The Becker-Döring equations for the kinetics of phase transitions

O. Penrose

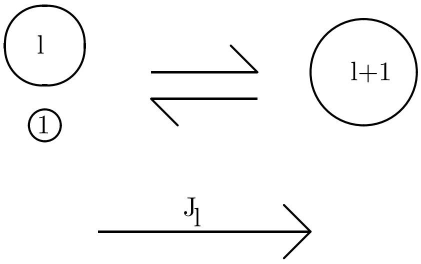
August 22, 2001

1 Formulation of the equations

In 1935 Becker and Döring [2] introduced a system of kinetic equations which can be used to model a variety of phenomena — the metastability of a ferromagnet magnetized in the opposite direction to the applied magnetic field, the coarsening of the granular structure during phase separation in a binary alloy, and the breakdown of metastability in a supersaturated vapour, such as the water vapour in the air on a cold evening. In each case we are dealing with a two-component system: in the case of the ferromagnet the two components are the two possible directions of spin for the elementary magnets (spinning electrons); in the case of the alloy, they are the two types of metal atom; in the case of water vapour they are air and water.

The equations apply to the case where the amounts of the two components are very unequal. The distribution of the molecules of the minority component is described by assuming that they clump together in clusters or droplets of various sizes. To describe the size of a droplet we use a variable l, defined as the number of particles (atoms or molecules) of the minority component in it. A cluster containing l minority particles will be called an l-cluster. A 1-cluster is usually called a *monomer* Let us define $c_l(t)$ to represent the concentration of l-clusters at time t in our system. 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. See diagram.



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 net effect of the corresponging interconversion between $(l-1)$-clusters and l clusters, whose 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 effects:

$$\frac{dc_l}{dt} = J_{l-1} - J_l \qquad (l \geq 2) \qquad \boxed{\text{dc/dt}} \tag{1}$$

In the case $l = 1$ the equation is different because the monomers participate in every process. The processes involving l-clusters and $(l+1)$-clusters use up monomers at a rate J_l, except in the case where $l = 1$ where they are used at a rate $2J_1$ because two monomers participate in the processes. So the total rate of change of c_1 is

$$\frac{dc_1}{dt} = -2J_1 - \sum_{l=2}^{\infty} J_l \qquad \boxed{\text{dc/dt1}} \tag{2}$$

These two equations have the character of conservation laws. 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 coefficient a_l is independent of time.. At the same time, 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}; therefore this type of process contributes a term $-b_{l+1}c_{l+1}$ to J_l. The complete constitutive relation is thus

$$J_l = a_l c_l c_l - b_{l+1} c_{l+1} \qquad (l \geq 1) \qquad \boxed{\text{J1}} \tag{3}$$

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

In their original paper, Becker and Döring did not use eqn (2). Instead they made the approximation of treating c_1 as a constant. This approximation has the disadvantage that the resulting equations do not have the density-conserving property to be proved in the next section. The full form of the equations including (3) appears to be due to Burton [3].

There is also a slightly different form of the equations appropriate to the case where the objects constituting the clusters are not something whose number is conserved, as for example in a ferromagnet where the clusters could be clusters of up-spins. For purposes of comparison I give these equations below:

$$\begin{aligned} \frac{dc_l}{dt} &= J_{l-1} - J_l \quad (l \geq 1) && (4)\\ J_l &= a_l \zeta c_l - b_{l+1} c_{l+1} \quad (l \geq 1) && (5)\\ J_0 &= a_0 \zeta - b_1 c_1 && (6) \end{aligned}$$

where ζ is a parameter which in the case of a ferromagnet is given by

$$\zeta = e^{-2H/kT} \tag{7}$$

with H the magnetic field (in suitable units). These equations are very similar to the original treatment of Becker and Döring, in which c_1 was held fixed instead of varying with time according to (2)

2 Existence, Uniqueness, Density conservation

Since the B-D equations (1), (2), (3) are infinite in number, it is not obvious that they have a solution at all. A theorem proved in [1] (page 663) proves that they do: provided that

$$\begin{aligned} a_(l) &= O(l) \quad (l \to \infty)\\ c_l(0) &\geq 0\\ \sum_l^\infty l c_l(0) &< \infty && (8) \end{aligned}$$

then the equations do indeed have a solution for all positive times t (on the other hand if a_l increases more rapidly than l as $l \to \infty$, then they do not.) Moreover, if the initial conditions obey the stronger condition

$$\sum_l^\infty l^2 c_l(0) < \infty \tag{9}$$

then ([1], p. 624) the solution with the given initial not only exists but is also unique.

Since the B-D 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 density (overall number of particles per unit volume) at time t is defined as

$$\rho(t) := \sum_{l=1}^{\infty} l c_l(t) \qquad \boxed{\text{rho}} \tag{10}$$

where the colon indicates a definition. Using equations (1) and (2) we can calculate the time derivative of ρ as

$$\begin{aligned} \frac{d\rho}{dt} &= -2J_l - \sum_{l=2}^{\infty} J_l + \frac{d}{dt}\sum_{l=2}^{\infty} l c_l \quad \text{by (1)} \\ &= -2J_1 - \sum_{l=2}^{\infty} J_l + \sum_{l=2}^{\infty} l(J_{l-1} - J_l) \quad \text{by (2)} \\ &= \sum_{l=2}^{\infty}(-1 + (l+1) - l)J_l \quad \text{by rearrangement} \\ &= 0 \qquad \boxed{\text{drho/dt}} \end{aligned} \tag{11}$$

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

$$\rho = \sum_{l-1}^{\infty} l c_l(0) \qquad \boxed{\text{rho=}} \tag{12}$$

Because we are dealing with an infinite system of equations, it is not obvious that the steps used in lines two and three of (11) are justified, and indeed systems of equations do exist for whiche ρ is not constant in time but instead decreases. The physical interpretation of such behaviour would be that the series defining ρ includes only the material in clusters that are of finite size, albeit indefinitely large. If any of the material goes into infinitely large clusters, which might for example correspond to the formation of a liquid phase, then there is that much less material for the finite clusters that make up ρ. However, for the BD equations Ball *et al* ([1], p.668) show that if the above conditions for the existence of a solution are satisfied then the density conservation result (12) is indeed true.

3 Equilibrium

To find out something about the solutions of the BD equations, consider first the equilibrium solutions. An equilibrium solution is one where all the c_l's are constant in time. For such a solution we must, by (1), have every J_l 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

$$a_l c_1 c_l - b_{l+1} c_{l+1} = 0 \quad (l = 1, 2, \ldots) \qquad \boxed{\text{eqmRR}} \tag{13}$$

The solution of this recurrence relation is

$$c_l = Q_l c_1^l \qquad \boxed{\text{eqm}} \tag{14}$$

where the Q_l's are defined by

$$Q_l = \frac{a_1 a_2 \ldots a_{l-1}}{b_2 b_3 \ldots b_l} \qquad \boxed{\text{Q}} \tag{15}$$

If the forces between the molecules are known, the Q_l's can be found in terms of those forces using equilibrium statistical mechanics (see Appendix 2 for the formula). In that case eqn (15) can be used to give information about the kinetic coefficients — the ratios a_l/b_{l+1} to be specific — in terms of the known Q_l's. The formula is

$$a_l Q_l = b_{l+1} Q_{l+1} \qquad \boxed{\text{db}} \tag{16}$$

The equilibrium states (14) form a one-parameter family labelled by values of c_1. The eqilibrium density at that value of c_1 is given by (10) as

$$\rho = \rho(c_1) := \sum_{l=1}^{\infty} l Q_l c_1^l \qquad \boxed{\text{rhoeqm}} \tag{17}$$

For the Q_l that arise in practice the series has a finite radius of convergence, which we shall call z_s, and the series converges when $c_1 = z_s$, so that

$$\rho_s := \rho(z_s) = \sum_{l=1}^{\infty} l Q_l z_s^l < \infty. \qquad \boxed{\text{rhos}} \tag{18}$$

The physical reason for this is that ρ_s is the density of a saturated gaseous phase (i.e. one that can be in thermodynamic equilibrium with another phase, which in this theory can be thought of as a droplet of infinite size).

4 Long-time limiting behaviour

$\boxed{\text{LTAB}}$

Having found the equilibrium solutions, we want to know whether an arbitrary initial state $\{c_l(0)\}$ will approach some equilibrium state, and if so which one. A useful approach to problems connected with the long-time behaviour of any differential equation is to look for a Lyapunov function, that is a function which can be shown to change monotonically with time. For physicists the best-known such function is Boltzmann's H, essentially the negative of the entropy; Boltzmann's H-theorem, showing that H is a non-increasing function of time, is the key to proving that a gas obeying Boltzmann's kinetic equation approaches a Maxwellian distribution at late times.

We now show that

$$L := \sum_{l=1}^{\infty} c_l[\log(c_l/Q_l) - 1] \qquad \boxed{\text{L}} \tag{19}$$

is a Lyapunov function for the BD system of equations. Indeed, we have

$$\begin{aligned}
\frac{\partial L}{\partial t} &= \sum_{1}^{\infty} \frac{dc_l}{dt} \log\left(\frac{c_l}{Q_l}\right) \qquad \text{by (19)} \\
&= (-2J_1 - \sum_{2}^{\infty} J_l) \log(c_1/Q_1) + \sum_{l}^{\infty} (J_{l-1} - J_l) \log(c_l/Q_l) \quad \text{by (2) and (1)} \\
&= J_1 \log\left(\frac{c_2 Q_1^2}{Q_2 c_1^2}\right) + \sum_{2}^{\infty} J_l \log\left(\frac{c_{l+1} Q_l}{Q_{l\ +1} c_l c_1}\right) \quad \text{after rearrangement} \\
&= (a_1 c_1^2 - b_2 c_2) \log\frac{b_2 c_2}{a_1 c_1^2} + \sum_{2}^{\infty} (a_l c_1 c_l - b_{l+1} c_{l+1}) \log\frac{b_{l+1} c_{l+1}}{a_l c_l c_1)} \quad \text{by (3) and (16)} \\
&\le 0 \qquad \boxed{\text{Lyap}}
\end{aligned} \tag{20}$$

It is not difficult to show (see Appendix 1) that L has a lower bound; therefore it 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 (20) are non-positive it follows that the individual terms approach zero:

$$a_l c_1 c_l - b_{l+1} c_{l+1} \to 0 \ \text{ as } \ t \to \infty \qquad \boxed{15} \tag{21}$$

so that, as in the discussion of (13)

$$c_l - Q_l c_1^l \to 0 \quad \text{as } \ t \to \infty \qquad \boxed{16} \tag{22}$$

To complete the argument we need to know how c_1 behaves as $t \to \infty$. From the conservation of density, eqn (11), we know that

$$\lim_{t\to\infty} \sum_{l=1}^{\infty} l c_l(t) = \rho_0 := \sum_{l=1}^{\infty} l c_l(0) \qquad \boxed{17} \tag{23}$$

Eqn (22) tells us that

$$\sum_{l=1}^{\infty} \lim_{t\to\infty} l c_l(t) = \sum_{l=1}^{\infty} l Q_l [\lim_{t\to\infty} c_1(t)]^l \qquad \boxed{18} \tag{24}$$

The question is whether we can interchange the two limit operations $t \to \infty$ and $l \to \infty$ to get (using (11) as well)

$$\rho(\lim_{t\to\infty} c_1(t)) = \rho_0 \qquad \boxed{19} \tag{25}$$

The answer to this question is given by the rigorous analysis of Ball et al [1]. They prove, subject to suitable conditions on the coefficients a_l, b_l and the initial data $c_l(0)$, that

(i) if $\rho_0 \leq \rho_s$, then

$$\lim_{t\to\infty} c_l(t) = Q_l z^l \quad (l = 1, 2, \cdots) \qquad \boxed{20} \tag{26}$$

where z is the solution of

$$\rho(z) = \rho_0 \qquad \boxed{21} \tag{27}$$

with $\rho(\cdot)$ the function defined in (11). In this case the convergence is strong in the sense that

$$\lim_{t\to\infty} \sum_{l=1}^{\infty} l|c_l(t) - Q_l z^l| = 0, \qquad \boxed{22} \tag{28}$$

and so the interchange of limits leading to (25) is justified.

(ii) if $\rho_0 > \rho_s$, then

$$\lim_{t\to\infty} c_l(t) = Q_l z_s^l \quad (l = 1, 2, \cdots) \qquad \boxed{23} \tag{29}$$

where z_s is the radius of convergence of the series in (11). In this case the convergence is weak; i.e. the individual terms of the series in (28) converge to zero, but their sum does not. Consequently the interchange of limits leading to (25) is *not* justified; in fact the right-hand side of (24) is equal to $\sum lQ_l = z_s^l = \rho_s$ and is therefore different from the right-hand side of (23) which equals ρ_0. A mathematical example showing how the two expressions can be unequal is (assuming for simplicity that t only takes integral values)

$$c_l(t) = Q_l z_s^l + (\rho_0 - \rho_s)\delta_{l,t}/l \qquad \boxed{24} \tag{30}$$

where $\delta_{l,t} := 1$ if $l = t$ and $:= 0$ otherwise. The physical interpretation of this non-uniform convergence is that the excess density $\rho - \rho_s$ is contained in a set of clusters which get larger and larger as time progresses.

5 Metastability

If $c_1 > z_s$ then the series (17) diverges; nevertheless if c_1/z_s is small enough (small supersaturation) the successive terms may become very small before they eventually start to grow beyond all bounds. The value of l at the smallest term is called the critical cluster size. Clusters that are smaller than this size will tend to shrink, though from time to time they grow as the result of fluctuations; clusters that are larger than this size tend to grow and are called super-critical clusters. A metastable state, if it exists initaially, will persist so long as the concentration of supercritical clusters remains negligibly small. Slowly, supercritical clusters will form and then grow, but this may happen very slowly. Eventually, when their concentration has become significant, one can say that the metastable state has broken down through homogeneous nucleation (it can, of course break down from other causes too, for example nucleation due to inhomogeneities such as particles of dust, which are ignored in the BD equations.)

In the original Becker-Döring treatment of metastability, the idea is to look for a very slowly varying solution of the basic equations (1), (2), (3), in which c_1 has a value slightly greater than the critical value z_s:

$$c_1 > z_s \qquad \boxed{\text{M0}} \tag{31}$$

Since the solution is slowly varying, we replace eqn (2) by the approximation

$$\frac{dc_1}{dt} = 0 \qquad \boxed{\text{M1}} \tag{32}$$

The physical interpretation sometimes given for this approximation is that any cluster that exceeds a prearranged value L larger than l^*, perhaps $2l^*$ say, is artificially removed from the system and recycled (i.e. broken up into monomers which are then restored to the system). To implement this idea systematically one would have to change the $l \geq L$ contributions in eqns (1), (2) and (3). Since the resulting equations are completely unrealistic I will not pursue the idea further here.

We seek a steady solution of the remaining equations (1), (3). From (1) we see that J_l must be independent of l, a constant which we call simply J. This constant is called the nucleation rate: it gives the number of large clusters being formed per unit volume per unit time. Replacing the J_l in (3) by this constant we get a recurrence relation for the c_l's which is to be satisfied subject to the conditions that c_1 has the value already assumed (see eqn (31) and that c_l aproaches 0 for large l. To solve the recurrence relation, divide both sides by $a_l Q_l c_1^{l+1}$ and sum from $l = r$ to ∞, where r is any positive integer. In particular, taking $r = 1$ we get a formula for J:

$$J = J(c_1) \tag{33}$$

where

$$J(z) = \frac{1}{\sum_{l=0}^{\infty} 1/(a_l Q_l z^{l+1})} \qquad \boxed{\text{M2}} \tag{34}$$

Since a_l varies only slowly with l, no faster than a power of l, the series converges; but if c_1 is only just greater than z_s the sum of the series can be very large, and in that case the nucleation rate J is very small, indicating that large clusters are formed only very slowly so that the metastable state may be expected to last fo a very long time.

While this theory has had much success, it is not completely satisfactory from a mathematical point of view because eqn (2) is not satisfied : the left side is equal to zero, whereas the right side diverges to $-\infty$. A treatment of metastability that avoids this defect is given in [5]. The main result is this if the coefficients a_l, b_l, Q_l obey certain (reasonable) conditions, and if the the initial conditions are bounded above by the Becker-Döring approximate solution, denoted here by f_l and defined by

$$f_l(z) = Q_l z^l J(z) \sum_{r:=l}^{\infty} \frac{1}{a_r Q_r z^{r+1}}, \qquad \boxed{\text{fdef}} \tag{35}$$

for some $z > z_s$ then the following results hold:

- $c_l(t)$ is bounded above by $f_l(z)$ for all positive times, and
- the number of super-critical clusters, defined as

  $$M_0(t) = \sum_{l=l^*+1}^{\infty} c_l(t) \qquad \boxed{\text{M0def}} \tag{36}$$

  where l^* is defined as the value of l that maximizes $a_l Q_l z^{l+1}$, has the upper bound

  $$M_0(t) \leq M_0(0) + J^* t \qquad \boxed{\text{M0ub}} \tag{37}$$

  where

  $$J^* = a_{l^*} Q_{l^*} z^{l^*+1} \qquad \boxed{\text{J*}} \tag{38}$$

The theorem also gives a similar upper bound on $M_1(t) = \sum_{l>l^*} l c_l(t)$, the number of particles in supercritical clusters.

If z is close enough to z_s then the upper bound J^* on the nucleation rate implied by (38) is exponentially small, i.e. it goes to zero as $z \searrow z_s$ more rapidly than any power of $z - z_s$. The l^* used in the theorem is not precisely the same as the critical cluster size defined verbally in the first paragraph of this section, but the difference is unimportant since a_l varies much less rapidly with l than Q_l and z^l.

For the situation envisaged in this theorem to correspond to metastablity rather than a simple approach to equilbrium it is also necessary, of course, to have $\sum l c_l(0) > \rho_s$, so that (by the second theorem in section 4) M_0 does eventually become large.

6 Coarsening

There is very little rigorous theory about the way the final equilibrium is approached, but the theory of coarsening, due to Lifshits and Slyozov [4] does give some information. The theory applies to the case where the rate coefficients have (at least for large l) the special form

$$\begin{aligned} a_l &= a_1 l^{1/3} \\ b_{l+1} &= z_s a_1 (l^{1/3} + q) \qquad \boxed{\text{LSab}} \end{aligned} \tag{39}$$

where a_1, z_s and q are positive constants. According to eqn (15), the corresponding cluster partition functions are

$$Q_l = z_s^{-l} \prod_{r=1}^{l-1} (1 + q r^{-1/3})^{-1} \approx \text{const.} \exp(-\frac{3}{2} q l^{2/3}) \qquad \boxed{\text{LSQ}} \tag{40}$$

The assumption is made that c_l varies quite slowly with l when l is large, so that (let us say)

$$c_{l+1} = c_l (1 + O(l^{-1})) \qquad \boxed{\text{smoothc}} \tag{41}$$

Using the approximations (39) and (41) in the BD equations, we obtain for large l

$$J_l = v_l c_l \tag{42}$$

where

$$v_l = a_1 [(c_1 - z_s) l^{1/3} - z_s q] \tag{43}$$

It is further assumed that J_l varies smoothly enough with l to justify replacing the difference in eqn (1) by a derivative, so that it bevomes

$$\frac{dc_l}{dt} = -\frac{\partial (v_l c_l)}{dt} \tag{44}$$

Appendix 1: a lower bound for the Lyapunov function

Since $c_l[\log(c_l//l) - 1]$ has a positive second derivative with respect to c_l, it is a convex function of c_l, and can therefore be bounded below by the tangent to its graph at an arbitrary value of c_l, say c_l^*. Choosing for definiteness $c_l^* = Q_l z_s^l$ and using such a lower bound for every term in the sum (19), we obtain

$$L \geq \sum_{l=1}^{\infty} \{ c_l^* [\log(c_l^*/Q_l) - 1] + (c_l - c_l^*) \log(c_l^*/Q_l) \}$$

$$
\begin{aligned}
&= \sum_{l=1}^{\infty}[c_l l \log z_s - Q_l z_s^l] \\
&= \rho \log z_s - \sum_{l=1}^{\infty} Q_l z_s^l > -\infty
\end{aligned} \tag{45}
$$

as required.

Appendix 2: crude estimates for the plane square lattice

We may define the cluster partition function for clusters of size l at temperature T to be

$$Z_l := \sum_K e^{E(K)/kT} \tag{46}$$

where the sum goes over all translationally inequivalent clusters K of size l, and $E(K)$ denotes the energy of the cluster K, that is to say, the energy increase when that cluster is placed on a previously cluster-free region of the lattice. Then, assuming the density of clusters is sufficiently small to justify ignoring the interaction between clusters, it follows from the grand canonical formalism of statistical mechanics that the equilibrium concentration of clusters of size l is given by

$$c_l^{eq} = Z_l \lambda^l \tag{47}$$

where λ is the activity. Comparing with eqn (14) we see that

$$Q_l = Z_l/(Z_1)^l \qquad \boxed{\text{QZ}} \tag{48}$$

For our example we choose a lattice gas in which the clusters consist of A atoms and the cluster-free sites are B atoms, and the energy of a nearest-neighbour AA pair is $-U$, the other types of pair having zero energy. Our crude approximation, which may possible be reasonable at very low temperatures, is to consider only the largest term in the sum defining Z_l and to use for this term the formula for $E(K)$ appropriate to a square cluster. The number of nearest-neighbour bonds in a square cluster of side $\sqrt{l}$ is $2l - 2\sqrt{l}$, giving the approximation $Z \approx \exp(2l - 2\sqrt{l})U/kT$. Substitution into (48) then gives

$$Q_l \approx \exp 2\beta U(l - \sqrt{l}) \qquad \boxed{\text{A1}} \tag{49}$$

where $\beta := 1/kT$. Even at very low temperatures, (49) is a gross underestimate unless l or $l + 1/4$ is a perfect square, so the right side of (49) is really a lower bound rather than a realistic approximation. Nevertheless the formula (49) implies

$$z_s = e^{-2\beta U} \tag{50}$$

which is consistent with the Yang-Lee theorem which implies that on a finite lattice the singularities of the exact formula for the density must lie on the circle $|z| = e^{-2\beta U}$, indicating that $z_s \geq e^{-2\beta U}$.

The critical cluster size, according to this approximation, is

$$l^* \approx \left(\frac{\beta U}{2 \log(z/z_s)} \right)^2 \tag{51}$$

so that (assuming that a_l = const. = 1, say) the upper bound in (37) on the nucleation rate is

$$J^* \approx \exp - \frac{(\beta U)^2}{2 \log(z/z_s)} \tag{52}$$

which is indeed exponentially small as $z \searrow z_s$.

References

[1] J M Ball, J Carr and O Penrose. The Becker-Döring cluster equations: basic properties and asymptotic behaviour of solutions. Commun. Math. Phys. **104** 657-92 (1986).

[2] R Becker and W Döring. Kinetische Behandlung der Keimbildung in übersättigten Dämpfern. Ann. Phys. (Leipzig) **24**, 719-752 (1935).

[3] J J Burton. Nucleation theory. pp 195-234 of Statistical Mechanics, Part A: Equilibrium techniques, edited by B.J. Berne, Plenum 1977.

[4] I M Lifshitz and V V Slyozov, J Phys Chem Sol 19 35 (1961)

[5] O Penrose. Commun. Math. Phys. **124** 515-541 (1989)