CR-178862

THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

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OSTWALD RIPENING THEORY

QUARTERLY REPORT
April 1 - June 30, 1985

NAS8-35986

BY

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(NASA-CR-178862) OSTWALD RIPENING THEORY Quarterly Report, 1 Apr. - 30 Jun. 1985 (Alabama Univ., Huntsville.) 10 p HC A02/MF A01 CSCL 07D N86-27433 Unclas G3/25 43166

Prepared for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama 35812

(1) Personnel

Dr. Li Kao Lee continues to be supported under this contract.

(2) Expenditures

The cumulative amount, \$31,392.00, or 46% of the contract budget has been expended by the end of this the third quarter.

(3) Technical Accomplishments

3.1 Concentration Dependence of the Interdiffusion Coefficient.

It now seems certain that the proper coefficient of diffusion to be used in the theory of Ostwald ripening of a two component system is the interdiffusion coefficient. This is the diffusion coefficient measured with respect to the center of volume of the system. This diffusion coefficient is conveniently determined with the diaphragm cell.

In our first quarterly report, we showed that the concentration dependence of the interdiffusion coefficient can be easily measured using this cell if the volumes V_1 and V_2 of the top and bottom compartments are equal. In that report, we showed that the interdiffusion coefficient, $D(\bar{c})$, evaluated at $\bar{c}$, the arithmetic mean of the top and bottom concentrations satisfied the equation

$$\ell n \left[\frac{c'(t) - c''(t)}{c'(0) - c''(0)}\right] = - \frac{2AD(\bar{c})t}{\ell V} \qquad (3.1.1)$$

where ℓ and A are the thickness and cross-sectional area, respectively, of the cell; $V=V_1=V_2$; and $c'(t)$ and $c''(t)$ are the bottom and top concentrations, respectively, at time t, while $c'(0)$ and $c''(0)$ are the analagous concentrations at $t=0$. All other quantities being known, if $c'(t)$ and $c''(t)$ are followed as a function of t, $D(\bar{c})$ can be determined directly from Eq (1).

We have found a new and more direct derivation of Eq (1), which exploits a Taylor series expansion of D(c) <u>about $c = \bar{c}$</u> rather than c = 0 as done previously. The new derivation is <u>much shorter</u> and more direct. It leads to a new formula for estimating the systematic error, ε, associated with Eq (1) (which is approximate). We find

$$\varepsilon = \left(\frac{1}{6}\right) \cdot \frac{D^{(2)}(\bar{c})(\Delta c)^2}{D(\bar{c})} \times 100\% \qquad (3.1.2)$$

where $\Delta c = c'(0) - c''(0)$ and $D^{(2)}(\bar{c})$ is the second derivative of D(c) evaluated at $c = \bar{c}$. Using reasonable values for the quantities in Eq (2), we find

$$\varepsilon = 1.6\% \qquad (3.1.3)$$

which is well within the random error ordinarily encountered when using the diaphragm cell.

A research paper on this subject was delivered at the European Materials Research Society Meeting at Strasbourg, France May 13-15, 1985 and will be published in <u>Journal de Physicue</u>. A copy is attached.

3.2 Grain Size Distribution in Ostwald Ripening as a Function of Volume Fraction of Grains

We consider the precipitation of a single solute from a two component solution. Define the following quantities

$c(\infty)$ - Equilibrium solubility in molecules/Cm^3 of the solute in the solution.

v - molecular volume of the solute in a precipitate grain in Cm^3/molecule.

D - Interdiffusion coefficient of solute and solvent in the parent phase in Cm^2/sec.

γ - Surface tension between a precipitate grain and the parent solution in erg/Cm^2.

kT - Product of Boltzmann's constant times the absolute temperature, T, in ergs.

R - Radius in Cm of a given precipitate grain.

It is helpful to define some intermediate quantities. Let

$$\alpha = 2\gamma v/kT \tag{3.2.1}$$

Define a dimensionless time, τ,

$$\tau = tDvc(\infty)/\alpha^2 \tag{3.2.2}$$

and a dimensionless radius, a,

$$a = R/\alpha \tag{3.2.3}$$

We find that the grain distribution, $F(a,\tau)$ (where $F(a,\tau)da$ is the number of grains with radii between a and $a + da$) is given by

$$F(a,\tau) = \tau^{-4/3} F_0(z) \tag{3.2.4}$$

Here

$$z = a/\tau^{1/3} \tag{3.2.5}$$

and

$$F_0(z) = C_0 z^2 (z_0-z)^{-\theta}(z+3/z_0^2)^{-\beta} \exp(-\delta/(z_0-z)),\quad z \leq z_0 \tag{3.2.6}$$

where

$$\theta = 2 + \frac{3z_0^3(z_0^3 + 6)}{(z_0^3 + 3)^2} \tag{3.2.7}$$

$$\beta = 1 + \frac{27}{(z_0^3 + 3)^2} \tag{3.2.8}$$

$$\delta = \frac{3z_0^4}{(z_0^3 + 3)} \tag{3.2.9}$$

The cut-off radius, z_0, satisfies the quartic equation

$$\varepsilon z_0^4 + 2z_0^3 - 3\varepsilon^2 z_0^2 - 6\varepsilon z_0 - 3 = 0 \tag{3.2.10}$$

where

$$\varepsilon = (4.55\varphi)^{1/2} \tag{3.2.11}$$

and φ is the precipitate grain volume fraction which occurs once the steady state of the Ostwald ripening has been established. The normalization constant, C_0, depends upon φ.

Figure 1 shows the function $F_0(z)$ for various values of φ. These curves were computed as follows: A value of φ was chosen and ε was calculated using Eq (3.2.11). Eq (3.2.10) was solved for z_0 using this value of ε. Next, the exponents θ, β, and δ were computed using Eqs (3.2.7) - (3.2.9). The value of the normalization constant was determined from the integral

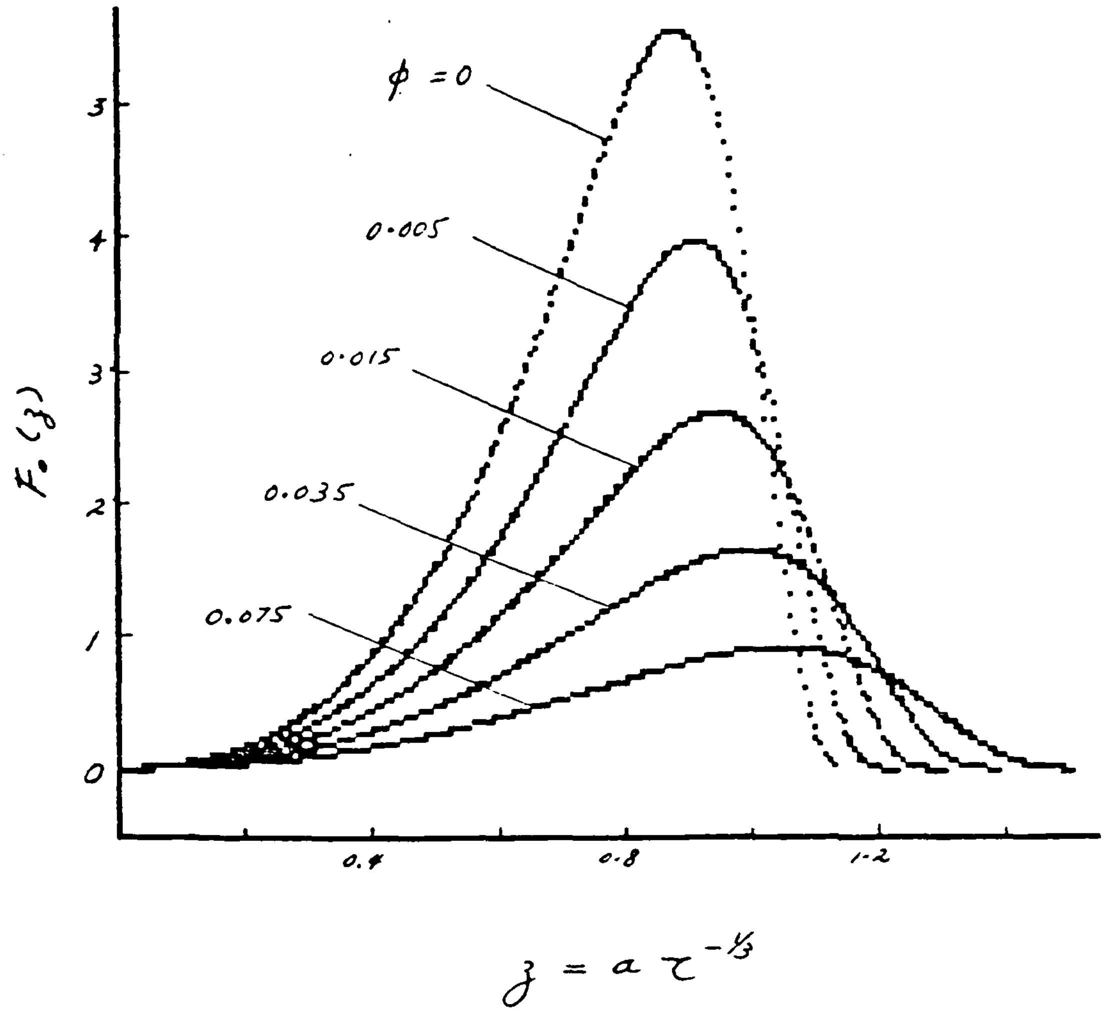
$$\int_0^{z_0} dz\, z^3\, F_0(z) = 1 \tag{3.2.12}$$

which guarantees the conservation of solute mass.

Figure 1 demonstrates that competition for solute between solute grains has a substantial effect on $F_0(z)$, even for small values of φ. The grain size distribution becomes broader and the maximum radius (cutoff radius) increases with φ. Because the area under $z^3 F_0(z)$ is conserved (See Eq (3.2.12)), the brodened distributions for $\varphi > 0$ are also shorter. Detailed derivations of Eqs (3.2.1) - (3.2.12) will be presented in the final report.

Fig. 1

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



Journal de Physique

ON THE CONCENTRATION DEPENDENCE OF THE INTERDIFFUSION COEFFICIENT

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Abstract - We derive an approximate analytical technique for extracting the concentration dependence of the interdiffusion coefficient from diffusion measurements carried out with the diaphragm cell. The systematic error incurred in using the technique is estimated and found to be no greater than the random error ordinarily encounted in these experiments.

I - INTRODUCTION

In microgravity, Ostwald ripening in phase separating immiscible liquids can be observed without interference from convection and sedimentation. Two component systems such as succinonitrile/water or succinonitrile/ethanol are easily studied, because they are optically transparent. In order to compare results obtained with these systems to the theory of Ostwald ripening /1,2,3/, the interdiffusion coefficient, and the interfacial energy and densities of the separating phases must be measured.

If the two components form an ideal solution, the interdiffusion coefficient is independent of composition and can be measured directly in earth's gravity using the diaphragm cell /4/. In the case of the two monotectic systems, $NC(CH_2)_2CN/H_2O$ and $NC(CH_2)_2CN/C_2H_5OH$, mentioned above, however, the interdiffusion coefficient is a function of composition. In as much as the diaphragm cell yields the integral of the interdiffusion coefficient over a range of concentration, the integral data must be unfolded to obtain the desired quantity /5/.

Below, we show that under certain conditions, the concentration dependence of the interdiffusion coefficient can be obtained directly from the data without unfolding. There is a systematic error incurred in this procedure, but it is of second order and no larger than the random error ordinarily incurred with the cell.

II - THEORY OF THE MEASUREMENT

The diaphragm cell consists of two volumes, V_1 and V_2, separated by a sintered glass diaphragm disk of cross sectional area, A, and nominal thickness, ℓ /4/. The sensitivity of cell depends upon the ratio, A/ℓ. Because of the torturous nature of the diffusion paths among the glass particles in the diaphragm, ℓ cannot be directly observed. Rather, the cell constant, A/ℓ, is determined by observing the diffusion coefficient of a solution (often aqueous KCl) whose interdiffusion coefficient is absolutely known.

This being done, we assume that the cell is loaded at $t=0$ with a solution of the two components of concentration $c'(0)$ occupying V_1 and concentration $c''(0)$ occupying V_2. (To prevent convection, the cell is ordinarily oriented so that ℓ is parallel to the gravity vector, and the less dense solution is above the more dense.) Thus take $c'(0) > c''(0)$. If the volumes V_1 and V_2 are well stirred, a concentration gradient, dc/dx, exists only across the diaphragm. The gradient is related to the flux, J, through Fick's first law

$$J = -D(c)\,\frac{dc}{dx} \tag{1}$$

where the interdiffusion coefficient /6/ is allowed to be a function of the concentration, c. Eq. (1) can also be written, $Jdx = -D(c)dc$, and integrated on the left side from 0 to ℓ and on the right side from c' to c'' to obtain

$$J\ell = -\int_{c'}^{c''} D(c)dc \tag{2}$$

By conservation of mass, the rate of loss of solute from V_1, $-V_1 dc'/dt$, must exactly equal the rate of gain of solute, $V_2 dc''/dt$ by V_2. Hence,

$$V_2\frac{dc''}{dt} = JA = -V_1\frac{dc'}{dt} \tag{3}$$

Eqs. (2) and (3) can be combined to obtain

$$\frac{d(c'-c'')}{dt} = -\frac{A}{\ell}\left(\frac{1}{V_1}+\frac{1}{V_2}\right)\int_{c''}^{c'} D(c)dc \tag{4}$$

As written, Eq. (4) cannot be integrated directly without knowledge of the functional form of $D(c)$, which is ordinarily not known.

In what follows, we shall show that Eq. (4) can be integrated accurately after a Taylor series development of $D(c)$, provided that $V_1 = V_2 = V$. In this circumstance, conservation of solute mass dictates that the mean concentration $\bar{c} = (c' + c'')/2$, is independent of time and if $c' = \bar{c} + \Delta c$, then $c'' = \bar{c} - \Delta c$. Define the variable $y = c - \bar{c}$ and transform the integral, I, on the right hand side of Eq. (4) to

$$I = \int_{c''}^{c'} D(c)dc = \int_{-\Delta c}^{\Delta c} D(\bar{c} + y)\,dy \tag{5}$$

Expand $D(\bar{c} + y)$ about $D(\bar{c})$ in a Taylor series in y,

$$D(\bar{c} + y) = \sum_{n=0}^{\infty} \frac{D_n(\bar{c})\,y^n}{n!} \tag{6}$$

where $D_n(\bar{c}) \equiv (d^nD(c)/dc^n)\,|_{c = \bar{c}}$. Substitute Eq. (6) into Eq. (5) and integrate term by term. The result is

$$I = \sum_{n=0}^{\infty} \frac{D_n(\bar{c})}{(n+1)!}\left((\Delta c)^{n+1} - (-\Delta c)^{n+1}\right) \tag{7}$$

When written to third order in Δc, Eq. (7) reads

$$I = 2D_o(\bar{c})\Delta c + (1/3)D_2(\bar{c})(\Delta c)^3 \qquad (8)$$

Note that the term of order $(\Delta c)^2$ cancels out. Factoring Eq. (8) and using $\Delta c = (1/2)(c'-c'')$, we have

$$I = D(\bar{c})(c'-c'')\left[1 + \left(\frac{1}{6}\right)\cdot\frac{D_2(\bar{c})(\Delta c)^2}{D(\bar{c})}\right] \qquad (9)$$

where the "zeroth" derivative $D_o(\bar{c}) = D(\bar{c})$. The integral, I, thus can be accurately represented by $D(\bar{c})(c'-c'')$ assuming that the systematic error, ϵ,

$$\epsilon = \left(\frac{1}{6}\right)\cdot\frac{D_2(\bar{c})(\Delta c)^2}{D(\bar{c})} \qquad (10)$$

is small.

We replace I by $D(\bar{c})(c'-c'')$ and integrate Eq. (4) to obtain

$$\ell n\left(\frac{c'(t) - c''(t)}{c'(0) - c''(0)}\right) = -\frac{2AD(\bar{c})}{\ell V}\, t \qquad (11)$$

Eq. (11) is identical with the usual result /4,7/, except $V = V_1 = V_2$ and the interdiffusion coefficient is a function of the mean concentration, $\bar{c}$. If the concentrations, $c'(t)$ and $c''(t)$, are monitored as a function of time, then a plot of the left hand side of Eq. (11) as a function of t, yields a straight line with slope $-2AD(\bar{c})/\ell V$ from which $D(\bar{c})$ can be extracted if V and A/ℓ are known.

III - DISCUSSION

If Δc is not too large, we can safely assume that $D_2(\bar{c})(\Delta c)^2$ is a small fraction of $D(\bar{c})$, say 1/10. In this circumstance, using Eq.(10), we estimate $\epsilon = 1/60$, which is the same order of magnitude as the random error ordinarily incurred with the diaphragm cell. To test Eqs. (10) and (11), a range of solutions of increasing Δc should be prepared and tried with the cell. So long as for each solution $D(\bar{c})$ determined using Eq. (11) is independent of Δc, it can be concluded that the systematic error is small. In as much as the diffusion will be slow when Δc is small, special care should be taken to keep the cell isothermal over the course of the experiment.

IV - ACKNOWLEDGEMENT

This work was supported by Grant NAS8-35986 provided by the National Aeronautics and Space Administration, Marshall Space Flight Center, Alabama, 35812, USA.

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FINANCIAL REPORT

NAS8-35986

Cumulative costs incurred as of report date	$33,647.48
Estimate of cost to complete contract as of June 30,1985	36,863.27
Estimated percentage of physical completion of contract	60%