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APPENDIX I

MINIMUM ENTROPY PRODUCTION RATE AND
OSTWALD RIPENING

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MINIMUM ENTROPY PRODUCTION RATE AND OSTWALD RIPENING

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INTRODUCTION

The previous treatments of the problem of Ostwald ripening undertaken by Wagner¹ and Lifshitz and Slyozov² attempted to predict the shape of the particle size distribution curves, for two possible mechanisms which can control the molecular transfer between the particle and matrix phases. They are the interface exchange of molecules and diffusion through the matrix phase, respectively. Of course the constancy of the positions of the discrete particles in space was always assumed. The rate of radial growth or shrinkage of a single particle was obtained from mean field approximation

$$v = \frac{dr}{dt} = \frac{K_o D V_m}{K_o r + D} (C - C^*) \quad (1)$$

where r is the radius of the spherical particle in question, K_o the rate constant of molecules exchanging between matrix and the particle, D the coefficient of diffusion in the matrix, V_m molar volume, C concentration of diffusing molecules in the matrix at the particle interface and C^* the average concentration of these molecules in the matrix at time t . C^* is a function of average r and through it, of time t . It is further assumed that the distribution function $f(r,t)dr$ which is defined as the number of particles or radius between r and $r + dr$ per unit volume of the time t , obeys the continuity equation

$$\frac{\partial f}{\partial t} + \frac{\partial (vf)}{\partial r} = 0 \quad (2)$$

Solution of the coupled system of these differential equations yields f , but the task is not a simple one.

Wagner obtained a solution in the form

$$f = f_1(t) f_2(\rho) \quad (3)$$

$\rho = r/r^*$ where

$$r^* = \frac{\int_0^\infty f(t, r) \frac{r^2}{K_0 r + D} dr}{\int_0^\infty f(r, t) \frac{r}{K_0 r + D} dr} \quad (4)$$

f_2 is of the form

$$f_2(\rho) \sim \rho^n \phi(\rho) \quad (5)$$

where $n = 1$ or 2 characterize interface-controlled and diffusion controlled processes, respectively and $\phi(\rho)$ an exponential function of ρ having a sharp cut off at high values of ρ . An experimental determination of the distribution function of particles or pores fits very poorly the theoretical curves. The discrepancy is most noticeable on the large particle side where experimental distribution curves as a rule display long tails.

MINIMUM ENTROPY PRODUCTION RATE PRINCIPLE

In the last technical report³ an idea was advanced that the distribution function of particles undergoing Ostwald ripening can, in principle, be obtained directly from a minimum entropy or minimum dissipation rate principle, first introduced by Prigogine.⁴ It is essentially an extension of LeChatelier's principle and can be stated simply, that if the open thermodynamic system is not far from equilibrium, then such a system approaches its equilibrium state by keeping the rate of production of entropy at a minimum. If the deDonder⁵ theorem is accepted, namely, that

$$\frac{dS}{dt} = - \frac{1}{T} \frac{dG}{dt} \quad (6)$$

where S is entropy of the system, the Prigogine principle also means that the rate of decrease of Gibbs free energy G is minimum. The acceptance of relation (6) is based on what is called by deDonder, the fundamental hypothesis, that if chemical reaction is the only cause of irreversibility in the system, the production of entropy depends only on the extent to which reaction has proceeded. This in turn is equivalent to the assumption often taken for granted that the free energy of the system has a real significance at any stage of the reaction process, its value being determined by the variables of state.

A system of N_v spherical particles per unit volume where N_v is a large number is described by some distribution function $f(r,t)$ of particle radius and time. If the rates of increase of entropies from various sources of the system could be expressed by an integral, the problem of finding function f which would satisfy the minimum entropy production rate would be reduced to a variational problem. The same idea was suggested in the last report, however its execution was incorrect. In the remainder of this report a new variational analysis of this problem is presented.

ENTROPY PRODUCTION RATES

The problem of Ostwald ripening discussed here will be limited only to the systems of spherical pores. In principle the same treatment can be applied to the system of particles of the second phase precipitated in the matrix of the first phase; however difficulty of such a problem is greatly increased by the fact that the composition of the particles of the second phase is a function of their radii.⁶

Let us start with stating the assumptions involved. Number N_v of spherical pores is dispersed randomly in a material matrix. N_v is only a function of time. The centers of these spheres are fixed permanently in space. The spheres can exchange volume by dissolving vacancies in the matrix and diffusing them from one pore to another. Total volume of pores and vacancies is constant and only capillary forces are in operation.

Instead of the distribution function $f(r,t)$ we shall use function $p(r,t)$ defined by the equation:

$$f(r,t) = N_v p(r,t) \quad (7)$$

with the condition

$$\int_0^{\infty} p(r,t) dr = 1 \quad (8)$$

By equation (8)

$$\int_0^{\infty} f(r,t) dr = N_v \quad (8')$$

Using p we can write the continuity equation in the form

$$\frac{\partial p}{\partial t} + \frac{\partial (vp)}{\partial r} = - \frac{d \ln N_v}{dt} p \quad (9)$$

There are two sources of entropy in the system. The first is that associated with configuration of the pores in space

$$S_1 = - N_v k \int_0^{\infty} p \ln p \, dr \quad (10)$$

By this definition, S_1 is the entropy per unit volume due to the distribution of particles in space. Equation (10) represents this entropy correctly only when the distribution of particles is perfectly random. k is the Boltzmann constant. Equation (10) yields at once an expression for the rate of the production of configurational entropy.

$$\frac{dS_1}{dt} = - N_v k \int_0^{\infty} \left(\frac{d \ln N_v}{dt} p \ln p + \frac{\partial p}{\partial t} (\ln p + 1) \right) dr \quad (11)$$

However from (8) we obtain

$$\int_0^{\infty} \frac{\partial p}{\partial t} \, dr = 0 \quad (8'')$$

hence (11) is reduced to the form:

$$\frac{dS_1}{dt} = - N_v k \int_0^{\infty} \left(\frac{d \ln N_v}{dt} p \ln p + \frac{\partial p}{\partial t} \ln p \right) dr \quad (11')$$

and upon applying (9) we obtain

$$\frac{dS_1}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \ln p \, dr \quad (11'')$$

where

$$u = v p \quad (12)$$

The second source of entropy is the fluctuations of the vacancy concentration near the pores, causing the fluctuations of free energy due to the vacancy concentrations and their gradients. The Helmholtz free energy increment

ΔF due to vacancy concentration is estimated in Appendix I and is given by equation (A9). The rate of entropy increase can be calculated from the deDonder theorem (6) using equation (A9)

$$\frac{dS_2}{dt} = -\frac{1}{T} \frac{d\Delta F}{dt} = -\frac{4\pi}{\Omega} \frac{d}{dt} \left[N_v k \int_0^{\infty} \left(-\frac{r^3 \Delta f(r)}{kT} \ln\left(\frac{r}{L}\right) + \frac{Kr}{kT} \Delta C(r)^2 \right) p dr \right] \quad (13)$$

This expression can be further transformed with the help of relations (9) and (12) yielding

$$\frac{dS_2}{dt} = N_v k \frac{4\pi}{\Omega} \int_0^{\infty} \frac{\partial u}{\partial r} \left(-\frac{r^3 \Delta f(r)}{kT} \ln\left(\frac{r}{L}\right) + \frac{Kr \Delta C(r)^2}{kT} \right) dr \quad (14)$$

Introducing $n = \frac{4\pi r^3 \Delta f(r)}{\Omega kT}$, we obtain

$$\frac{dS_2}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \left(-n \ln\left(\frac{r}{L}\right) + 4\pi \frac{Kr}{\Omega kT} \Delta C(r)^2 \right) dr \quad (14')$$

DERIVATION OF DISTRIBUTION FUNCTION

In order to obtain the distribution function $p(r, t)$ of pore radii the integral:

$$\frac{dS_1}{dt} + \frac{dS_2}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \left[\ln p - n \ln \left(\frac{r}{L} \right) + \frac{4\pi K r}{\Omega k T} \Delta C(r)^2 \right] dr \quad (15)$$

has to be minimized subject to the following auxiliary conditions. The first one is given by equation (8). Another expresses the fact that the total volume of pores and vacancies remains constant

$$4\pi \int_0^{\infty} \left[\frac{r^3}{3} + \int_r^L \Delta C x^2 dx \right] p dr = \text{constant} \quad (16)$$

for that time derivative of this integral is equal zero.

Although it is possible to proceed with the calculations based on equation (16), at present for our purpose to illustrate the method, it is sufficient to consider a simpler, though not exactly accurate assumption, that the total pore volume remains constant

$$\frac{d}{dt} \int_0^{\infty} r^3 p dr = \int_0^{\infty} r^3 \frac{\partial p}{\partial t} dr = 0 \quad (16')$$

Doing this we neglect the small vacancy contribution. With the help of (9) we can write

$$\int_0^{\infty} \left(r^3 \frac{\partial u}{\partial r} + \frac{d \ln N_v}{dt} r^3 p \right) dr = 0 \quad (16'')$$

as the second auxiliary condition. Multiplying (16'') by λ and (8) by μ and adding to (15) we obtain a Lagrange function

$$I = \frac{\partial u}{\partial r} \left[\ln p - n \ln \left(\frac{r}{L} \right) + \frac{4\pi K \Delta C_o^2}{r \Omega k T} + \lambda r^3 \right] + \left(\lambda \frac{d \ln N_v}{dt} r^3 + \mu \right) p \quad (17)$$

where $\Delta C_0 = r\Delta C(r) = \frac{2\Omega\gamma}{kT}$.

We can now write two Euler's equations

$$\frac{d}{dr} \left(\ln p - n \ln \left(\frac{r}{L} \right) + \lambda r^3 + \frac{4\pi K \Delta C_0^2}{r \Omega k T} \right) = 0 \quad (18)$$

$$\frac{1}{p} \frac{\partial u}{\partial r} + \mu + \lambda \frac{d \ln N_v}{dt} r^3 = 0 \quad (19)$$

Upon integration of equation (18) we obtain an expression for distribution function $p(r, t)$ in the form

$$\ln p = n \ln \frac{r}{L} - \lambda r^3 - \frac{4\pi K \Delta C_0^2}{r \Omega k T} + \phi(t) \quad (20)$$

where $\phi(t)$ is a function of time to be determined. Equation (20) can also be written as follows

$$p = \exp \phi(t) \left(\frac{r}{L} \right)^n \exp \left(- \frac{r_c}{r} - \lambda r^3 \right) \quad (20')$$

where $r_c = \frac{4\pi K \Delta C_0^2}{\Omega k T}$.

From (8), $\phi(t)$ can be determined as a function of the parameter λ .

It should be noted that for small values of r , function (20') behaves similarly to Wagner's distribution function, namely, it is proportional to r^n . However, for large values of r , two functions behave differently. While Wagner's function after going through a maximum has a sharp cut off at certain value of r , the function in (20') displays an exponential tail ($\lambda > 0$).

Integration of equation (19) yields

$$u(r, t) = - \int_0^r \left(\mu + \lambda \frac{d \ln N_v}{dt} r^3 \right) p dr + \psi(t) \quad (21)$$

where $\psi(t)$ is a function of time only, which can be determined from the condition that

$$u(0,t) = \frac{d \ln N_v}{dt} = \psi(t) \quad (22)$$

Therefore

$$u(r,t) = - \int_0^{\infty} \left(\mu + \lambda \frac{d \ln N_v}{dt} r^3 \right) p dr + \frac{d \ln N_v}{dt} \quad (21')$$

On the other hand

$$u(\infty,t) = 0 \quad (23)$$

Therefore

$$\frac{d \ln N_v}{dt} = \mu + \lambda \frac{d \ln N_v}{dt} \int_0^{\infty} r^3 p dr = + \lambda \frac{d \ln N_v}{dt} \overline{r^3}$$

or

$$\frac{d \ln N_v}{dt} = \frac{\mu}{1 - \lambda \overline{r^3}} \quad (24)$$

The expression for the rate of the change of pore radius $\frac{dr}{dt} = v(r,t)$ can be obtained from (21') and (12)

$$v(r,t) = - \frac{\int_0^r \left(\mu + \lambda \frac{d \ln N_v}{dt} r^3 \right) p dr + \frac{d \ln N_v}{dt}}{p} \quad (25)$$

or utilizing (24)

$$v(r,t) = \frac{\mu}{p} \left(\frac{1 - \int_0^r r^3 p dr}{1 - \lambda \overline{r^3}} - \int_0^r p dr \right) \quad (25')$$

It is readily seen from this equation that pores of certain radius r^* will have $v = 0$. This will happen when

$$\lambda = \frac{\int_{r^*}^{\infty} p dr}{\int_0^{r^*} r^3 p dr - \overline{r^3} \int_0^{r^*} p dr} \quad (26)$$

It should be pointed out that, in derivation of equation (25) or (25'), the mean field approximation was not necessary.

DISCUSSION

The variational treatment of the entropy production in a system composed of N_v pores per unit volume yielded expressions for the size distribution function $p(r,t)$ (20'), the radial change rate of the pores $v(r,t)$ (5) and the change of the number of pores N_v (24) with time. These equations contain two constants λ and μ and two time functions $\phi(t)$ and $\psi(t)$. To determine them we have four auxiliary equations, (8), (16''), (22) and (23). Therefore the problem is amenable to complete solution, though the actual determination of the constants and functions may be cumbersome and probably will require computer calculations.

Before closing a few words should be said about the function $L(t)$, which was defined as a distance from a pore at which $\Delta C(x)$ becomes vanishingly small.

L is the only function which is determined by the mechanism of matter transport.

It has been suggested at the end of Appendix I that $L \sim N_v^{-1/3}$. This assumption may be sufficient if the process is dominated by interface reaction. In case of diffusion control $L \sim r + \sqrt{Dt}$ where D is the diffusion coefficient. For well dispersed systems, $N_v^{-1/3} > r + \sqrt{Dt}$. These assumptions are obviously very crude.

It looks like the mean field hypothesis eliminated in derivation of $v(r,t)$ returns here and nests itself in the theory of vacancy concentration fluctuations treated in Appendix I.

Finally the term $\exp(-\frac{4\pi K \Delta C_o^2}{\Omega k T r})$ in equation (20') deserves a comment. This function decreases rapidly as r approaches zero. Therefore for $r < \frac{4\pi K \Delta C_o^2}{\Omega k T}$, $p(r,t)$ is practically zero. This may be interpreted that there exists a pore of smallest radius

$$r_c = \frac{4\pi K \Delta C_o^2}{\Omega k T}$$

All pores with radius less than r_c collapse catastrophically. As $K \sim 10^{-30}$ ergs cm^2 and $\Delta C = 2\Omega\gamma/kT$ where γ is the surface tension of the solid, $r_c \sim 10^{-7}$ cm.

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APPENDIX I

FREE ENERGY INCREASE DUE TO PORES

The increase of Helmholtz free energy ΔF , due to the vacancy concentration near a single spherical pore of radius r is according to Cahn et al⁶

$$\Delta F_1 = \frac{4\pi}{\Omega} \int_r^L \left[\Delta f + K \left(\frac{dC}{dx} \right)^2 \right] x^2 dx \quad (A1)$$

where Ω is atomic volume, C is the vacancy concentration, K the coefficient measuring response of the system to concentration gradients, assumed to be constant, and L , the distance at which $\Delta C = C - C_0$, where C_0 is equilibrium vacancy concentration, is zero or vanishingly small. f is the free energy per atom and $\Delta f = f - f_0$ where f_0 is this free energy at equilibrium (corresponding to C_0 concentration of vacancies). Of course f is a function of vacancy concentration C which, in turn, is a function of the distance from pore center, x . The use of Helmholtz rather than Gibbs free energy is to simplify the calculations. For condensed systems the difference between these two approaches is minimal.

The free energy function given by equation (A1) has to be minimized with the steady state auxiliary condition

$$\nabla^2 C = \frac{1}{x} \frac{d^2}{dx^2} (x \Delta C) = \frac{1}{x^2} \frac{d}{dx} \left(x^2 \frac{d\Delta C}{dx} \right) = 0 \quad (A2)$$

(A2) yields at once

$$\Delta C = K_1 + \frac{K_2}{x} \text{ with } K_1 = 0 \text{ and } K_2 = r \Delta C(r) \\ \Delta C = \frac{r}{x} \Delta C(r) \text{ and } \frac{dC}{dx} = - \frac{r \Delta C(r)}{x^2} \quad (A3)$$

The Lagrange-Euler function is

$$I = \Delta f x^2 + K \left(\frac{dC}{dx} \right)^2 x^2 + \beta \left(2x \frac{dC}{dx} + 2x^2 \frac{d^2 C}{dx^2} \right) \quad (A4)$$

where β is a Lagrange multiplier. The Euler's equation

$$\frac{\partial I}{\partial C} - \frac{d}{dx} \left[\frac{\partial I}{\partial \left(\frac{dC}{dx} \right)} \right] = \frac{\partial \Delta f}{\partial C} x^2 - 2K \left[x^2 \frac{d^2 C}{dx^2} + 2x \frac{dC}{dx} \right] - 2\beta = 0 \quad (A5)$$

and as the expression in the bracket is by (A2) equal 0,

$$\frac{\partial \Delta f}{\partial C} x^2 - 2\beta = 0 \quad (A5')$$

which with the help of (A3) is converted into:

$$\frac{d\Delta f}{dx} = - \frac{2\beta r}{x^4} \Delta C(r) \quad (A6)$$

yielding after integration

$$\Delta f(x) = \frac{2}{3} \frac{\beta r \Delta C(r)}{x^3} \quad (A7)$$

β has dimensions of K in equation (A1) and has the same magnitude. Introducing (A7) and (A5) into (A1) and integrating we obtain:

$$\Delta F_1 = \frac{4\pi}{\Omega} \left[-r^3 \Delta f(r) \ln\left(\frac{r}{L}\right) + Kr \Delta C(r)^2 \right]$$

If we assume that the system of pores is well dispersed, with little overlapping of the vacancy clouds around pores, the total increase of free energy ΔF due to N_v pores per unit volume is

$$\Delta F = \frac{4\pi N_v}{\Omega} \int_0^\infty \left[-r^3 \Delta f(r) \ln\left(\frac{r}{L}\right) + Kr \Delta C(r)^2 \right] p dr \quad (A9)$$

The assumption of good dispersion means that the distance L is of the order of $N_v^{-1/3}$.

REFERENCES

1. C. Wagner, Zeit f. Elektrochemie 65, 581 (1961).
2. M. Lifshitz and V. V. Slyozov, J. Phys. & Chem. of Solids 19, 35 (1961).
3. G. C. Kuczynski, "Minimum Entropy Production Principle and Ostwald Ripening," The U. S. Department of Energy Contract No. 77-S-02-4385, February 1978.
4. S. R. DeGroot, "Thermodynamics of Irreversible Processes," North-Holland Publishing Co., Amsterdam and Interscience Publishers, Inc., N.Y. (1952) p. 196f.
5. T. de Donder "L'affinité" Gautier-Villars, Paris (1936) or T. de Donder and P. Van Rysselberghe "Affinity", Stanford University Press, Stanford University (1936).
6. J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 31, 688 (1958).