Sections 3 and 4 for calculating the coefficients in the Becker–Döring kinetic equation for nucleation. This method, it will be recalled, was to calculate coefficients for cluster sizes 1 to 6 using a diffusion model, and then to extrapolate to larger values of l using the idea of Lifshitz and Slyozov that these coefficients should be proportional to $l^{1/3}$ for large l .

Our work shows that the resulting system of differential equations is helpful in representing the behavior of both real and simulated clusters, for a three-dimensional lattice gas at temperature $0.59T_c$ and density 0.075. The most apparent defect in the representation provided is that the time scale is wrong, the theory predicting rates of change which are too small by a factor of about 3.3. The reason for this discrepancy is not understood at present, but it appears to be due to the fact that the low-density theory upon which our calculations are based needs modification before it can be applied at densities as high as 0.075.

In the low-density theory the only processes considered are the absorption or emission of a monomer by some cluster; but at higher densities a significant fraction of the particles are in dimers and larger clusters, so that processes such as the absorption and emission of dimers, ignored in this paper, may have quite a large effect on the transport of matter near a cluster. In the present paper these density effects were lumped together in the empirical parameter μ whose value appears to depend mainly on the concentration of monomers rather than on the overall density. It is hoped to return in a later paper to the question of whether this procedure has any theoretical justification, and if so whether μ can be calculated from first principles.

Ours is not the first calculation in which the Becker–Döring system of equations, or some generalization of them, was used to predict the time variation of the cluster size distribution. Calculations using the Becker–

Döring equations themselves have been reported by Courtney⁽¹⁴⁾ and Abraham,⁽²⁾ and calculations using a generalized form of these equations, which allows for processes involving clusters none of which are monomers, were reported by Mirolid and Binder.⁽¹⁵⁾ However, in all these calculations $a_l(0)$ was taken to be proportional, at large l , to $l^{2/3}$ —that is to the surface area of a sphere of volume l —rather than to $l^{1/3}$ as required by the Lifshitz–Slyozov diffusion mechanism. Moreover, in the calculations of Courtney and of Abraham, the time variation of c_1 was neglected; this is a legitimate approximation at very low concentrations, for which nearly all the small clusters are monomers, but not at the higher concentrations, such as 0.075, which interest us here. The reason for our interest in higher concentrations is that we wished to compare our results with those of computer simulations, and at very low concentrations such simulations are too slow and costly to be useful. The calculations of Mirolid and Binder,⁽¹⁵⁾ on the other hand, do apply at concentrations as high as 10% and 20% and their results show some similarity to ours. A more detailed comparison of their treatment with ours might provide useful information; but it would require, among other things, more information about the value of l^* and the results for clusters with $l > 50$ than is provided in Mirolid and Binder's paper.

Finally, it remains to discuss our neglect of the time variation of the spatial distribution of one-body clusters near a given cluster; in Section 3 this approximation enabled us to pass from the non-steady-state kinetic equation (3.3), which is analogous to the diffusion equation, to the steady-state equation (3.4) which is analogous to the Laplace equation. In order to judge the validity of the approximation we want to estimate the importance of two effects: (i) the time variation of the size of the central cluster, which affects the “inner” boundary condition (3.21), and (ii) the time variation of the overall concentration of one-body clusters, which affects the “outer” boundary condition (3.6).

The first effect, time variation of the size of the central cluster, can be estimated by imagining this cluster to be a sphere of radius R , where $\frac{4}{3}\pi R^3 = l$ is the number of particles in the cluster. Assuming that $l > l^*$ so that on average the cluster is growing, let us denote the flux of particles diffusing inwards at the surface of the sphere by J , so that $dl/dt = 4\pi R^2 J$ and $dR/dt = J$. Now the inward flux J is mainly due to diffusion of one-particle clusters, and therefore corresponds to a mean drift velocity for these clusters of J/c_1 . Thus the mean velocity of advance of the surface of the cluster, dR/dt , is about c_1 times the mean drift velocity: this indicates that when formulating the diffusion problem we may neglect the variability of mean cluster size provided that c_1 is not too large. In the simulation that mainly interests us here the value of c_1 was never greater than about 0.05

and hardly ever greater than about 0.025; so this neglect is unlikely to be a serious source of error.

The other effect noted above is the time variation of c_1 , the overall concentration of one-body clusters. If c_1 changes with time, it is because one-body clusters are being created or destroyed as a result of net emission or absorption of one-body clusters from larger clusters. Except in the vicinity of the central cluster, these large clusters may be assumed to be uniformly distributed, on the average, so that one-body clusters are being created or destroyed at the same rate, namely, dc_1/dt , everywhere. In the vicinity of the central cluster, however, the rate of creation of one-body clusters may be nonuniform, and there will also be some rearrangement of the spatial distribution of clusters as c_1 changes.

A crude estimate of the resulting flux of diffusing particles can be obtained by supposing the region near the central cluster to be a sphere of radius (say) $3R$ and that the rate at which particles accumulate in it or leave it as a result of changes in c_1 is (at most) dc_1/dt times its volume, i.e., $\frac{4}{3}\pi(3R)^3 dc_1/dt$. Dividing this quantity by the area of the sphere, which is $4\pi(3R)^2$, we find that the flux is roughly $R(dc_1/dt)$. Using the formula (5.3) in the simplified form

$$c_1 \cong c_s \left(1 + \frac{C}{l^{*1/3}} \right) \quad (8.1)$$

where c_s is the saturation (i.e., equilibrium) value of c_1 , we find

$$\begin{aligned} \frac{dc_1}{dt} &= \frac{c_s - c_1}{3l^*} \frac{dl^*}{dt} \\ &= \frac{c_s - c_1}{3t} \end{aligned} \quad (8.2)$$

since $l^* \propto t$ according to the Lifshitz-Slyozov theory.⁽⁷⁾ Thus we may estimate of the fluxes due to the changes in c_1 to be at most $R|c_s - c_1|/3t$, whereas the fluxes accounted for in the main calculation are, as we have just seen, of order dR/dt or crudely R/t . So the fluxes due to the changes in c_1 are smaller by a factor estimated here as $|c_s - c_1|/3$, which was hardly ever as large as 1% in the simulations associated with this paper. Thus both sources of time variation lead to particle fluxes which are small compared with the fluxes taken into account in our main calculation, and our neglect of time variation in solving the basic equation (3.4) is justified.

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