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OSTWALD RIPENING THEORY

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ON LAST STAGE OF PRECIPITATION - OSTWALD RIPENING

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ABSTRACT

Ostwald-ripening theory is deduced and discussed starting from the fundamental principles such as Ising model concept, Mayer cluster expansion, Langer condensation point theory, Ginzburg-Landau free energy, Stillinger cutoff-pair potential, LSW-theory and MLSW-theory. Mathematical intricacies are reduced to an understandable version. Comparison of selected works, from 1949 to 1984, on solution of diffusion equation with and without sink/source term(s) is presented. Kahlweit's 1980 work and Marqusee-Ross' 1984 work are more emphasized. Odijk and Lekkerkerker's 1985 work on rodlike macromolecules is introduced in order to stimulate interested investigators.

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I. INTRODUCTION

1.1. Theory of Ostwald-ripening, pioneers´ work and development

Theories for liquid or solid binary mixture-nucleation, coagulation and droplet growth have been discussed extensively by Binder and Stauffer [1]. The works of pioneers such as Ising model concept [2], Mayer cluster expansion [3], and the Langer-condensation point theory [4], lead to the analytical continuation of the free energy, beyond the experimentally unobservable singularity [3], by conventional droplet model.

Ising-spin system in a magnetic field and a lattice gas are proved to be mathematically equivalent [2]. Mayer cluster expansion considers that the negative sum of the magnetic field and free energy, -(H + F), which is equivalent to pressure of the gas, can be expanded into cluster integrals b_i as $p=kT\sum_{i=1}^{N} b_i z^i$. In which k is Boltzman constant, z is the active number density, T is the absolute temperature, and b_i the cluster integrals defined over the coordinates of i molecules in volume V. The cluster integral depends on the potential energy and coordinates of the i molecules [3]. However, the statistical theory of condensation phenomena developed by Mayer and his coworkers and subsequently by Kann and Uhlenbeck, and Born and Fuchs [5], with its mathematical intricacy, was hardly applied to experimental works.

According to Langer´s condensation theory [4], the stage of degree of evolution is expressed most naturally in terms of the wave number $\vec{k}$. At $\vec{k}_m$ the structure function S(k,t) is a maximum. The structure function S(k,t) is defined as the Fourier transform of the spatial correlation function

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$G(\bar{r},t)$. In principle the structure function can be obtained experimentally by light scattering.

Immediately following the pioneers´ works, Frenkel [6] proposed in 1939 a simplified format of mathematical derivation, which emphasizes that the importance of a droplet radius, therefore the velocity of condensation of a oversaturated vapor and the growth of the droplet can be deduced by the number of molecules (or atoms for monoatomic species) in cluster, since the number of molecules in cluster is related to the average radius of the clusters each containing the same number of molecules or atoms.

Hill [7a,b] applied the cluster-theory in 1955 to imperfect gases and protein solutions. Greenwood [7c] analyzed theoretically the diffusion flow, the smaller to the larger particles for the growth of dispersed precipitates in solutions. Perhaps all these works were related to Bigelow and Trimble´s extensive experimental work [7d] on vapor pressure and particle size. They repeated Ostwald´s experiments [7e] on sulfur, since Ostwald found that, the vapor pressure difference between two droplets of unequal size. Sulfur was the species Ostwald suggested other ones to use for verifying his finding [7d,e]. Finally Greenwood [7c] tried to verify the particle size and vapor pressure relationship, and the growth rate, by use of the well known Thomson-Freundlich equation [7f]. All these lead to the name Ostwald-ageing [9b] and or Ostwald-ripening [18,21a,b].

Greenwood [7c] derived the formulas for the rate of change of particle size and performed calculationss or growth rate for highly dispersed particles. He applied the theory to experimental results of growth in uranium-lead and uranium-sodium slurries.

Stillinger [8] proposed in 1963 a concept of "physical cluster integral" by overlap of spheres drawn each molecule, which are not regarded as statistically independent, but their mutual exclusion property gives rise to free energy of formation, work for cavities necessary to contain those clusters. Stillinger´s work gives a connection between these free energies and a suitable generalization of the Mayer´s irreducible cluster sum. Above all, the most important points are:

1. Hill included the external forces (such as gravitational field) upon the system considered.
2. Stillinger [8] based on Frenkel-Bank theory of association equilibrium intensively and introduced the idea cutoff-potential, V(r), which vanishes identically beyund $r = b$, where $b/2$ is the molecular radius (see Fig. 1).

The kinetics of precipitation from supersaturated solutions, known as Ostwald ripening [7d,e], were examined in detail by Lifshitz and Slyozov [9a], and by Wagner [9b] independently and conventionally termed LSW-theory. Formulas for the asymptotic grain size distribution, for the number of grains per unit volume, and for the supersaturation as a function of time, were all established by the LSW-theory.

1.2. Phase separation, its hydrodynamic/chemical-kinetic analogy

A thermodynamically unstable system separates into its components is termed spinodal decomposition [10a,b]. Phase separation is clearly a nonequilibrium and nonlinear phynomenon. For this reason, Siggia [10a] used models of fluid systems that typically would manifest themselves in the so called later stage of spinodal decomposition. Prior to Siggia´s work, Langer

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and his coworkers [10b] performed series of calculations with the theory of spinodal decomposition through reagion in which it is difficult to distinguish from nucleation and growth. The experimental part concerning this topic was carried out by Cahn and Hilliard in metallurgical systems [10c,d]. Light scattering experiments were carried out by Huang, Goldburg, Bjerkaas, Wong, Knobler and Chou [10e-h], in order to verfy Siggia´s theoretical argument [10a] and Langer, Bar-on, and Miller (LBM) theory [10b]. More detail can be found in Section IV.

The interaction between molecules or between ions, which leads to cluster formation and eventually to the evolution of crystals, has been likened to a chemical reaction so that the chemical kinetic theories can apply [11a]. Similar to chemical reaction, the activation energy the barrier to nucleation must be overcome before crystallization can occur, so that the intermeadiate stage and the last stage of precipitation can follow. One result of the energy barrier is the necessary creation of some degree of supersaturation before spontaneous crystallization will occur [11aii]. The cluster formation can be dealt with chemical equilibrium expressions [22c], for instance, $\beta = A_n/A^n$ for $nA = A_n$ and $\beta_{n+k} = A_{n+k}/A_n A_k$ for $A_n + A_k = A_{n+k}$. However, in adding or subtracting monome(s) to or from a growing aggregate, thousands of steps forward and backward may be needed to consider.

Siggia [10a] discussed in detail the influence of hydrodynamic interaction on the coarsening rate of a mist of droplets combining through diffusive coalescence. He emphasized that the "volume fraction" of precipitate actually produced in most off-critical quench experiments probably favors direct coalescence (the zero volume fraction was taken as in LSW - theory).

According to Landau's theory the free energy can be expanded in a power series of the order parameter ρ and its derivative. By minimizing the free energy one obtains the most probable value of ρ. Landau made assumption that the most probable value of ρ coincides with the mean value $\bar{\rho}$. Ginzburg modified Landau's theory to a more realistical form which bears the name Ginzburg-Landau free energy [10a].

I.3. Theories of crystal growth, LSW-theory and MLSW-theory

The theories of crystal growth have been divided into two categories:

1. Those describing the rate-limiting process in terms of transport to the crystal surface are called diffusion controlled (or limited) growth (dl-cases).
2. Those relating the rate control to processes occuring in the interface region (i.e., precipitation of crystals from a stirred liquid solution) are called interface controlled (or kinetic) growth (ik-cases).

Diffusion controlled growth has been a subject of continued interest for decades [11], starting probably with the old Noyes-Whitney [11b], Nernst [11c] equations and developing to the sophisticated approaches by Frisch [12], Ham [13], finally by Lifshitz and Slyozov and Wagner [9].

The theory of diffusion-controlled particle coarsening developed by LSW was modified by Ardell [14], to take into account the volume fraction, ϕ, of the precipitate [15]. The characteristic distance chosen for computational purpose was related to the mean free path between a particle and its nearest neighbor. Also spherical symmetry was assumed. It was named the modified LSW theory (MLSW-theory) by Ardell [14]. The MLSW-theory

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predicts that while the basic $t^{1/3}$ kinetic of the LSW theory is maintained, the coarsening rate increases with increasing volume fraction even at very small volumes of ϕ [14-16,21b].

At zero volume fraction ($\phi = 0$) the MLSW-theory is equivalent to the LSW-theory. The MLSW theory was justified for several alloys such as with the available data in the coarsening rates of A-precitates in A-B alloys such as Co in Cu-Co alloy. Ardell discussed [14] the works by Sarian and Weart and Asimow [16] as they proposed that the mean particle diameter d_{av} and number of particles per unit volume N_v are functioin of temperature T, volume fraction ϕ, and time t,

$$d_{av} = f(T, \phi)\, t^{1/3}, \quad N_v = f(T, \phi)\, t^{-1}$$

Ardell also emphasized that the Dirichlet region for a 2-dimensional distribution of circular particles (see Fig. 2), the concentration of solute in the matrix must approach

$$C(r) \Big|_{r=r'} = C(r') = C'$$

at a distance from the ith particle, where

$$r' = r_i + L/2, \quad L = \text{mean free path}$$

Felderhof and Deutch [17] dealt with the concentration dependence of the rate of diffusion-controlled reactions, particularly in steady state situation for a random distribution of the sinks (precipitate particles). The sink concentcration is a function of rate constant k, the size distribution function P. The rate constant is predicted to increase with concentration of sinks and the dependence on concentrationis shown to be nonanalytic.

I.4. Time rate of changing particle radius-growth law

Brailsford and Wynblatt [18] derived the spatially homogeneous rate theory model, to describe the time rate of change of radius of a spherical particle embedded in a confgurational random array of particles of like nature but differing in size only. The growth rate so derived by B & W is incorporated with LSW-hydrodynamic model of particle coarsening and the asymptotic size distribution determined as a function of the particle volume fraction ϕ, is in agreement with earlier workers. It is shown that the diffusion controlled coarsening the basic kinetic form r_{av}^3 is proportional to kt, where r_{av} is the mean particle radius r_{av}, t is time as usual, and k is the rate constant a function of the volume fraction Φ.

Bixon and Zwanzig [19a] reexamined the diffusion problem in a median with static traps (sinks), and obtained the first order in density. They obtained a long time tail solution for its steady state situation included more complicated dynamical processes that appear to lead to contributions of higher order in the trap density. The work of B & Z was extended by Kirkpatrick [20] in which the time dependent transport situation is well discussed by adding a class of density corrections which are divergent for long times and that when these divergent terms are resummed they modified the lowest order result of B & Z.

I.5. Works by Marqusee-Ross and by Kahlweit

Marqusee and Ross [21a] presented a new derivation for the last stage of phase separation in the kinetics of a first order phase transition, precipitation, where Ostwald ripening is the dominant mechanism. They used a time scaling [21a,c,d] technique and derived the power law time dependence and distributions for the size of the particles of the new phase. The derivation classifies and corrects prior size of the particles of the new phase. Equations are derived for the corection terms to the distribution in power laws. The derivation classifies and corrects prior work. In a succeeding paper [21b], M & R extend the theory of Ostwald ripening to include the dependence of the volume fraction [14-16,18,21b] of the minority the precipitate (see Appendix A), the multiscattering [18-20,21b,d] approaches (see Appendix C), and the power laws of the time dependences for the late stages of phase separation, Ostwald ripening.

The work of LS and Wagner (the so called LSW-theory) has been criticized by Kahlweit in a series of papers [22a,b]. He claims that their asymptotic solutions are not those of the last stage of phase separation but rather those of earlier intermediate stage. A 3-dimensional schematic representation [22aii] and a 2-dimensional one [22b,c], in distribution of particule number density on particule size, demonstrate his idea very clearly.

Marqusee and Ross [21a] claim that LSW´s solution are correct and that they are the leading terms in the expansion of long time solution. As for the contradiction in fixed total mass of precipitate yet allowing the monomer concentration to change, M & R show that the assumption does not affect the lowest order term in the expansion.

I.6. The main goal of this work

The present paper is intended to reduce the mathematical intricacy of all the pioneers´ theories (LSW-theory, MLSW-theory) in order to simplify them to an understandable version. Several appendices are added for this purpose. Some discussions are also included for stimulating new ideas for latter improvement of Ostwald ripening theory.

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Following this introduction, we emphasize the fundamental concepts (Section II) and asymptotic distribution for particle sizes (Section III), which obeys an equation of continuity in R space (Section III, Eq. 3.1). Key points for approximate solution of complicated process, experimental efforts following theories, and the theory applicability to alloys are discussed (Section IV). A comparison of related works on solution of diffusion equation withand or without sink/source term(s) in time period of four decades is presented (Section IV, Table 2). We evaluate the growth law (appendix A), deduce continuity equation and its Laplace transform (Appendix B), demonstrate multiscattering representation and its Fourier transform (Appendix C), and show example for solution of Fick's 2nd law (Appendix D). Two figures contain in Section I, one table and seven figures are in section III, and one table in Section IV. All these effortcs are for simplifying the theory and drawing the distance between ideality and reality more closer.

Most of the related works containing in literature are for systems with spherical sinks (precipitate particles). For more complicated system Odijk and Lekkerkerker [47] have recently reported a theoretical approach on the phase separation for a solution of bidisperse rodlike macromolecules. It is worthwhile to pay attention to such a system (see Section IV, Subsection IV.6).

(Figures 1 and 2 are in this Section I, see Figure Captions, p. 69, and the Figures followed.)

II. FUNDAMENTAL CONCEPTS

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II.1. Diffusion equations

Consider a general equation for diffusion,

$$\partial C/\partial t = D_o \, v^2 C + A \qquad (2.1)$$

in which C is the concentration of a supersaturated solution, D_o is the diffusion coefficient and A is the sink/source term. If replace C by T (the temperature), D_o by $\kappa/\rho s$ (the thermal-conductivity divided by density-times-specific-heat), A by $A'/\rho s$, then the expression becomes equation of heat conduction [23a].

For steady state case, $\partial C/\partial t = 0$, Eq. (2.1) reduces to

$$v^2 C = - A/D_o \qquad (2.2)$$

Eq. (2.2) is called the Poisson's equation. In case A =0, no sink/source and is also in steady state, then, Eq. (2.2) reduces to

$$v^2 C = 0 \qquad (2.3)$$

which is called the Laplace's equation. Another case is, no sink/source but is not under steady state, from Eq. (2.1) one obtains

$$\partial C/\partial t = D_o \, v^2 C \qquad (2.4)$$

Eq. (2.4) is called the equation of continuity. In fluid dynamics, if consider v as the velocity of the fluid of density ρ, then $V= \rho v$ is called the flux density and represents the total flow of fluid per unit cross section in unit time. If no fluid is created or distroyed within the small volume element $d\tau$, this loss of mass (if any) must equal $-(\partial\rho/\partial t)d\tau$, so that

$$v.V = -\partial\rho/\partial t \qquad (2.5)$$

Eq. (2.5) is called the equation of continuity [23a] in fluid dynamics. If replace ρ by C and V by j, $j=-D_o v^2 C$, then Eq. (2.5) becomes Eq. (2.4) the equation of continuity. If consider steady state and without sink/source, Eq. (2.5) reduces to (2.3), the Laplace´s equation. Laplace´s equation and the equation of continuity are very important in solving diffusion equation problems.

For the last stage of phase separation, when the nucleation is neglible, the distribution of particle size obeys a continuity equation in R space, where R is the radius of the partice,

$$\partial n(R,t)/\partial t + \partial\{V[R,C(t)]n(R,t)\}/\partial R = 0 \qquad (2.6)$$

Where n(R,t) is the number density of the precipitate particles, and

$$V[R,C(t)] = dR/dt$$

is the growth rate of a precipitate particle, here C(t) is the average monomer concentration [21a],

$$\begin{aligned} C(t) &= C_{in} - \text{change of concentration due to precipitation} \\ &= C_{in} - \int_C^{\infty} [(4/3)\pi R^3/v_m] n(R,t)dR \qquad (2.7) \end{aligned}$$

$$\begin{aligned} V[R,C(t)] &= dR/dt \\ &= (Dv_m/R)[C(t) - C_{eq}(R)] \qquad (2.8) \end{aligned}$$

where C_{in} is the initial monomer concentration and v_m is the molecular volume of the solute.

If the solution is not stirred (the diffusion limited case), the first step is to transport C to the interface (by diffusion), and the second step is to incorporate monomers into the precipitate particle. Therefore the quasistationary solution [9b] for diffusion limited growth (dl-case) of a spherical particle is

$$V^{dl}[R,C(t)] = [C(t)-C_{eq}(R)]Dv_m/R \qquad (2.9)$$

For the precipitation of crystals from a stirred liquid solution (the ik-case), the growth rate follows a first order law [9b] as

$$V^{ik}[R,C(t)] = kv_m[C(t)-C_{eq}(R)] \qquad (2.10)$$

Where k is a constant and in dimension $cm^5 molecule^{-1} sec^{-1}$,

$k = D/\delta = \mathcal{D}$ ($\mathcal{D}$ is Lifshitz-Slyozov's notation [9a]), δ is density,

$$dR/dt = V[R,C(t)] \begin{cases} > 0, & \text{if } C(t) > C_{eq}(R) \\ < 0, & \text{if } C(t) < C_{eq}(R) \end{cases}$$

Therefore, we may call $[C(t)-C_{eq}(R)]$ the driving force for crystal growth or dissolution.

II.2. LSW - theory and Kahlweit's deduction

According to LSW-theory, the size distribution asymptotically approaches a time independent shape,

$$n(R,t) \rightarrow f(t)g(\rho) \quad \text{for } t \rightarrow \infty$$

where $\rho=R/R_c$, a dimemsionless length, and R_c is the critical radius. This result follows from the assumption that the ageing rate , $d\Phi/dt$, defined in the particular case (22aii) according to LSW-theory [9].

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$$d\Phi/dt = d(R_c)^2/dt \rightarrow b > 0, \text{ for } t \rightarrow \infty \qquad \text{(see Fig. 1)}$$

where $b = 2kv_m 2\sigma C(\infty)/(k_B T)$, in which k_B is the Boltsmann constant, the other constants have the usual meaning. Kahlweit's derivation (22aii) follows from the conclusion that the ageing rate defined in this particular case by $d\Phi/dt = d(R^2)/dt$. Since according to LS-theory [9a, Eq.2],

$$dR/dt = (\mathcal{D}/R)(\Delta - \alpha/R), \quad \Delta = \alpha/R_c, \quad \alpha/R = C(R) - C(\infty), \text{ so that}$$

$$\begin{aligned} d\Phi/dt &= 2R\, dR/dt \\ &= 2k(\Delta - \alpha/R) \\ &= 2k[(\alpha/R_c) - C(R) + C(\infty)] \end{aligned}$$

Since as $t \rightarrow \infty$, $C(R) \rightarrow C(\infty)$, therefore

$$d\Phi/dt \rightarrow 2k\alpha/R_c = 2k[2\sigma v_m C(\infty)/k_B T]/R_c = b > 0$$

in which $\mathcal{D} = D/\delta$ has been replaced by k, the rate constant for this particular case, precipitation of crystals from a stirred liquid solution [22aii]. However, Kahlweit (22ai) showed that the latter conclusion is incorrect. Instead, $d\Phi/dt$ may be seen as a measure of $-dC/dt$ as shown in Figure 3, increases rather rapidly after the nucleation period and then passes through a maximum during the early stages of precipitation to slowly approach zero for $t = \infty$.

II.3. Sink density and competition of sinks in precipitation

Consider the total number of molecules (or moles) in one sink changes with time as

$$\begin{aligned} d(4\pi R^3/3v_m)/dt &= k(R)\,\rho \\ &= k(R)[C_{av} - C_{eq}(R)] \end{aligned}$$

$$= 4\pi R^2 dR/dt \qquad \text{(see Appendix A)}$$

The above expression is for one sink only. In competition with other sinks the expression [21b] will be

$$4\pi R^2 dR/dt = 4\pi D_o R[1+R\sqrt{4\pi\rho\langle R\rangle}][C_{av}-C_{eq}(R)]$$

$$dR/dt = (D_o/R)[1+R\sqrt{4\pi\rho\langle R\rangle}][C_{av}-C_{eq}(R)] \qquad (2.11)$$

II.4. Particle size plays an important role in precipitation competition

The driving force for ageing of the precipitate is originated from the surface free energy difference between different sizes of molecules. The surface free energy is related to the size of the droplet for a liquid-vapor system in the following way: The vapor pressure of smaller droplet will be higher than that of the bigger droplet as follows,

$$\ln (p_2/p_1) = (2\gamma M/\rho_d RT)(1/a_2 - 1/a_1)$$

$$= (2\gamma v_m/kT)(1/a_2 - 1/a_1) \qquad (2.12)$$

where ρ_d is the density of the condensed phase precipitate, γ is the surface tension, p_1, p_2 are the vapor pressures of the droplets with radii a_1, a_2 respectively. M/RT is the molecular weight divided by RT, gas constant times the absolute temperature. This fact or principle favors the growth of larger particles and derives the precipitate to decrease its surface/volume ratio, that is growing bigger in expense of dissolving the smaller particles.

Similar deduction can be applied to solid-liquid phase transitions. A number of observations of the growth of solid particles in a liquid medium at the expense of smaller particles have previously been reported [7c,d].

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Greenwood [7c] proposed a general analysis of particle growth using Thomson-Freundlich equation [7f]:

$$\ln(S/S_a) = 2M\sigma/(RT\rho_d a) \tag{2.13}$$

Where S is the true solubility, S_a the solubility in contact with a particle of radius a, σ the interfacial tension between solid phase and liquid phase, and M/RT has the usual meaning. Bigelow and Trimble [7d] repeated Ostwald's experiment [7e] on sulfur and perhaps led the name Ostwald ageing [9b] and or Ostwald ripening [18,21a,b] for the last stage of precipitation in binary or multicomponent systems.

For a special particle and an ideal solution, the R depencence of $C_{eq}(R)$ is

$$\begin{aligned} C_{eq}(R) &= C_{eq}(\infty)\exp(\alpha/R) \\ &= C_{eq}(\infty)(1+\alpha/R) \end{aligned} \tag{2.14}$$

where $\alpha = 2\gamma v_m/k_B T$ [21a,b].

Conventionally, a set of reduced variables are used as follows:

$r=R/\alpha$, $\tau = t/T$, $T^{di} = \alpha^2/Dv_m C_{eq}(\infty)$ and

$$T^{ik} = \alpha/[kC_{eq}(\infty)], \quad \sigma(\tau) = [C(t)-C_{eq}(\infty)]/C_{eq}(\infty) \tag{2.15}$$

in which $T=(R_{co})^3/\alpha\pounds$ in LS-notation [9a].

Briefly, there exists a critical radius R_c which is the particle radius in equilibrium with the surrounding solution, and R is the effective particle radius [9b] defined as

$$R = 2\,dV/dO = 2\,d[(4/3)\pi R^3]/d(4\pi R^2) \tag{2.16}$$

The statistical theory of number density as a function of particle size first established by Smoluchovski [24c] as a linear function of time t is

$$1/n = 1/n_o + \text{const}.t \tag{2.17}$$

where const = $4\pi DA$, in which A is the radius of action, D is the diffusion coefficient, and n and n_o are the number densities at time t and t_o respectively. Smoluchovski also reached a mathematical deduction formula for the number of monomers in cluster in such a way

$$n_k = n_o(t/T)^{k-1}/(1+t/T)^{k+1} \tag{2.18}$$

where n_k is the number density of clusters, in which each cluster contains k monomers, and T is a constant which equals $(4\pi DAn_o)^{-1}$.

II.5. Mass transfer in crystal growth

The interface of a crystal grain represents not only a sink for matter but also a source of both heat and matter. The rate with which crystal building blocks are incorporated into the solid is governed by the difference of their chemical potential in the two phases in contact. Though for the time dependent position and shape of an interface one must simultaneously consider the conservation of mass, momentum and energy for the system in question, however. one may simplify the problem by reasonable assumptions (such as steady state approximation, isothermal condition, etc.).

A critical discussion on diffusive mass transfer in crystal growth was given by Westphal and Rosenberger [27]. The discrepancies between predicted and measured growth rates were attributed to the formal description which ignored the limited analogy between heat transfer and mass transfer and the

Nernst-Brunner unstirred film model. However, the intricacy of mass transfer in crystal growth can be simplified by proper approximations. Drastic simplications can be made for the crystal growth continuity equations - rate of gain in mass, in momentum, in internal and kinetic energy [27b, Eqs. 5.1 - 5.3]. As for convection may be neglected when the crystal grains are smaller than about 10 μ, because the crystals move with the fluid [28]. Under such circumstances one would expect the growth rate to be insensitive to stirring. Furthermore, the diffusion fields of the particles have been found to be independent of one another if the average distance between them is larger than about 10 times their diameter. Under such circumstances diffusion controlled growth has been observed [29,30].

Phase equilibria and chemical equilibria depend on temperature, thus a temperature difference can cause a solid to dissolve in a fluid at one temperature and deposit elsewhere at a different temperature. Gradients of many types cause relative motion of the components of a mixture with respect to one another. Hurle et. al. pointed out [31] that transport takes place whenever a difference in chemical potential exists, such as between stable and metastable phases of the same material.

By experimental measurements one may reduce the intricacy of the diffusion mass transport problem by imposing an isothermal condition. Also one may focus attensions to the reference frames chosen for the flows of the entire system.

For studies on multicomponent isothermal diffusion it is customary to describe the transport matter by means of flow equations which are extensions of Fick's first law. These equations express the flow of current J_i of component i as a sum of concentration gradients each multiplied by a diffusion coefficient D_{ij} (named as practical diffusion coefficients) of one type. In theoretical work the corresponding phenomenological equations are usually written as sums of forces, i.e., the negative gradients of chemical potentials each multiplied by a diffusion coefficient D'_{ij} of another type [32]. The two sets of diffusion coefficients dependent on the frame of reference selected. Onsager's reciprocal relations [33] hold between certain of the D'_{ij} and the testing of these relations by using data for the D_{ij} together with certain thermodynamic data. Correct tests of the Onsager reciprocal relations require proper specification of the reference frame. Usually, the solvent fixed frame and the volume fixed frame are used. The former is used when the chemical potential gradient of the solvent is eliminated from the flow equations, and which is used for computing D'_{ij} from D_{ij}, and then for evaluating these D_{ij} from those for the volume fixed frame. The volume fixed frame is important to the experimental measurements of diffusion. For the solvent fixed or mass fixed frames some auxiliary data such as partial specific volumes are required for determination of partial diffusion coefficients. Kirkwood [32] considered, for certain frames of reference, as is the problem of measuring practical diffusion coefficients correctly where the partial specific volumes are dependent on concentration and the solutions therefore exhibit a change of volume on mixing [32].

In addition to isothermal condition, the phenomenological description of diffusion in isotropic mixtures has been developed from the expression for the entropy production and the relation between the diffusion coefficients in accordance with Onsager reciprocal relations [34].

II.6. Entropy production and Onsager reciprocal relations

The phenomenological description of diffusion in isotropic mixtures is derived from the expression for the entropy production and the relation between diffusion coefficients, resulting from the Onsager relations [34a]. The entropy production σ of the vectorial irreversible phenomena can be written in the form

$$\sigma = \sum_{k=1}^{n} J_k \cdot X_k \tag{2.19}$$

where J_k are the components of fluxes and X_k are the forces. In isotropic media

$$J_k = \sum_{j=1}^{n} L_{kj} X_j, \quad k=1,2,\ldots.n \tag{2.20}$$

In the absence of magnetic field, the Onsager relations [4b,d] state that

$$L_{kj} = L_{jk}, \quad j,k=1,2,\ldots.n \tag{2.21}$$

The system described by Eq. (2.15) can be solved for the X_j, the new scheme of phenomenological coefficients again being symmetrical, i.e.,

$$X_j = \sum_{k=1}^{n} L_{jk}^{-1} J_k, \quad L_{jk}^{-1} = L_{kj}^{-1} \tag{2.22}$$

The entropy flow J_s and entropy production σ can be deduced from the thermodynamics equation $TdS = dE + PdV - \sum_{i=1}^{n} \mu_i dC_i$. It demonstrates that the entropy prodection contains four different contributions [35, Eq. 21]:

1) heat conduction (due to temperature gradients),

2) diffusion (due to concentration gradients),

3) viscous flow (due to velocity gradients), and

4) chemical reaction.

For systems without heat conduction and without chemical reaction the contributions reduce to two.

II.7. Thermodynamical argument on crystal growth

Since by controlling the heat removal from the fused metal the metallugist can give the casting the requisite structures, Ivantsov studied the growth kinetics of different crystal structures [36a]. When the crystal is small and the growth rate very small, the system will be almost isothermal, i.e., the effect of uneven temperature distribution will be vanishingly small.

In addition to the diffusion process, the molecular kinetic process in crystallization under supersaturation is equally important [36b], especially for controlling the crystal-grain sizes [36c]. The fundamental aspects of crystal growth concern: a) the atomic processes of phase change, b) surface energy, and c) heat and matter transfer. a) and b) influence the geometry of the interface. c) determines the temperature and compositions of crystal growth [36d]. The interface roughness is a measure of entropy of fusion since the interface being rough for metals and smooth for most nonmetals, and the entropy of phase change is small for rough surfaces and large for smooth surfaces. According to this fact one may find, for some reason, compounds which may have low entropy of fusion freeze like metals [36e].

The spontaneous precipitation is a process toward a state of low entropy. However, from the point of view of statistical mechanics, all

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molecular processes must be reversible. Besides, there is a theorem in dynamics due to Poincare, which states that in a system of material particles under the influence of forces which depend only on the spatial coordinates, must, in general, be able to return to the initial state to any desired degree of accuracy [24bii].

In accordance with Boltsmann's point of view bsed on probability, Smoluchowski's theory of fluctuation in molecular concentrations [24] allows us to bridge the gap between the region of the macroscopically irreversible diffusion and the microscopically reversible fluctuation.

thermodynamically a spontaneous process can occur when the free energy change is less than zero even if the entropy of the system is decreased. The Gibb's thermodynamic potential, i.e., the Gibb's free energy, can be deduced for the precipitation in supersaturated solution as follows:

1) $$dG = -Sdt + VdP + \gamma dA + \sum_i \partial G/\partial n_i dn_i$$

$$dG_p = -SdT + \gamma dA + \sum_i \overline{G}_i \, d\, n_i, \qquad (2.24)$$

during the latent period, $dT > 0$, so $-SdT<0$, where S is the entropy of the entire system. The 3rd term of Eq. (2.24) is < 0, since $dn_i < 0$ for the solute while precipitation occurs and n of the solvent is unchanged, hance $dG<0$. Note that though the 2nd term γdA should be >0 (the interfacial tension $\gamma>0$, $dA >0$) for one crystal growing, however for the crystal growth in expenditure of smaller particles a summation of $\gamma_i dA_i$ should be used. As long as $\{dA_i\}$ are negative except the one of the crystal which is growing, therefore the 3rd term has no significant contribution to the free energy change.

2) Consider the phase change being isothermal,

$$dG = d(H - TS) + \gamma\, dA + \sum_i \overline{G}_i\, dn_i$$

$$= dH - TdS + \gamma\, dA + \sum_i \overline{G}_i\, dn_i \qquad (2.25)$$

in which $dH < 0$, $-TdS > 0$ (sinc $dS<0$ in precipitation), the 4th term is less than zero, and the 3rd term has small significance as discussed above, therefore we expect $dG<0$.

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III. ASYMPTOTIC DISTRIBUTION FOR PARTICLE SIZES

III.1. Fundamental equations and reduced variables

Define n(R,t) as the number density of particles with radius R per unit volume of solution. N(R,t) can only change by growth from nuclei or dissolution of precipitate particles. It must obey a continuity equation in R space in the specific dynamic system,

$$\partial n(R,t)/\partial t + \partial/\partial R\{V[R,C_{av}(t)]n(R,t)\} = 0 \qquad (3.1)$$

Where $\{V[R,C_{av}(t)]n(R,t)\}$ is called the flux density and represents the total flow of fluid per unit cross section in unit time [23a]. It is also assumed that the particles are stationary and nucleation is neglected, i.e. the sink/source term in Eq. (A.1) of Appendix A is nearly zero and is omitted. The precipitate-particle density at time t is N(t) (see Fig. 3), which is conventionally termed (t), and expressed as

$$N(t) = \int_0^\infty n(R,t)dR \qquad (3.2)$$

One can see from Fig. 3

$$\int_0^\infty n(R,t_1)dR = N(t_1) \text{ and } \int_0^\infty n(R,t_2)dR = N(t_2)$$

The $(n,t)_{R=0}$ plane, in Fig. 3, illustrates the course of development of the mean concentration of monomers with time [22aii], which is related to cavity theory [36,45] and theory of fluctuations [24bii]. The $(R,t)_{n=0}$ plane shows the trajectoory of the projections of critical radius of the clusters changes with time. The planes parallel to the $(n,R)_{t=0}$ plane represent the size distribution as it changes with increasing time.

The distribution function can change by: 1) growth of particles, 2) dissolution of particles, and 3) the creation of new particles due to nucleation. For last stage of phase separation, in case the nucleation rate is negligible, the distribution obeys an equation of continuity in R space as shown in Eq. (3.1) above.

As mentioned in Section II, by introducing reduced variables "r" or "a", τ, and $\sigma(\tau)$ [21a,b], the continuity equation in reduced variables [21e] becomes:

$$\partial/\partial\tau F(a,\tau) + \partial/\partial a\{F(a,\tau)V[a,\sigma(\tau)]\} = 0 \qquad (3.3)$$

with the growth law [21f] as:

$$V[a,\sigma(\tau)] = a^{-\lambda}[\sigma(\tau) - 1/a],\ \lambda=1 \text{ for dl-cases}$$
$$=0 \text{ for ik-cases} \qquad (3.4)$$

The dimensionless reduced variables are defined [21g] as:

$$a=R/\alpha,\quad \tau=t/T,\quad \sigma(\tau) = [C(t)-C_{eq}(\infty)]/C_{eq}(\infty) \qquad (3.5)$$

III.2. Decay function in supersaturation

$\sigma(\tau)$ is the supersaturation at $t \geqslant 0$, at $t = 0$ $\sigma(0)$ is called σ_{in}. As time goes on, as Ostwald ripening begins, $\sigma(\tau)$ decreases, so that it is a measure of the decay of the supersaturation, i.e.,

$$\sigma(\tau) = \sigma_{in} - \kappa\int_0^\infty a^3 F(a,\tau)da \qquad (3.6)$$

The constants in Eqs. (3.5) and (3.6) [21h] are:

$\alpha = 2\gamma' v_m/k_B T$,

$T^{ik} = \alpha/kC_{eq}(\infty)$, $T^{dl} = \alpha^2/D_o v_m C_{eq}(\infty)$, and

$$\mathcal{K} = 4\pi\alpha^3/[3v_m C_{eq}(\infty)] \tag{3.7}$$

where γ is the surface tension and $C_{eq}(\infty)$ is the concentration in equilibrium with a macroscopic particle.

The ageing rate and the time development of the size distribution of a precipitate have been analyzed both experimentally and theoretically [22] on micelle association and dissociation in surfactant solutions. Kinetic equations have been given a form which suggests an analogy with heat conduction. Experimental methods, mostly in relaxation times, have been deduced for the net distribution of the rearrangement among the micelles [37].

Equations (3.3) to (3.7) are the starting point of the analysis of the last stage of phase separation [21a]. In order to find the asymptotic solution of the partial differential equation, the continuity equation, (3.3), one has to analyze $N(t)$ and $\sigma(\tau)$. After the rapid growth of the newly formed nuclei, the number of the precipitate particles $N(t)$ and the supersaturation $\sigma(\tau)$ are known to decay slowly. The number of colloidal particles decreases slowly. The supersaturation $\sigma(\tau)$ decreases slowly from $\sigma<1$ to approaching zero. The total mass of precipitate increases slowly. The average radius $\langle R \rangle$ increases slowly. All these imply that no exponential law of decay but power laws [21a,b].

III.3. Power expansion and scaled distribution function

Since $\partial F/\partial t \neq 0$ (in the sense of fluid dynamics, it is not incompressible), therefore

$$v.\underline{V} \neq 0, \quad \underline{V} = V[a,\sigma(\tau)]F(a,\tau), \text{ i.e.,}$$

$$v.\underline{V} = \partial/\partial a\ \{[V(a,\sigma(\tau)]F(a,\tau)\},$$ for a spherical-function-solution.

A power expansion which is sufficient for the determination of the properties of spherical function defined in the interval $0 < a < a^*$, where a^* is a characteristic constant, which can be used as the asymptotic solution of the differential equation. In such cases the differential equation can be integrated "asymptotically" for very great values of the variable [23b], so that the solution can be interpreted asymptotically.

In extracting the lowest decay from the distribution function and write it in the long-time limit [21b], Marqusee-Ross's scaled form for the distribution takes the following form:

$$F(a,\tau) = \tau^{-y}F_o(z); \quad z=a\tau^{-x}$$

or, takes the form as in their preceding paper [21a], but setting r = a, one obtains:

$$F(a,\tau) = \tau^{-4x} \sum_{n=0}^{N} \tau^{-nx} F_n(z) \tag{3.8}$$

$$z = a\tau^{-x} \quad \text{and} \quad \partial/\partial a = \tau^{-x}\partial/\partial z \tag{3.9}$$

Substituting Eqs. (3.8) and (3.9) into (3.3) and (3.4), one may solve the continuity equation and deduce the growth law in reduced variable forms, as showing in (3.10) and (3.11) respectively (see below).

$$\partial F(a,\tau)/\partial\tau + \partial/\partial a\ \{F(a,\tau)\ V[a,\sigma(\tau)]\} = 0 \tag{3.10}$$

$$V[a,\sigma(\tau)] = (z\tau^{x})^{-\lambda}[\sum_{n=1}^{\wedge} \sigma_n \tau^{y_n} - (1/z)\tau^{-x}] \tag{3.11}$$

In which $\sigma(\tau) = \sum_{n=1}^{\wedge} \sigma_n \tau^{-y_n}$ has been introduced. The distribution of long time limit in its scaled form is:

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$$F(a,\tau) = \tau^{-y} F_o(z), \quad z = a\tau^{-x}$$

As in the method of series expansion, (3.10) can be solved by substituting (3.8) and (3.11) into (3.10) with the aid of (3.9). By collecting the coefficients on both sides of the ultimate equation, for a certain n, the following rules hold:

a_n of $F_n(z)$ on LHS = a'_n of $F_n(z)$ on RHS

b_n of $dF_n(z)/dz$ on LHS = b'_n of $dF_n(z)/dz$ on RHS

where a_n, a'_n are coefficients of $F_n(z)$ on LHS and RHS respectively; b_n, b'_n are coefficients of $dF_n(z)/dz$ on LHS and RHS respectively.

Using these rules one finds that $(2+\lambda)x - 1 = 0$, therefore

$$\begin{aligned} x &= 1/(2+\lambda) \\ &= 1/2 \quad \text{for } \lambda = 0 \quad \text{ik-case} \\ &= 1/3 \quad \text{for } \lambda = 1 \quad \text{dl-case} \end{aligned}$$

Consider two values of n, n=0 and n=1, one obtains:

$$4x\, F_o(z) + xz\, d/dz\, F_o(z) = d/dz\, \{z^{-\lambda}(\sigma_1 - 1/z)F_o(z)\} \tag{3.12}$$

$$5x\, F_1(z) + xz\, d/dz\, F_1(z) = d/dz\, \{z^{-\lambda}(\sigma_1 - 1/z)\, F_1(z) - \sigma_2\, F_o(z)\} \tag{3.13}$$

The operator d/dz, on the RHS in both Eq. (3.12) and Eq. (3.13), may generate $dF_o(z)/dz$ and $F_o(z)$ terms which can be combined with the LHS proper terms. In this way one obtains the scaled continuity equations, and scaled growth rates $\omega(z, \sigma_n)$ as follows,

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$$-F_o(z) + d/dz\,\{\omega(z, \sigma_1)\, F_o(z)\} = 0 \qquad (3.14)$$

$$-F_1(z) + d/dz\,\{(3/4)\omega(z, \sigma_1)\, F_1(z)\} + d/dz\,\{\omega(z, \sigma_2)\, F_o(z)\} = 0 \qquad (3.15)$$

$$\omega(z, \sigma_1) = z^{-\lambda}\,[\,\sigma_1 - 1/z]/3x - z/3 \qquad (3.16)$$

$$\omega(z, \sigma_2) = z^{-\lambda}\,\sigma_2/4x \qquad (3.17)$$

Here $\omega(z, \sigma_n)$ are the "scaled growth rate" expressions.

III.4. Scaled growth rate as function of scaled radius

Plottings for $\omega(z, \sigma_1)$ versus z with different λ and σ_1 are shown in Fig. 4 and Fig. 5. The calculated data for the plottings are listed in Table 1.

Figs. 4 and 5 show that as $\omega(z, \sigma_1) = 0$ and $d\,\omega(z, \sigma_1)/dz = 0$, one obtains the optimum values of z, as z_o, and σ_1 the decacy function of the supersaturation, for different values of λ and x, i.e.,

$$\lambda = 0,\ x = 1/2,\ z_o = 2^{1/2} = \sigma_1$$

$$\lambda = 1,\ x = 1/3,\ z_o = (3/2)^{1/3},\ \sigma_1 = (9/4)^{1/3} = z_o^{\,2} \qquad (3.18)$$

The general form of the distribution function, $F_n(z)$, in the last stage of phase separation. can be solved by integration using separation of variable and other techniques. For instance, consider Eq. (3.14), by separation of variables, one obtains:

$$dF_o(z)/F_o(z) + d\,\omega(z,\sigma_1)/\omega(z,\sigma_1) = [\omega(z, \sigma_1)]^{-1}\,dz \qquad (3.19)$$

which is $d \ln\{F_o(z)\,\omega(z, \sigma_1)\} = [\omega(z, \sigma_1)]^{-1}\, dz$ (3.19)′

III.5. Scaled Distribution in Zero Volume Fraction of Sinks

After integration Eq. (3.19)′ the scaled distribution function, $F_o(z)$, is obtained as:

$$
\begin{aligned}
F_o(z) &= \text{const}[\,\omega(z, \sigma_1)]^{-1} \\
&\qquad \times \exp\int_0^z [\omega(z', \sigma_1)]^{-1} dz', \quad z <= z_o; \\
&= 0, \quad z > z_o
\end{aligned}
\tag{3.20}
$$

Substituting (3.16) into (3.20) for $\lambda=0$ and $\lambda=1$ respectively, and using the proper values of z_o and σ_1 (i.e. using Eq. (3.18)), then by tedious manipulations, one obtains:

1. For $\lambda = 0$, $x = 1/2$, $z_o = 2^{1/2}$, $\sigma_1 = z_o = 2^{1/2}$

$$[\,\omega(z, \sigma_1)]^{-1} = -3z/(2^{1/2} - z)$$

$$
\begin{aligned}
F_o(z) &= (C_o\,\sigma_{in}/\kappa)\,z(2^{1/2}-z)^{-5} \\
&\qquad \times \exp[-3z/(2^{1/2}-z)], \quad z <= 2^{1/2}; \\
&= 0, \quad z > 2^{1/2}
\end{aligned}
\tag{3.21}
$$

2. For $\lambda = 1$, $x = 1/3$, $z_o = (3/2)^{1/3}$, $\sigma_1 = (9/4)^{1/3} = z_o^{\,2}$

$$[\,\omega(z, \sigma_1)]^{-1} = -3z^2/[z^3 - 3z_o^{\,2}z + 3]$$

$$
\begin{aligned}
F_o(z) &= (C_o\,\sigma_{in}/\kappa)\,z^2(2z_o+z)^{-7/3}(z_o-z)^{-11/3} \\
&\qquad \times \exp[-z/(z_o-z)], \quad z <= (3/2)^{1/3};
\end{aligned}
$$

$$= 0, \quad z > (3/2)^{1/3} \qquad (3.22)$$

The above results are obtained by using various integrating techniques, including change of variable and rational fractions [23c]. Eq. (3.22) is for the dl-case and with the assumption of negligible nucleation, i.e., $\phi = 0$.

By use of the imposed normalization condition for $F_o(z)$ [21a],

$$\sigma_{in} = \kappa \int_0^\infty z^3 F_o(z)dz \qquad (3.23)$$

one may substitute $F_o(z)$ for $z <= z_o$, in expression (3.22), into (3.23), to obtain the constant c_o. Numerical calculation method may be used for evaluating c_o. Since $\sigma_{in} c_o / \kappa$ is just the normalization constant for $z^3 F_o(z)$. The justification may be made by rearranging Eq. (3.23) to the following expression:

$$\begin{aligned} \sigma_{in}/\kappa &= \int_c^\infty z^3 F_o(z)dz \\ &= \text{const} \int_0^\infty z^3 f_o(z)dz \\ &= \text{const}/c_o \end{aligned} \qquad (3.23)'$$

in which $c_o^{-1} = \int_0^\infty z^3 f_o(z)dz$ has been imposed, so that

$$(\sigma_{in}/\kappa)c_o = \text{const}$$

That is to say, if the integral can be evaluated, c_o^{-1} is obtained, so is the constant in Eq. (3.23)'.

For expression (3.21) of $z <= z_o$, evaluation of c_o may be evaluated by change of variable several times, then the integral may be reduced to a standard form named "exponential integral", so that proper mathematical table can be used [23d].

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III.6. Scaled distribution in nonzero volume fraction of sinks

With $\phi \neq 0$, correction term should be added, it can be written [21b], after another tedious manipulation, for instance, for $\lambda = 1$, dl-case,

$$\omega(z, \sigma_1) = (1/z)[\ \sigma_1 - 1/z][1 + z\epsilon\ ] - z/3$$

$$F_o(z) = C_o z^2 (z_o - z)^{-\alpha} (z + 3/z_o^2)^{-\beta}$$

$$\times \exp[-\delta z/(z_o - z)], \quad z <= (3/2)^{1/3}$$

$$= 0, \ z > (3/2)^{1/3} \tag{3.24}$$

Here $\alpha = 2 + (3z_o^7 + 18z_o^4)/(z_o^3 + 3)^2$

$$\beta = 1 + 27/(3 + z_o^3)^2$$

$$\delta = 3z_o^4/(3 + z_o^3) \tag{3.25}$$

and $\epsilon = [3\phi_\infty a_o \rho_o]^{1/2}$

$$\phi_\infty = (4\pi/3)\int_0^\infty R^3 n(R, \infty) dR \tag{3.26}$$

Here ϕ_∞ is the equilibrium volume fraction of precipitate in solution (or in melt) after given quench, or equivalently $\phi_\infty = [C_{in} - C_{eq}(\infty)]v_m$ [21b]. The effect of equilibrium volume fraction ϕ_∞ on the scaled distribution function can be seen from a set of plottings, $F_o(z)$ vs z in dl-case for different ϕ_∞ (ϕ_∞ =0, 0.005, 0.015, 0.035, and 0.075) as shown in Fig. 6.

It is interesting to note that,

$R\,[4\pi\rho\langle R\rangle]^{1/2}$

$= a\,[4\pi\rho\langle a\rangle]^{1/2}$, when replace R by $\alpha\, a$, and ρ by $\overline{\rho}/\alpha^3$

$= z\,[3\phi_\infty a_o\, \rho_o]^{1/2}$, when the following conditions are imposed:

1) $n(R,t)dR = [3\phi_\infty/(4\pi\alpha^3)]F(a,\tau)da$,

2) $\int_0^\infty z^3 F_o(z)dz = 1$, and

3) $a = z\tau^x$, $\langle a\rangle = a_o\tau^x$, and $\overline{\rho}(a) = \rho_o\tau^{-x}$.

By numerical calculation method, plottings for z_o vs ϕ_∞, ζ(reduced coarsening rate) vs ϕ_∞, and a_o, σ_1, ρ_o, vs ϕ_∞ are shown in Figs. 7, 8, 9 respectively. From Fig. 9 one can see that, as ϕ_∞ slowly increases with time, the average radius $a_o(\phi_\infty)$ increases slowly, the supersaturation $\sigma_1(\phi_\infty)$ decreases slowly, but the density of particles or droplets of the minority phase $\rho_o(\phi_\infty)$ decreases faster than the change of degree of supersaturation. It can be deduced in this way, even if the supersaturation reaches a minimum ρ_o still changes fast because the expenditure of smaller particles in growing the bigger ones should drastically reduce the number density ρ_o. Therefore the following power laws may be considered as the time rate as if ϕ_∞ instantaneously being kept constant.

$a_o \sim t^{1/3}$,

$\sigma_1 \sim t^{-1/3}$, and

$\rho_o \sim t^{-1}$.

Table 1. $\omega(z, \sigma_1) = z^{-\lambda}(\sigma_1 - z^{-1})/3x - z/3$, $x = (2+\lambda)^{-1}$

z	$\lambda=0$, $x=1/2$, ik-case, $\omega(z, \sigma_1)$			$\lambda=1$, $x=1/3$, dl-case, $\omega(z, \sigma_1)$			
	$\sigma_1=1$	$=2^{1/2}$	$=2$	$\sigma_1=1$	$=(9/4)^{1/3}$	$=2^{1/2}$	$=2$
1/2	-0.83	-0.56	-0.17	-2.17	-2.05	-1.34	-0.17
1	-0.33	-0.06	0.33	-0.33	-0.02	0.08	-0.67
$(3/2)^{1/3}$					0		
$2^{1/2}$		0					
3/2	-0.28	-0.002	0.39	-0.28	-0.07	-0.002	-0.40
2	-0.33	-0.06	0.33	-0.42	-0.26	-0.21	0.08
3	-0.56	-0.28	0.11	-0.78	-0.68	-0.64	-0.44
4		-0.56	-0.17	-1.15	-1.07	-1.04	-0.90
graphs, ω vs z	(See Fig.4, $\omega = \partial\omega/\partial z = 0$, as $z_o = \sigma_1 = 2^{1/2}$.)			(See Fig.5, $\omega = \partial\omega/\partial z = 0$, as $z_o = (3/2)^{1/3}$, $\sigma_1 = (9/4)^{1/3}$.)			

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IV. DISCUSSION AND CONCLUDING-REMARKS

IV.1. Concentration gradient as driving force in diffusion

Consider one of the precipitate particles (sinks), around it there is a concentration gradient for the other species, and that the rate of flow of solute molecules in this concentration gradient is governed by Fick´s law of diffusion. The Smoluchowski´s theory on the kinetics of colloid coagulation as a diffusion-controlled process using Fick´s law of diffusion [24a,38] led series of investigations and applications in this field both theoretically and experimentally [39].

The mathematical solution for the fundamental differential equation governed by Fick´s 2nd law drew attentions of a great number of physicists, chemists, and scientists of related fields [39,40]. Here we deal with the situation around one sink particle in very law sink concentration. In this case, the concentration gradient for the unprecipitated solute in solution is set up and the rate of flow of monomers of the solute into (or out from) the sink (or source) can be solved by imposing proper boundary conditions. For instance, in case the system is increasing supersaturation, i.e., the sink shrinks and is becoming a source (giving up monomers instead of absorbing monomers), the concentration gradient of the monomer is negative, $\nabla C(r,t) < 0$. As the Ostwald ripening begins, the concentration gradient will be reversed, i.e., $\nabla C > 0$. so that the monomers diffuse into the precipitate (the sink).

IV.2. Solution of Fick´s law, comparison between selected works

For $\nabla C > 0$, $C(R,t) = 0$ is a proper boundary condition for Ostwald

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ripening process both in physical meaning and mathematical logic. Since in Ostwald ripening the monomer whenever strikes the surface of the sink, shall be incorporated with the sink encountered. However, if not every monomer reaching the reaction radius incoporates with the sink, an obvious modification is to be assumed [38].

In Table 2, we outline several representative works in this field, in different time period (1949 to 1984), from which techniques in solving the fundamental partial differential equation, $\partial C/\partial t = D\nabla^2 C + A$, with $A = 0$ and or $A \neq 0$, in accordance with imposed boundary condition (B. C.) and initial condition (I. C.), are worth learning. For instance, the boundary and initial conditions for the last stage of precipitation (Ostwald ripening) are $C(R,t)=0$ and $C(r,0)=C_0$ $R<r<=\infty$ respectively in most of the methods cited in Table 2. However, there is a singularity at $t=0$ for the solution chosen by Collins & Kimball [38], since they used the technique in solving second order partial differential equation on linear flow of heat [41]. Also, since $C(R)=0$ can not be correct if not every monomer which reaches the reaction radius reacts. Their modification for the boundary condition is $C(R)=\gamma(\partial C/\partial r)_R$. We can see that the modified B. C. still holds if $C(r)_R$ = constant so that $(\partial C/\partial r)_R = 0$.

IV.3. Approximate solution for complicated process, example

Reiss and La Mer [42] proposed a very interesting idea: moving boundaries, connected with the growth of coilidal particles. For this complicated process, the differential equation is difficult to treat mathematically. In considering the boundary being not stationary, the boundary value problem is not soluble by means of the familiar methods. So that approximate solution techniques were used [42a].

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Interference of growing spherical precipitate particles were treated by Wert and Zener [43a] using approximate method in a relatively simple manner. A transformation law to fit the experimental data was developed by Wert [43b], and results of derivations of Zener [43c] were used to calculate the mean distance between nucclei [43b]. Following are the concepts and equations they developed and applied for experimental fitting:

1. The amount of precipitate formed at any time is proportional to $C_o - C(t)$.

2. The rate of transformation of the particles of a second phase growing in a matrix without mutual interference may be written as,

   $$dW(t)/dt = f(t) \qquad (4.1)$$

   where W(t) is the fraction of transformed material and f(t) is some function of time. However, if interference between precipitate particles are considered, the rate will be lessened and the decrease will be proportional to the fraction already transformed, so that the modified equaztion becomes,

   $$dW(t)/dt = [1 - W(t)]f(t) \qquad (4.2)$$

3. Eq. (4.2) can be integrated directly and the integrated form is

   $$W(t) = 1 - \exp[- \int_0^t f(t')dt'] \qquad (4.3)$$

   An explicit form used by Wert [43b] for Eq. (4.3) is

   $$C(t)/C_o = 1 - \exp[(- (t/\tau)^n] \qquad (4.4)$$

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where $\Delta C(t)$ is the amount of transformed material, $\Delta C(t)=C_0-C(t)$, C_0 is the initial concentration of solute, τ is a time constant depending on C_0, T (the temperature of the system), and other undertermined factors.

4. τ can be determined by fitting experimental data to log-ln-form of Eq. (4.4), i.e.,

$$\log \ln[C_0/\Delta C(t)] = n \log t - n \log \qquad (4.4)'$$

by plotting $\ln[C_0/\Delta C(t)]$ versus t in log-scale, for a certain temperature T, the slope is n and the intercept is τ^{-n}, so that

$$\tau = \text{intercept}^{-1/\text{slope}}$$

Data for the precipitation of Fe_3C in α-iron at various temperatures were used for fitting [43b]. By taking average of the slopes for different temperatures they obtained

$$n=1.45$$

Which can be approximated as $n=3/2$ as being used conventionally [43d]. The slope, n, varies between 1.2 to 1.7 from 43°C to 312°C, while τ varies from about 12000 minutes to 0.5 minute [43b].

5. The radius of the spherical precipitate particle, S, varies with time [43c] according to,

$$S = \alpha_\lambda (Dt)^{1/2} \qquad (4.5)$$

where D is the atomic diffusion coefficient, α_λ is the dimensionless growth coefficient, in which λ is the number of dimensions. For shperical particles $\lambda=3$ of course. α_3 takes the form:

$$\alpha_3 = K_3[(n_\infty - n_1)/(n_o - n_\infty)]^{1/2} \qquad (4.6)$$

Where n_o = concentration of solute in precipitate,

n_1 = concentration of solute in the matrix which is in equilibrium with the precipitate, and

n_∞ = concentration of solute in the matrix far away from the precipitate.

IV.4. Experimental efforts following Theories

Light scattering studies of phase separation in fluid mixtures [10e-10h] have provided a wealth of information about the complex, highly nonlinear processes by which a new phase forms in a system that was originally homogeneous. By light scattering and by direct microscopic observation Chou and Goldburg [10g] confirmed the early conjecture of Cahn and Moldover (Ref. 1 of [10g]) that hydrodynamic effects are important in the late stage of the process, since droplet growth is speeded up by fluid flow which in turn is driven by the curvature of irregular surfaces which interpenetrate the nucleating fluid. Wong and Knobler [10f], using an ingenious pressure-jump technique to quench the system, made extensive light scattering measurements of phase separation in isobutyric acid and water. They found that when the critical mixture is quenched, the two-phase region scatters light in the form of a ring which brightens, sharpens, and decreases in diameter as the system evolves toward its final equilibrium state.

In accordance with Siggia's theoretical hydrodynamic arguments [10a], Wong and Knobler [10h] experimentally found that the crossover wave number corresponding to the maximum in the scattering, k_m, decreases initially as $t^{-1/3}$ and at long times as t^{-1}. Their earlier work [10f] shows an initial t^2 growth in $I(k_m)$, the intensity of scattering, followed by a slower growth $t^{1/2}$, correspondingly Siggia [10a] proposed a crossover from $r \sim t^{1/3}$.

THe existence of crossover can be related to the volume fraction of the new phase, ϕ. Wong and Knobler [10h] found that in dilute mixtures

$$k_m = At^{-1/3} \text{ with } A=A(\phi) \text{ for } 0.02 <= \phi <= 0.10 \qquad (4.7)$$

and they found their case for $\phi < 0.02$ is equivalent to Lifshitz-Slyozovc growth in which A is supposed to be independent of ϕ. Wong and Knobler [10h] aalso compared their results with the quantitative nonlinear theory by Langer, Bar-on, and Miller [10b] usually called LBM-theory, and with computer simulation on model systems, they found close agreement between experiment, theory, and computer simulation [10h].

IV.5. Application of theory to alloys

It is well known, in fluid dynamics, the diffusion constant of a spherical drop of one fluid in another of similar viscosity [10a,26b] is

$$D = k_BT/5\pi\rho\mu a \qquad (4.8)$$

Where a is the radius, ρ is density, and μ is viscosity. Consider drops of radius R_i, diffusion constant D_i, and number density ρ_i, for i=1,2, one finds that, according to collision theory, the number of collosions between the two populations per unit time per unit volume [10a] is:

$$I_{1,2} = 4\pi(R_1+R_2)(D_1+D_2)\rho_1\rho_2 \qquad (4.9)$$

If each collision causes one new droplet formation, then one may expect a population of drops agglutination at a rate given by (4.9) approches a stationary distribution when scaled by average values R, D, and ρ, i.e., $R_1+R_2=2R$, $D_1+D_2=2D$, and with the assumption $\rho_1 \rho_2 \sim \rho^2$, then

$$\partial \rho / \partial t = -16\pi D(R) R \rho^2 \qquad (4.10)$$

with $(4\pi/3)R^3 \rho = \phi \qquad (4.11)$

Where D(R) is the diffusion coefficient for a particle of radius R and ϕ is the volume fraction of particles.

By using the definition of kinematic viscosity [26c], $\nu = \eta / \rho$ and substituting η / ρ for ν into (4.8), also replace "a" in (4.8) by R just for convenience, one obtains

$$D(R) = k_B T/5\ \pi R \qquad (4.12)$$

Substituting (4.12) into (4.10) with the aid of (4.11), after integration, one obtains the power laws

$$\rho \sim t^{-1} \quad \text{and} \quad R \sim \phi^{1/3}\, t^{1/3} \qquad (4.13)$$

However, for the case of a binary alloy where we have a solid particle in a solid matrix or in very high viscous fluid, the diffusion coefficient at low temperatures is estimated [16b,21b] to depend on the radius as

$$D(R) \sim 1/R^4 \qquad (4.14)$$

and at high temperatures as

$$D(R) \sim 1/R^3 \qquad (4.15)$$

By use of the same deduction one can obtain the power laws as

$$\rho \sim \phi^{1/2}\, t^{-1/2} \quad \text{and} \quad R \sim \phi^{1/6}\, t^{1/6}$$

for low temperature case, and

$$\rho \sim \phi^{2/5}\, t^{-3/5} \quad \text{and} \quad R \sim \phi^{1/5}\, t^{1/5}$$

for high temperature case. Similar but simplier analyses can be found elsewhere [21b].

One may use Gibbs-Kelvin (Gibbs-Thomson) equation [46a], and write into the following form

$$C(R) = C(\infty)\exp[\Delta\mu(R)/kT] \simeq C(\infty)[1+\Delta\mu(R)/kT]$$

If higher order term(s) being added [46b], such as

$$C(R) = C(\infty)[1 + a_{-1}R^{-1} + a_{-4}R^{-4}]$$

with $a_{-1}=f(\sigma, v_m)$, $a_{-4}=f(q, \epsilon, v_m)$ [46b]. In which σ is surface tension, q is charge of the particle, approximated as $|q_i q_j|=q^2$, ϵ is dielectric constant of the medium, and v_m is molecular volume of the monomer as usual. However, the surface tension is also a function of droplet size and is expected to decrease with decreasing in droplet size over wide range of circumstances [46c], therefore the absolute value of a_{-1} and a_{-4} are governed by v_m, $\sigma(R)$, q, and ϵ. Note that $a_{-1} > 0$, since $2\sigma v_m > 0$ [46d]; and $a_{-4} < 0$ [46b] as long as $q_i q_j < 0$. For colloidal particles, always with residing charges, the above inverse power law in droplet radius is worthwhile to apply.

IV.6. System containing nonspherical sinks

So far we only discussed systems with assumed spherical particles.

Odijk and Lekkerkerker recently reported [47] their work on theory of the isotropic-liquid crystal phase separation for a solution of bidisperse rodlike macromolecules. They used Gaussian trial functions that depend on adjustible parameters which were found by minizing the free energy of the system. Since the rods are never ideally hard particles, they are always flexible, therefore Odijk and Lekkerkerker took only the leading terms from the asymptotic expansion of the Onsager theory in studying the complicated influence of bidispersity. They found that the longer rods more highly ordered than the shorter ones [47].

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Table 2. Comparison of Selected Works on Solution of

$\partial C/\partial t = D\nabla^2 C + A$, with A=0 and or A≠0 *

Ref.	B. C. and I. C.	Solution, C(r,t), while A=0 or A/0
Collins & Kimball 1949 [38]	$C(R,t)=0$ $C(\infty,t)=C_o$ $C(r,0)=C_o$, r>R R=sink radius	$C(r,t)=C_o\{1-(R/r)\mathrm{erfc}[(r-R)(4Dt)^{-1/2}]\}$ Proposed B.C.: $C(R)=(\ C/\ r)_R$, $\gamma=D/k$ D=diffusion coeff., k=rate constant (See Appendix D.)
Reiss & La Mer 1950 [42a]	$C(r,0)=C_o$ $C(x,t)=C_o e^{-\gamma Bt}$ $(\partial C/\partial r)_{r=h}=0$ γB=constant x=sink radius h=higher limit of boundary $C(h,t)=\langle C(t)\rangle$ (See Fig. 2 b)	(1) A=0 $C(r,t)=C_o e^{-\gamma Bt}+C_o x/r\sum_{n=1}^{\infty}\sin\alpha_n(r-x) \times \dfrac{\gamma B[\exp(-\alpha_n^2 Dt)-\exp(-\gamma Bt)]}{(\gamma B-\alpha_n^2 D)\alpha_n\beta_n^2}$ *** (2) A=-k(t)/D and C(x,t)=0 assumed $C(r,t)=C_o x/r\sum_{n=1}^{\infty}\exp(-\alpha_n^2 Dt)[\sin\alpha_n(r-x)]/\alpha_n\beta_n$ + higher order terms (x<r<h)
Lifshitz & Slyozov 1961 [9a]	$C=C(t)$, $C(0)=C_o$ $C_R=C_{eq}$ at the boundary C_∞=sat. conc. R_{co}=critical radius at t=0	$C_R=C_\infty+\alpha/R$, $\alpha=(2\sigma/kT)v_m C$ $j=\mathcal{D}(\partial C/\partial r)_{r=R}=(\mathcal{D}/R)(C-C_R)$ $=(\mathcal{D}/R)(\Delta-\alpha/R)$, $\mathcal{D}=D/\delta$, δ=density $\Delta=C-C_\infty$=degree of supersaturation at t>0 $\Delta_o=C_o-C_\infty$=degree of supersaturation at t=0 $dR/dt=\mathcal{D}/R\,(\Delta-\alpha/R)$

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Table 2. (continued)

Wagner 1961 [9b]	C=average conc. C_r'=surface conc. of particles with radius=r C_r=saturated conc for particles with radius=r C_o=sat. sol'n of particles of $r=\infty$	$C_r=C_o[1+2\sigma v_m/\nu rRT]$, $\nu=1$ for undissociated $dr/dt=[kDv_m/(kr+D)](C_r-C)$ $= -(Dv_m/r)(C_r'-C)$, for kr>>D, dl-case $= -kv_m(C_r'-C)$, for kr<<D, ik-case R=gas constant T=absolute temperature
Felderhof & Deutch 1976 [17]	$n(r)=0$, $r=R$ $=C$, $r=\infty$ Here n(r) is equivalent to C(r).	(1) $A=0$, $n(r) = n_o - n_oR/r$ $J=\int_S jds=4\pi D_oRn_o=k_on_o$, $j=-D_o\nabla n$ (2) $A=-k_o\rho\langle n\rangle$, $\partial\langle n\rangle/\partial t=D_o\nabla^2\langle n\rangle-k_o\rho\langle n\rangle$ ρ= sink density $n(r)=n_o+e_o.r-n_o(R/r)-e_o.r(R/r)^3$ (See Appendix B.)
Marqusee & Ross ** 1984 [21b]	$C(r,t)_R=C_{eq}(R)$ $C(r,t)_{r\to\infty}=C_o$	(1) $A=0$, $C(r,t)=C_o[1-R/r]+C_{eq}(R)R/r$ $J_T=4\pi D_oR[C_o-C_{eq}(R)]$ (2) $A=-4\pi\rho/v_m\int_0^\infty R^2V[R,\langle C\rangle]P(R)dR$ $V[R,C]=dR/dt=(D_ov_m/R)[\langle C\rangle-C_{eq}(R)]$ C(r,t) see Appendix B. $\underline{C}(r,\lambda)$ and $\hat{C}(q,\lambda)$ see Appendix C.

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* A=sink/source term(s), B.C.=boundary condition, I.C.=initial condition.

** Similar works in period of 1979-83 have previously reported [18-21b].

*** α_n and β_n see definitions defined in [42a]-Eqs. 11 and 12.

(Figures 3 to 9 are in this Section IV, see Figure Captions, p. 89, and the Figures followed.)

APPENDIX A

EVALUATION OF THE GROWTH LAW

Consider a spherical sink (the precipitate particle) of radius R,

$(4\pi/3)R^3/v_m$ = volume of the sink/molecular volume

= total number of molecules in one sink = n (per sink)

Let $I = dn/dt$ = rate of molecular adsorption or desorption on the sink surface

$$= d/dt[(4\pi/3)R^3/v_m]$$

$$= (4\pi/v_m)R^2 dR/dt \qquad (A.1)$$

or equivalently, $d[(4\pi/3)R^3]/dt = v_m\, dn/dt$.

Note that, since, $I = J_T$ and J_T is the total flux of mass getting into a single isolated particle, i.e.,

$$J_T = -\int_s ds.j = -4\pi R^2 \underline{n}.J \qquad (A.2)$$

where $\underline{n}$ is the out normal unit vector on the sink surface. The negative sign in Eq. (A.2) takes care of the case for negative ∇C, in order to make j positive (see Appendix B). By definition,

$$j = -D_o \nabla C(r,t) = -D_o\, \partial C(r,t)/\partial r$$

and since [21b],

$$C(r,t) = C_o[1-R/r] + C_{eq}(R)\, R/r$$

is the solution of Laplace-equation in the concentration field arround a single sink, which satisfies boundary conditions

$C(r,t)_{r=R} = C_{eq}(R)$ and

$C(r,t)_{r=\infty} = C_o$, therefore

$$j = -D_o[C_o - C_{eq}(R)]/R \qquad (A.3)$$

Substituting (A.3) into (A.2), one obtains,

$$J_T = 4\pi R D_o[C_o - C_{eq}(R)] \qquad (A.4)$$

After equating (A.1) and (A.4), one obtains for one single sink and consider t=0,

$$dR/dt = (D_o v_m/R)[C_o - C_{eq}(R)] \qquad (A.5)$$

For $t > 0$ and for a distribution of particles with number densioty, ρ, and probability size distribution function, $P(R)$, we define an average concentration $C_{av}(r,t)$ under the asumption of particle independence, such that,

$$C_{av}(r,t)/\ t = D_o v^2 C_{av}(r,t) - (4\pi\rho/v_m)\int_0^{\infty} R^2 dR/dt\ P(R)dR \qquad (A.6)$$

The microscopic concentration field [20, 21b] obeys the steady state diffusion equation (see Appendix B).

Now, consider the rate of molecular absorption or desorption, $I(=J_{total})$, number-density of sinks $n(R,t)$ or (R,t) as used by some authors, the super saturation $[C-C_{eq}]$, and the volume fraction ϕ [14-16,18,21b] of the sinks,

$$I = k(R)\ \rho_o = 4\pi D_o R\ \rho_o$$

$$= 4\pi D_o R[C_o - C_{eq}(R)], \text{ as } t=0, \ \phi=0 \qquad (A.7)$$

$$I = k(R)$$

$$= 4\pi D_o R[C_{av} - C_{eq}(R)], \text{ as } t>0, \ \phi=0 \qquad (A.8)$$

$$I = k(R)$$

$$= 4\pi D_o R\ [1+R\sqrt{4\pi\rho\langle R\rangle}][C_{av} - C_{eq}(R)], \text{ as } t>0, \ \phi>0 \qquad (A.9)$$

Here $4\pi D_o R$ is responsible for the effect of the size of the single particle, $[1+R\sqrt{4\pi\rho\langle R\rangle}]$ is responsible for the effect of particle concentration, and $[C_{av} - C_{eq}(R)]$ is responsible for the effect of concentration field difference, the extent of supersaturation.

The growth law now becomes:

$$V(R, C_{av}) = dR/dt$$

$$= (D_o v_m/R)[1+R\sqrt{4\pi\rho\langle R\rangle}][C_{av} - C_{eq}(R)] \qquad (A.10)$$

This is the growth law and competition of sinks (precipitate particles) and under the influence of the concentration field gradient as well. now, the rate constant in (A.9) becomes

$$k(R) = 4\pi D_o\ R[1+R\sqrt{4\pi\rho\langle R\rangle}] \qquad (A.11)$$

APPENDIX B

CONTINUITY EQUATION AND ITS LAPLACE TRANSFORM

As consider the sinks to be completely at rest, the monomer concentration, C(r,t), satisfies the diffusion equation

$$\partial C(r,t)/\partial t = D_o \nabla^2 C(r,t) \qquad (B.1)$$

in the part of the space occupied by the solution. The microscopic concentration field obeys the steady state diffusion equation

$$\nabla^2 C(r,t) = 0 \qquad (B.2)$$

The so called Smoluchowski-boundary condition [24] requires C(r,t) to vanish at the surface of the sink. the problem has the obvious electrostatic analogue of finding the potential for a collection of ideally grounded metal spheres.

According to Smoluchowski-theory [24] for the steady state reaction rate in a dilute system of spherical sinks, at sufficiently low sink density the competitiuon for solute molecules between sinks can be neglected and one needs consider only the effect of a single sink. One assumes that a monomer diffusing toward the sink is absorbed instantaneously upon contact and expresses this by requiring C(r,t) to vanish at the surface of the sink. In a steady-state situation one therefore must solve Eq. (B.2). The boundary condition imposed on Eq. (B.2) is

$$C(r,t) = 0, \text{ at } |r-r_i| \le R \qquad (B.3)$$

where R is the sink radius (see Fig. 2). The initial condition is

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$$C(r,t) = C_o(r) \text{ at } t = 0 \qquad (B.4)$$

For uniform concentration C_o at infinity, the solution is

$$C(r) = C_o - (C_o R/r) \qquad (B.5)$$

For convenience, one may choose the coordinate origin located at the center of the sink, so that from r=0 to r=infinity, there are numerous vectors with r=R located on the surface of the sink. In this manner the meaning of k_o is self-evident, since

$k_o = 4\pi D_o R$ implying k_o proportional to R (see below)

The molecular flux encountering the sink surface is

$j = -D_o \nabla C$, by operating ∇ on Eq. (B.5) one obtains

$\nabla C = C_o R/r^2$

$J = \int_S j.ds$ = the total flux absorbed per second per sink after integrating over the surface of the sink

$$= \int_0^{2\pi}\int_0^{\pi}(D_o C_o R/r^2)\, r^2 \sin\theta \, d\theta \, d\phi$$

$$= 4\pi D_o R C_o = k_o C_o$$

On a macroscopic scale the equation for the average monomer concentration is $C_{av} = \langle C \rangle$, therefore the continuity equation becomes

$$\partial \langle C \rangle / \partial t = D_o \nabla^2 \langle C \rangle - k_o \rho \langle C \rangle \qquad (B.6)$$

with the rate constant $k_o = 4\pi D_o R$ and sink number density ρ.

Since C(r,t) in a concentrated solution varies rapidly, therefore it is no longer true that the concentration tends to a constant at a large distance from a single sink. The magnitude of the effect of gradients may be estimated by solving Eq. (B.2) with the condition

$$C(r) = C_o + e_o \cdot r \quad \text{as } r \text{ approaches infinity [17]}$$

The solution is:

$$C(r) = C_o + e_o \cdot r - C_o(R/r) - e_o \cdot r(R^3/r^3) \qquad \text{(B.7)}$$

The particle flux into the sink is still $J = 4\pi D_o R$, so that it appears that concentration gradients have no effect. However, the dipolar disturbance (the last term in Eq. (B.7)) makes itself felt at large distances and, when summed over a large number of sinks, contributions significantly to the average local particle density.

If replace Eq. (B.1) by a microscopic equation valid for all space with added sink terms representing the monopole and dipole contributions [17],

$$\partial C(r,t)/\partial t = D_o[v^2 C(r,t) - 4\pi \sum_{j=1}^{N} q_j \delta(r-r_j)$$

$$+ 4\pi \sum_{j=1}^{N} p_j \cdot v\delta(r-r_j)] \qquad \text{(B.8)}$$

where $C(r,t)=0$ at $r-r_j <= R$ (inside the sink or at the sink surface). By use of (B.8) one may take average as follows:

$$\text{LHS: } \langle \partial C(r,t)/\partial t\rangle = \partial C_{av}/\partial t = \partial \langle C\rangle/\partial t$$

$$\text{RHS: } \langle D_o{}^2 C(r,t)\rangle = D_o v^2 \langle C\rangle - 4\pi D_o \langle \sum_{j=1}^{N} q_j \delta(r-r_j)\rangle + 4\ D_o \langle \sum_{j=1}^{N} p_j \cdot v\delta(r-r_j)\rangle$$

After equating the two sides, one obtains:

$$\partial\langle C\rangle/\partial t = D_o v^2\langle C\rangle - 4\pi D_o Q(r,t) + 4\pi D_o P(r,t)$$

$$= v.[D(\rho)v\langle C\rangle] - k(\rho)\,\rho\langle C\rangle \qquad (B.9)$$

with $k(\rho)\rho\langle C\rangle=4\pi D_o Q$ and $D(\rho)v\langle C\rangle=D_o v\langle C\rangle+4\pi D_o P$ [17]. Eq. (B.9) accounts for the competition for monomers between sinks, as implied by $k(\rho)$. It also shows, by $D(\rho)$, the diffusion motion will be affected by sink concentration ρ.

If choose only the monopole sink term which only approximates the boundary condition but not affects the first order correction. The steady state solution of $D_o v^2 C(r,t)=$ (r)+ q_j $(r-r_j)$ has the formal solution [21b],

$$C(r,t)=G_o*\phi(r) + \sum_{j=1}^{N} G_o(r-r_j)q_j$$

Here the symbol G_o* denotes the convolution, as an integral operator,

$$G_o*\phi(r)=\int dr' G_o(r-r')\,\phi(r')$$

and $G_o(r)=-1/4\pi D_o r$ is the free diffusion propagator. The Green's function for the operator $D_o v^2$ is, according to Green's Theorem [23a,p.242],

$$G(r-r') = -1/(4\pi D_o|r-r'|)$$

Actually, "Smoluchowski" boundary condition, $C(R,t) = 0$, at the surface of the particle is not self-evidently valid [25a], so that the "radiation" boundary condition [25b] may be employed. Wilemski and Fixman [25c] compared these two boundary conditions and made them equal as set $\epsilon=0$ in $C(R+\epsilon$..

The continuity equation (B.1) with boundary condition and initial condition (B.3) and (B.4) respectively is more convenient to work with the

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Laplace representation obtained by Laplace transformation of Eq. (B.1) as follows:

$$L\ f(t)=\text{Laplace transform of } f(t)=\int_c^{\infty} f(t)e^{-\lambda t}dt=\underline{f}(\lambda)$$

$$L\ \{\partial C(r,t)/\partial t = D_o\nabla^2 C(r,t)\}=\text{Laplace transform of Eq. (C.1)}$$

$$\text{LHS: } L\ \partial C(r,t)/\partial t = \int_0^{\infty} \partial C(r,t)/\partial t\ e^{-\lambda t}dt = C(r,t)e^{-\lambda t}\Big|_0^{\infty} + \int_0^{\infty} \lambda C(r,t)^{-\lambda t}dt$$

$$= -C_o(r) + \lambda\underline{C}(r,\lambda)$$

$$\text{RHS: } L\ D_o\nabla^2 C(r,t) = D_o\nabla^2\int_0^{\infty} C(r,t)\ e^{-\lambda t}dt = D_o\nabla^2\underline{C}(r,\lambda)$$

The Laplace representation for (B.1), with boundary condition (B.3) and initial condition (B.4), now becomes:

$$\underline{C}(r,\lambda) - C_o(r) = D_o\nabla^2\underline{C}(r,\lambda),\ \lambda \text{ is the Laplace transform variable,}$$

$$\underline{C}(\left|r-r_i\right| <=R,\ \lambda) = 0,\quad i=1,2,\ldots\ldots N.$$

This difussion problem can be viewed as a case of multiple scattering, and the above equations are equivalent to a set of simultaneous equations by statistical averaging and mean field approximation [17,18] or by Fourier-Laplace transform to obtain a configurational average Green's function [19]. The latter method has been used by many aurthors [20,21]. A brief discussion is shown in Appendix C.

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APPENDIX C

MULTISCATTERING REPRESENTATION AND ITS FOURIER TRANSFORM

As shown in Appendix B, the Laplace transformed representation for the partial differential equation, $\partial C(r,t)/\partial t = D_o \nabla^2 C(r,t)$, is an ordinary differential equation in the form

$$\underline{C}(r,\lambda) - C_o(r) = D_o \nabla^2 \underline{C}(r,\lambda) \qquad \text{(C.1)}$$

where λ is the Laplace transformation variable amd $\underline{C}=C_o(r)$ at $t=0$ and $\underline{C}(|r-r_i| <= R_i, \lambda)=0$ are initial and boundary conditions respectively. Where $i=1,2......N$ for the radii of the N traps (sinks) located at $\{r_i\}$ respectively. Many authors use "R" or "a" for all $|r-r_i|$, just for convenience. Rearranging (C.1) we obtain:

$$(\lambda - D_o \nabla^2)\underline{C}(r,\lambda) = C_o(r)$$

$$\underline{C}(r,\lambda) = (\lambda - D_o \nabla^2)^{-1} C_o(r)$$

$$= G_o(r) C_o(r) \quad \text{in absence of sinks.}$$

If more than one sinks are considered, one should add the sink terms. In this case the solution becomes:

$$\underline{C}(r,\lambda) = G_o(r) C_o(r) + \sum_{i=1}^{N} G_o(r) t_i \underline{C}_i(r,\lambda)$$

where t_i is the t-operator for one sink located at r_i and $\underline{C}(r,\lambda)$ is the Laplace transform of the concentration in the system which the sink at r_i is eliminated. $G_o(r)$ is the Green's function in the absence of traps. According to Green's theorem in handling boundary conditions in

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electrostatic or analogy [26], a simple application of the divergence theorem leads to the solution of $D_o\nabla^2 C(r) = f(r)$ being $C(r) = \int G(r,r')f(r')dr'$, provided $G(r,r') = [D_o\nabla^2]^{-1}\delta(r-r')$ is imposed, where $\delta(r-r')$ is the Dirac delta function. The solution of

$$D_o\nabla^2\underline{C}(r,\lambda) = \phi(r) + \sum_{i=1}^{N} q_i\delta(r-r_i) \quad \text{is}$$

$$\underline{C}(r,\lambda) = \int dr' G(r,r')[\phi(r') + \sum_{i=1}^{N} q_i\,\delta(r'-r_i)]$$

The physical meaning is that $\underline{C}(r,\lambda)$ can be obtained by integration with an inverse operator of $[\lambda - D_o\nabla^2]^{-1}$. The inverse operator is equivalent to Green's function in such a way

$$\underline{C}(r,\lambda) = \int G(r,r')[\phi(r') + \sum_{i=1}^{N} q_i\delta(r'-r_i)]dr'$$

$$= \int [\lambda - D_o\nabla^2]^{-1}[\phi(r') + \sum_{i=1}^{N} q_i\delta(r'-r_i)]dr' \qquad (C.2)$$

In (C.2), only monopole terms are considered. Replacing $[\lambda - D_o\nabla^2]^{-1}$ by $G_o(r)$ and introducing another t-operator, one has

$$\underline{C}(r,\lambda) = G_o(r)C_o(r) + \sum_{i=1}^{N} G_o(r)t_i\underline{C}_i(r,\lambda) \qquad (C.3a)$$

$$\underline{C}_i(r,\lambda) = G_o(r)C_o(r) + \sum_{j=1,\neq i}^{N} G_o(r)t_j\underline{C}_j(r,\ ) \qquad (C.3b)$$

where $\underline{C}_i(r,\lambda)$ is the Laplace transform of the concentration in the system from which the sink at r_i is eliminated, and t_i is the t operator for one sink located at r_i.

By substituting (C.3b) into (C.3a) one obtains the multiscattering [18-20,21b,d] representatioins, where t_i is an integral operator [23e],

$$\underline{C}(r,\lambda) = G_o(r)C_o(r) + \sum_{i=1}^{N} G_o(r)t_i\{G_o(r)C_o(r)$$

$$+ \sum_{j=1,\neq i}^{N} G_o(r)t_j\underline{C}_j(r,\lambda))\} \qquad \text{(C.3c)}$$

$$t_k\underline{C}_k(r',\lambda) = \int T_k(r,r',\lambda;r_k)\underline{C}(r',\lambda)dr'$$

$$t_j\underline{C}_j(r'',\lambda) = T_j(r',r'',\lambda;r_j)\underline{C}_j(r'',\lambda)dr''$$

To solve (C.3a) it is convenient to use Fourier transform technique. The Fourier transform of a function, say f(r), is defined as

$$F\ f(r) = \int_{-\infty}^{\infty} f(r)e^{-iq.r}dr = \hat{f}(q)$$

therefore the Fourier transform of Eq. (C.3a) is

$$\text{LHS: } F\ \underline{C}(r,\lambda) = \int_{-\infty}^{\infty} \underline{C}(r,\ )e^{-iq.r}dr = \hat{C}(q,\lambda)$$

$$\text{RHS: } F\ [G_o(r)C_o(r) + \sum_{i=1}^{N} G_o t_i\ \underline{C}_i(r,\lambda)] = \text{(I)} + \text{(II)},\ \text{where}$$

$$\text{(I)} = \int G_o(r)C_o(r)e^{-iqr}dr$$

$$= \int \{C_o(r)dr/[(\lambda-D_o v^2)e^{iqr}]\}$$

$$= \int \{C_o(r)dr/[\lambda-D_o(iq)^2e^{+iqr}]\},\quad (iq)^2=-q^2$$

$$\text{so, (I)} = \int C_o(r)[\lambda+D_o q^2]^{-1}e^{-iqr}dr$$

$$= [\lambda-D_o q^2]^{-1}\int C_o(r)e^{-iqr}dr$$

$$= G_o(q)C_o(q),\ \text{where } G_o(q)=[\lambda+D_o q^2]^{-1},\ \text{similarly}$$

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$$(II) = F\sum_{i=1}^{N} G_o t_i \underline{C}_i(r,\lambda)$$

$$= \sum_{i=1}^{N} G_o(q)T_i(q)\hat{C}_i(q,\lambda)$$

After equating both sides, one obtains:

$$\hat{C}(q,\lambda) = G_o(q)\hat{C}_o(q) + \sum_{i=1}^{N} G_o(q)T_i(q)\hat{C}_i(q,\lambda) \tag{C.4}$$

and $T_i(q) = (3\ )^{-3}\int dq' T_i(q,q',\lambda;r_i)P(q,q')$

$T_i(q)$ is an integral operator, in which $P(q,q')$ is a permutation operator that changes the index q of the operand to q′, and $T_i(q,q',\ ;r_i)$ is a convolution integral operator, in Fourier transform,

$$T_i(q,q',\lambda;r_i) = \int dr\int dr' e^{-i(qr-q'r')}T_i(r,r',\lambda;r_i)$$

Substituting $\hat{C}(q,\lambda)=G_o(q)\hat{C}_o(q) + \sum_{j=1}^{N} G_o(q)T_j(q)\hat{C}_j(q,\lambda)$

into (C.4), one obtains

$$\hat{C}(q,\lambda)=G_o(q)C_o(q) + \sum_{i=1}^{N} G_o(q)T_i(q)\{G_o(q)\hat{C}_o(q)$$

$$+ \sum_{j=1,\neq i}^{N} G_o(q)T_j(q)\hat{C}_j(q,\lambda)\} \tag{C.5}$$

in such a way one may substitute

$\hat{C}_j(q,\lambda)=G_o(q)C_o(q)+\sum_{k=1,\neq j}^{N} G_o(q)T_k(q)\hat{C}_k(q,\lambda)$ into (C.5), and so on.

The ultimate representation will be:

$$\begin{aligned}\hat{C}(q,\lambda) = {} & G_o(q)\hat{C}_o(q) + \sum_{i=1}^{N} G_o(q)T_i(q)\{G_o(q)\hat{C}_o(q) \\ & + \sum_{j=1,\neq i}^{N} G_o(q)T_j(q)[G_o(q)\hat{C}_o(q) + \sum_{k=1,\neq j}^{N} G_o(q)T_k(q) \\ & X\ \{G_o(q)\hat{C}_o(q) + \sum_{m=1,\neq k}^{N} G_o(q)T_m(q)[- - - -]\}]\}\end{aligned} \qquad (C.6)$$

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APPENDIX D

SOLUTION OF FICK´S 2nd LAW, EXAMPLE

The solution of 2nd order partial differential equation, Fick´s second law of diffusion,

$$\partial C/\partial t = D \nabla^2 C \qquad (D.1)$$

chosen by Collins and Kimball [38a] with the boundary condition C(R,t)=0 on the surface of a sink of radius R (see Table 2), is similar to the solution of linear flow of heat [41]. For the normalization constant $(4\pi D)^{1/2}$, the particular solution should be like this:

$$C(x,t) = t^{-1/2}\exp(-x^2/4Dt) \qquad (D.2a)$$

since by change of variable, $x^2/(4Dt)=u^2$, $du=dx/(4Dt)^{1/2}$,

$$\int_{-\infty}^{\infty} C(x,t)dx = 2\int_0^{\infty} C(x,t)dx \quad \text{(since } C(x,t) \text{ in (D.2a) is an even function),}$$

$$= 2(\pi D)^{1/2}\int_0^{\infty}\exp(-u^2)\,du$$

$$= 2(\pi D)^{1/2} = (4\pi D)^{1/2} \qquad (D.2b)$$

$(4\pi D)^{1/2}$ is the normalization constant of the chosen function, the error function solution. Now, consider one spherical sink of radius R and located at the origin, then the error-function-solution takes the following form

$$C(r,t) = C_0\{1 - (R/r)\,\mathrm{erfc}\,[(r-R)/(4Dt)^{1/2}]\} \qquad (D.3)$$

The solution satisfies the boundary condition

$$C(r,t) = 0, \quad \text{for} \quad 0 <= r <= R$$

so that the concentration field of the monomer is only defined in the range of r-R to ∞ . In other words, the concentration of monomer is not defined in the region from r=0 to R, i.e., inside the precipitate-particle of volume $4\pi R^3/3$, since inside this volume monomers not exist.

The total flux J, which is $\int_S j.ds$ over the entire surface of the assumed spherical precipitate particle, was defined by collins and Kimball as Φ , i.e.,

$$\Phi = J = \int_S j.ds \qquad (j=-D\nabla C,\ ds\ \text{is negative to}\ j\ \text{in this case})$$

$$= 4\pi R^2\ D(\partial C/\partial r)_{r=R}$$

$$= 4\pi R^2\ D\,\partial/\partial r\ C_o\{1-(R/r)\ \mathrm{erfc}[(r-R)/(4Dt)^{1/2}]\}_{r=R}$$

$$= 4\pi R^2\ DC_o\{(1/R)\ \mathrm{erfc}[(r-R)/(4Dt)^{1/2}]\}_{r=R}$$

$$+ \{(R/r)\ \mathrm{erf}\ [(r-R)/(4Dt)^{1/2}]\}_{r=R} \qquad (D.4)$$

To obtain Eq. (D.4), the following Leibnitz-rule [44] should have been used,

$$d/dt\int_{a(t)}^{b(t)} f(x,t)dx = f[b(t),t]b'(t)-f[a(t),t]a'(t)$$

$$+\int_{a(t)}^{b(t)} [\partial f(x,t)/\partial t]dx$$

Besides, by definition,

$$\mathrm{erf}\ (x) = (2/\pi)^{1/2}\int_0^x \exp(-x'^2)dx'$$

$$\mathrm{erfc}\ (x) = 1 - \mathrm{erf}\ x$$

one can see that

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$$\mathrm{erf}\ (0) = 0,\ \mathrm{erfc}\ (0) = 1 - \mathrm{erf}\ (0) = 1$$

$$\mathrm{erf}\ (\infty) = 1,\ \mathrm{erfc}\ (\infty) = 1 - \mathrm{erf}\ (\infty) = 0$$

Since r-R=0 if r=R, so that erf $(r-R)/(4Dt)^{1/2} = 0$ as r=R, therefore we obtain a very neat form for the total flux as follows:

$$\Phi = 4\pi DRC_o[1 + R/(\pi Dt)^{1/2}] \qquad (D.5)$$

Moreover, Collins and Kimball defined Φ (=J) as the time derivative of the total amount of the diffusion species, from the amount presented at t=0. i.e.,

$$\Phi\ (=J) = dM/dt$$

We can see from Eq. (D.3), the total amount of the precipitate is just equal to the integration of the second term on the right hand side of Eq. (D.3) over the entire region of the precipitate-particle sizes, for spherical-size assumption, the volume element is $dV=4\pi r^2 dr$, i.e.,

$$M = C_o \int_R^\infty 4\pi r^2 \{(R/r)\ \mathrm{erfc}[\{r-R)/(4Dt)^{1/2}]\} dr$$

$$= C_o \int_R^\infty 4\pi rR\ \mathrm{erfc}[(r-R)/(4Dt)^{1/2}] dr \qquad (D.6)$$

which is the total amount of precipitate in all sizes of particles at time t>0. By taking time derivative of Eq. (D.6), and by use of Leibniz Rule again, one obtains

$$dM/dt = d/dt\{C_o \int_R^\infty 4\pi rR\ \mathrm{erfc}[(r-R)/(4Dt)^{1/2}] dr$$

$$= C_o 4\pi R \int_R^\infty r(d/dt)\{2/(\pi)^{1/2} \int_{(r-R)/(4Dt)^{1/2}}^\infty \exp(-x^2) dx\} dr$$

$$= C_o 4\pi R(4D\pi)^{-1/2}\ t^{-3/2}\int_R^{\infty} r(r-R)\exp[-(r-R)^2/(4Dt)]dr$$

then, by change of variable: $(r-R)^2=u$, $dr=(4u)^{-1/2}du$, and change of integrating limits from $r=(R,\infty)$ to $u=(0,\infty)$, then

$$\Phi = dM/dt = 2\pi RC_o(4D\pi)^{-1/2}\ t^{-3/2}\{\int_0^{\infty} u^{1/2}\ \exp[-u/(4Dt)]du$$
$$+ R\int_0^{\infty}\exp[-u/(4Dt)]du\} \qquad (D.7)$$

Eq. (D.7) can be evaluated by use of the following integrating formula,

$$\int_c^{\infty} x^{1/2}\ \exp(-ax)dx = (\pi/a)^{1/2}1/(2a)$$

provided we set the constant "a" equal to $(4Dt)^{-1}$. The integrated form of Eq. (D.7) is,

$$\Phi = dM/dt = 2\pi RC_o(4D\pi)^{-1/2}t^{-3/2}[2Dt(4Dt\pi)^{1/2}+4RDt]$$
$$= 4\pi RC_o D(D\pi t)^{-1/2}[(D\pi t)^{1/2} + R]$$
$$= 4\pi RDC_o[1 + R/(D\pi t)^{1/2}] \qquad (D.8)$$

Eq. (D.8) is just the total flux, Φ, represented by Eq. (D.5). From the above argument one can see that the significance of the solution of the second order differential equation of Ficks law of diffusion chosen by Collins and Kimball [36a].

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FIGURE CAPTIONS

Fig. 1. Cutoff - pair potential, which vanishes as $r >= b$.

Fig. 2. (a) Two dimentional schematic representation of circular particles in Dirichlet region.

(b) Reiss & LaMer's model [42a], h-x = thickness of the diffusion region (see Table 2).

Fig. 3. Schematic representation of $N(t) = \quad n(R,t)dR$. See Section III.1, and Kahlweit and Teubner's 1976 and 1980 works [22aii, 22b].

Fig. 4. $\omega(z, \sigma_1)$ vs z, ik-case (see Table 1).

Fig. 5. $\omega(z, \sigma_1)$ vs z, dl-case (see Table 1).

Fig. 6. Scaled distribution function $F_o(z)$ vs z, dl-case, for different equilibrium volume fraction ϕ_∞.

Fig. 7. Cutoff size distribution, z_o vs ϕ_∞.

Fig. 8. Reduced coarsening rate vs equilibrium volume fraction, ξ vs ϕ_∞, $\xi(\phi_\infty) = \langle a(\phi_\infty)\rangle^3/\langle a(0)\rangle^3$ [21b].

Fig. 9. Amplitude for the density of particles $\rho_o(\phi_\infty)$ vs ϕ_∞, average radius $a_o(\phi_\infty)$ vs ϕ_∞, and the supersaturation decay function $\sigma_1(\phi_\infty)$ vs ϕ_∞. In which $a_c(0)=(4/9)^{1/3}$, $\sigma_1(0)=(9/4)^{1/3}$, and $\rho_o = 1.99$ are used [21b]. The $t^{1/3}$, $t^{-1/3}$, and t^{-1} factors are taken as $[1 + 0.815(\phi_\infty)^{1/2}]$, $[1 - 0.815(\phi_\infty)^{1/2}]$, and $[1-2.445(\phi_\infty)^{1/2}]$ respectively.

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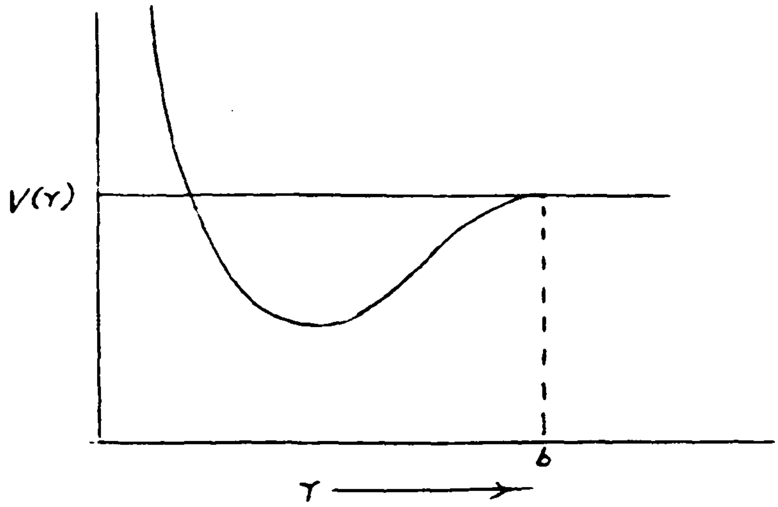
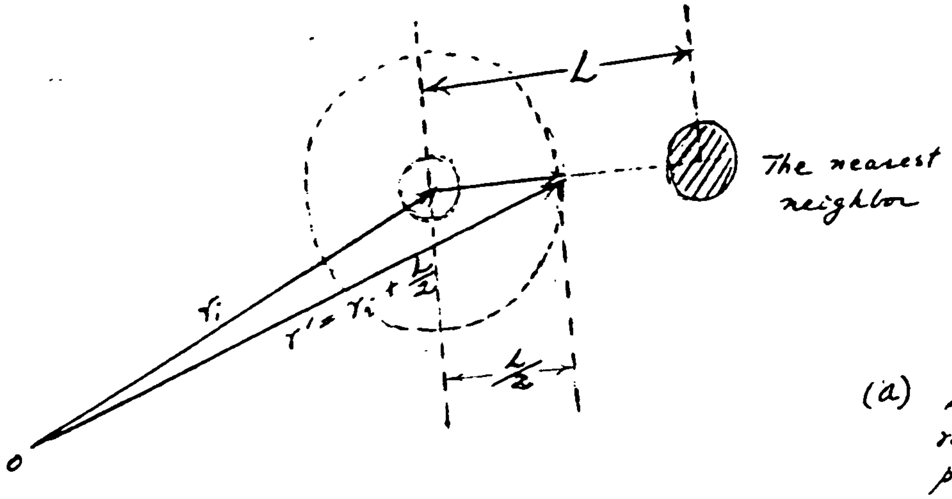


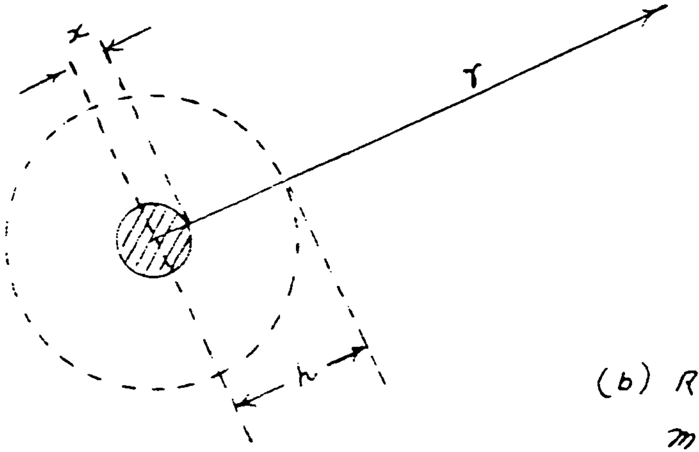
Fig. 1
Cutoff-pair-potential, which vanishes as $r \geq b$.

Baird, Fig. 1.

Fig. 2.



(a) 2-dimensional schematic representation of circular particles in Dirichlet region.



(b) Reiss & La Mer's model [42a], $h - x$ = thickness of the diffusion region (see Table 2).

Fig. 5.

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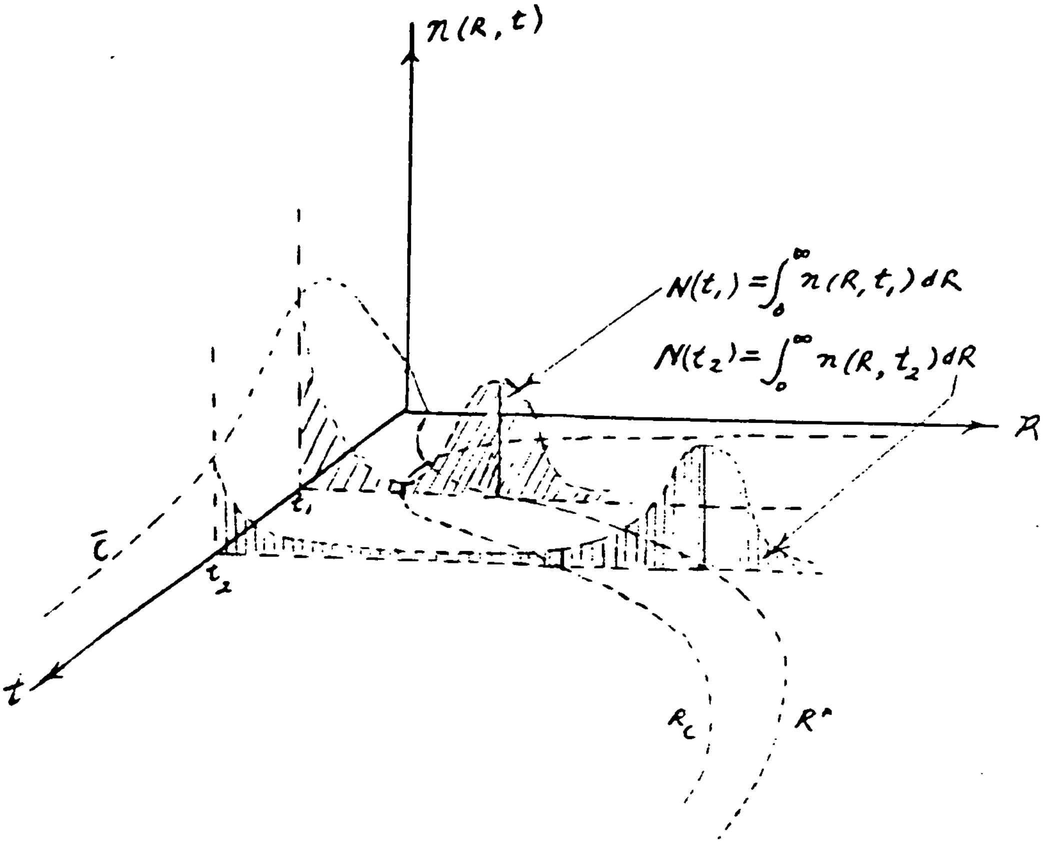

Fig. 3. Schematic representation of $N(t) = \int_c^\infty n(R,t)\,dR$.

—ee & Baird, Fig. 3.

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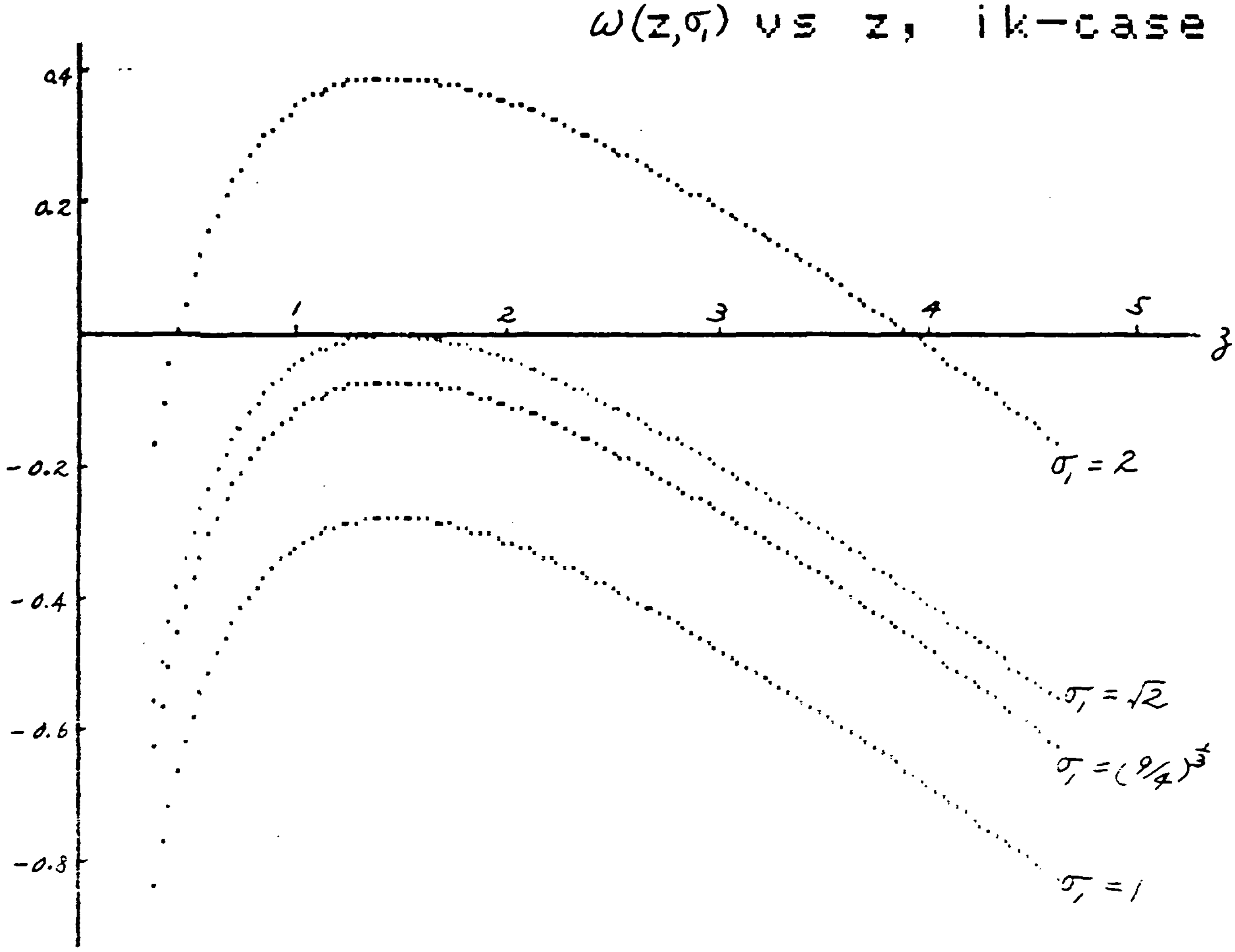
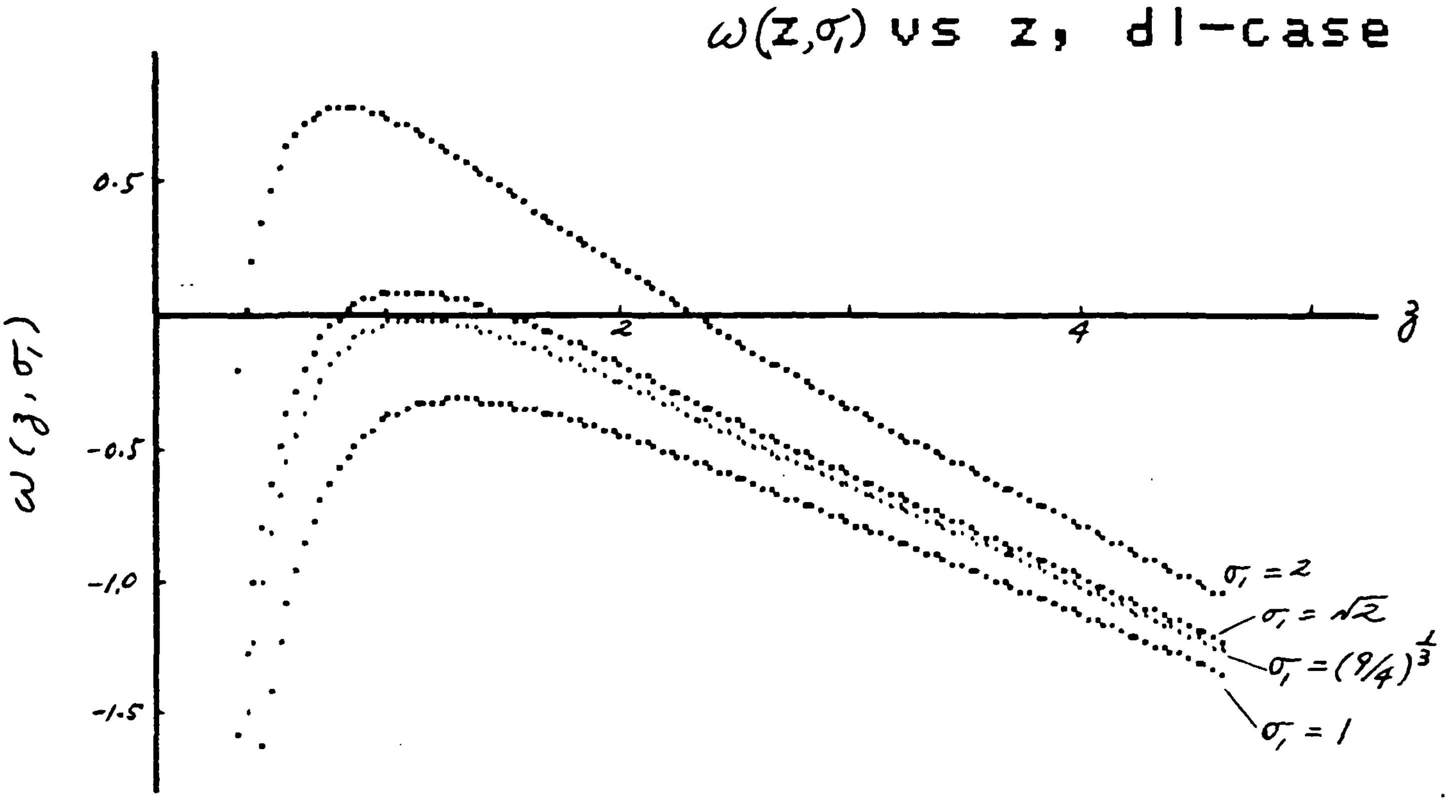


—— & Baird, Fig. 4.

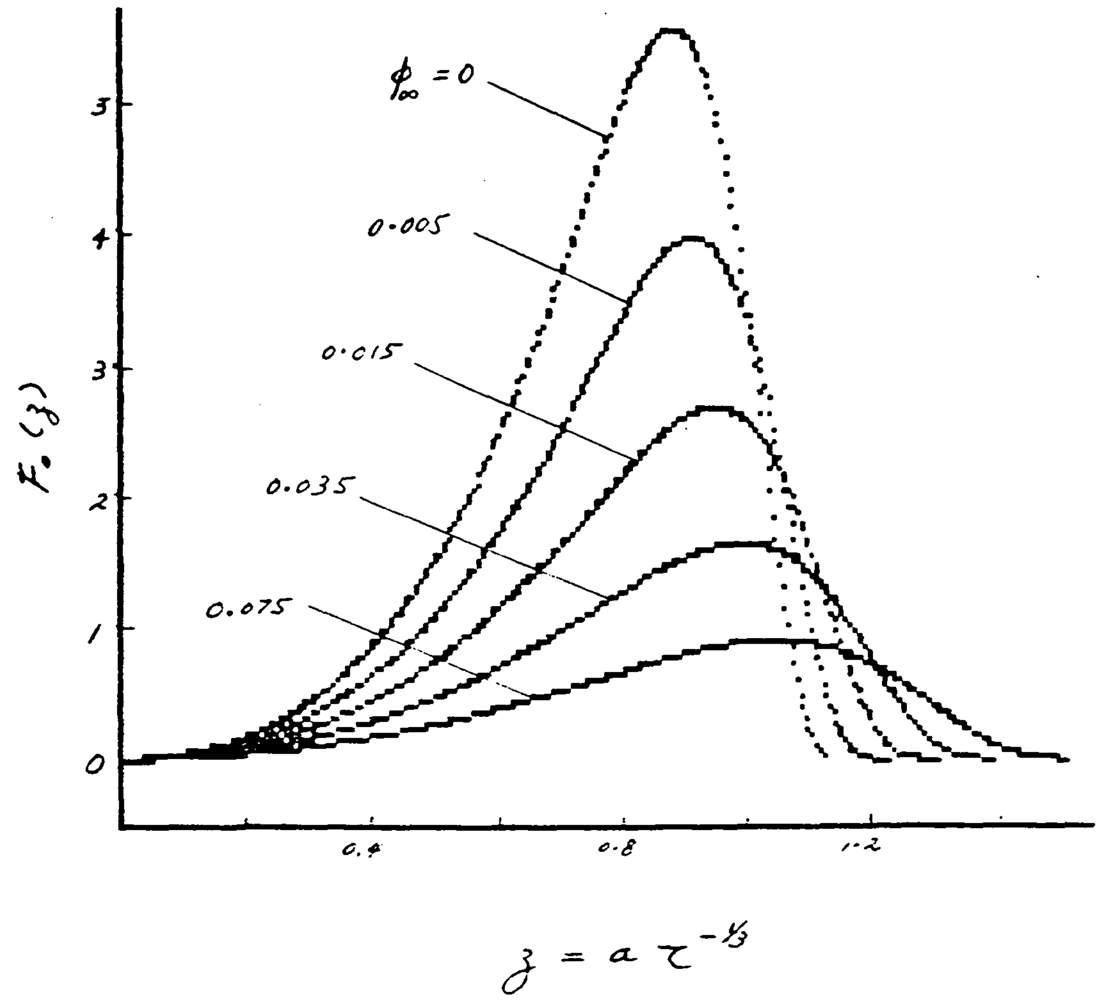
Fig. 5.



Lee & Baird, Fig. 5

Fig. 6.

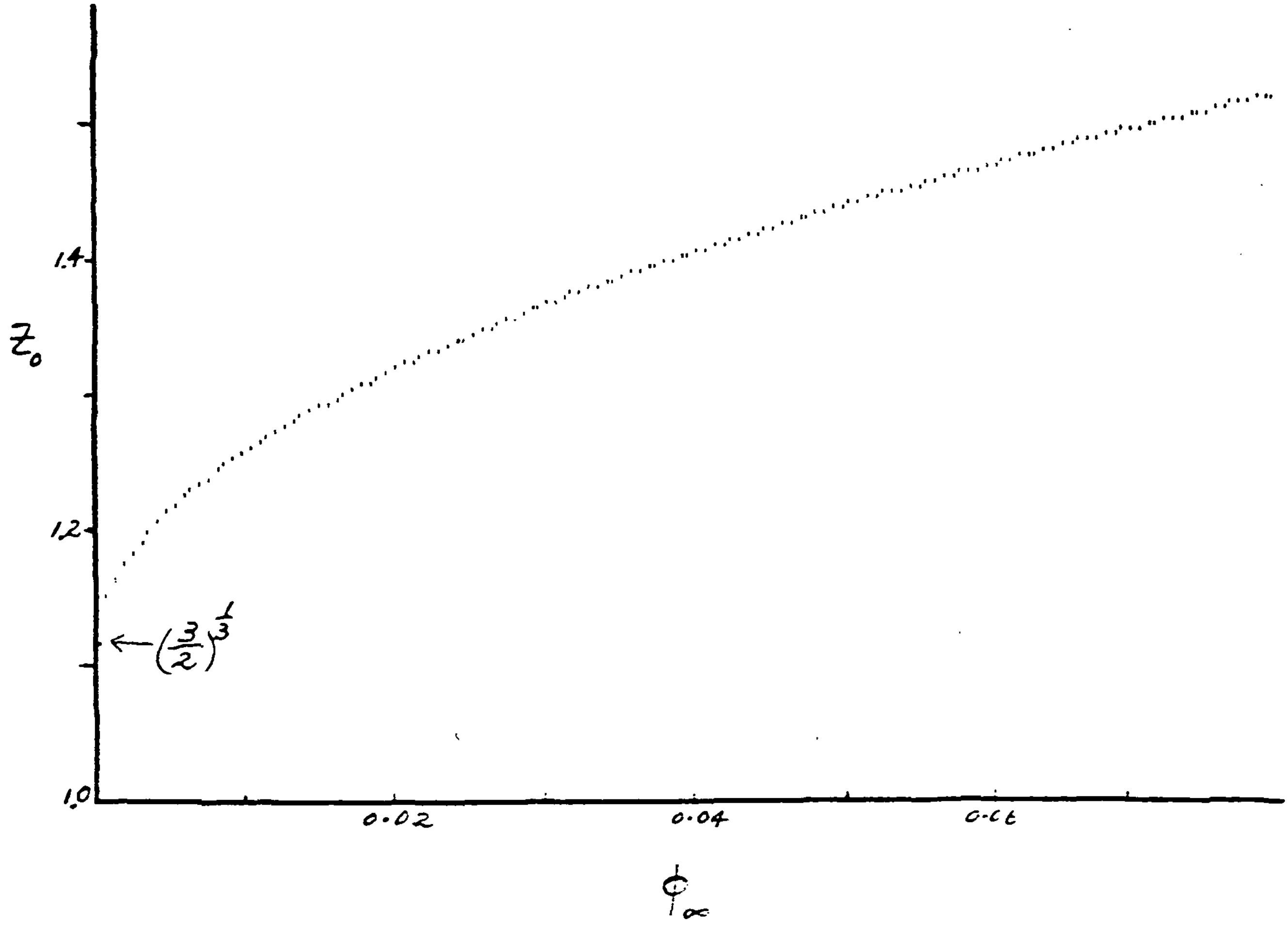
Fo(z) vs z in dl case for different equilibrium volume fractions



Lee & Baird, Fig. 6

Fig. 1.

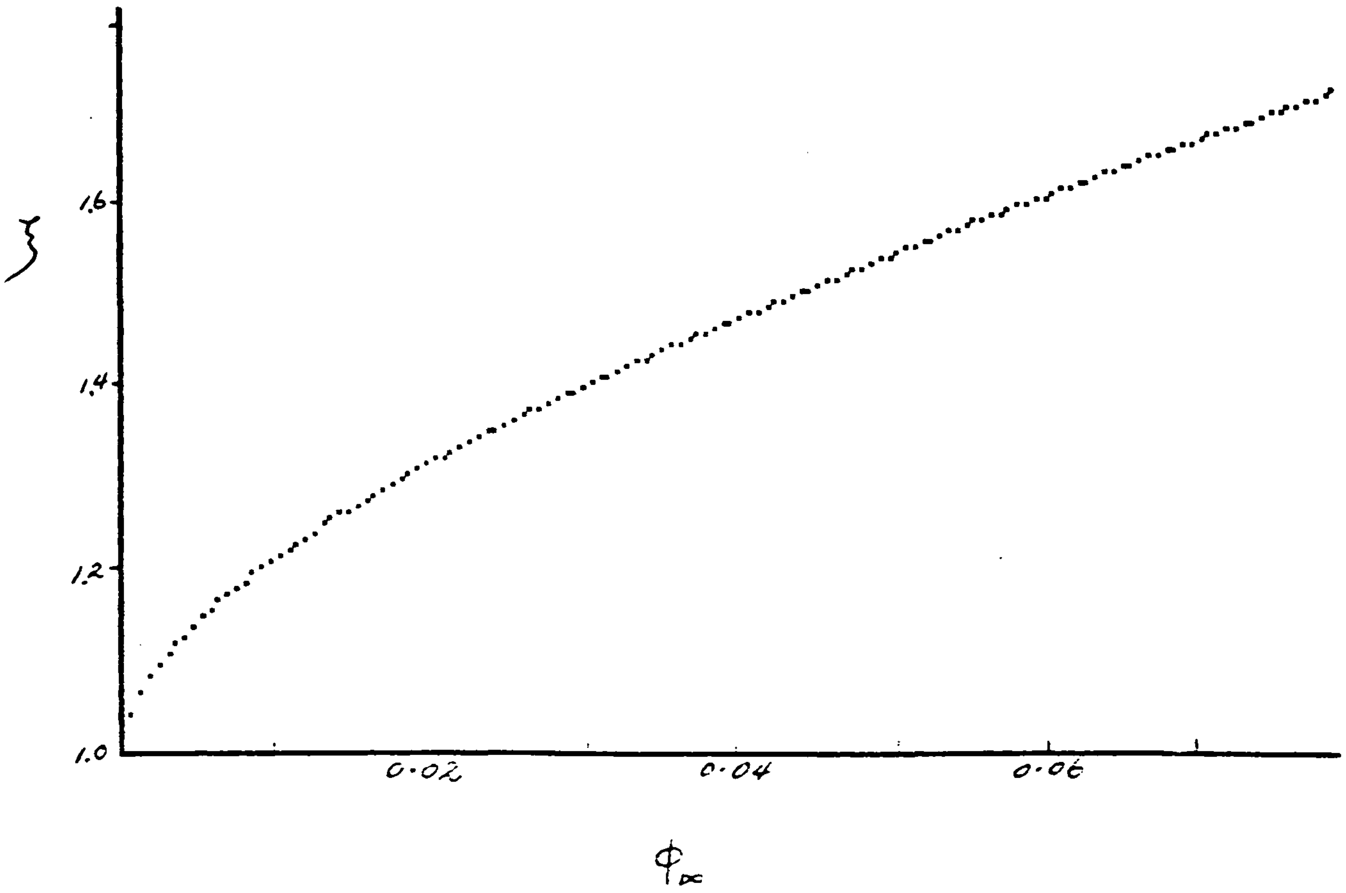
Cutoff size distribution, Z_0 vs ϕ_∞



Lee & Baird, Fig. 7

Fig. 8.

Reduced coarsening rate vs equilibrium volume fraction



Lee & Baird, Fig. 8.

Fig. 9.

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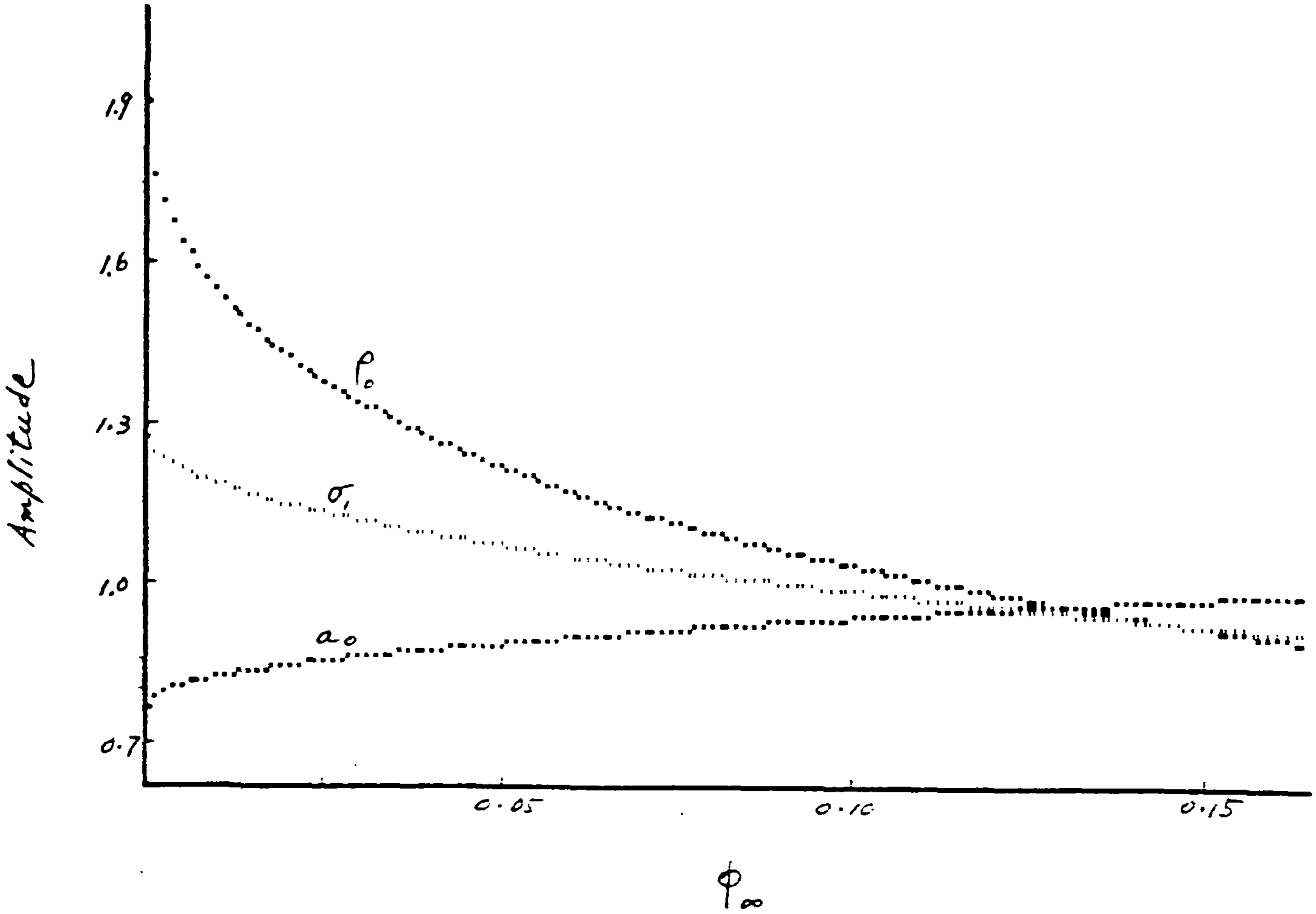
Amplitude for the density of particles vs phi, average radius vs phi, & sigma (supersat. decay function) vs phi.



Lee & Baird, Fig. 9