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MINIMUM ENTROPY PRODUCTION PRINCIPLE
AND OSTWALD RIPENING

Scientific Report

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INTRODUCTION

The problem of growth of particles in a medium capable of transmitting matter has been a subject of several theoretical treatments.^{1,2,3} All of them have tried to find a steady state solution to a continuity equation containing a distribution function for particle size, coupled with an expression for rate of change of particle size, usually obtained from a mean field approximation. No attempt has been made to derive the distribution function from a more general principle.

The objective of this note is to demonstrate that a distribution function can be obtained from a general principle such as the principle of minimum rate of entropy production.⁴

GENERAL RELATIONS

Let us consider N_v spherical particles of phase β dispersed in a phase α . N_v is a function of time only. The distribution function of radii of the particles $f(r,t)$ is defined as $f(r,t)dr$ being the number of particles having radius between r and $r+dr$, at a time t , per unit volume. The interaction among the particles is expressed by a known rate of the change of the particle radius with time, $\frac{dr}{dt} = v(r,t)$. The continuity equation can be written in the form

$$\frac{\partial f}{\partial r} + \frac{\partial(fv)}{\partial r} = 0 \quad (1)$$

We can normalize function $f(r,t)$ by introducing function $p(r,t) = f(r,t)/N_v$. Obviously

$$\int_{r_c}^{\infty} f(r,t)dr = N_v \text{ and } \int_{r_c}^{\infty} p(r,t)dr = 1 \quad (2)$$

where r_c is the radius of the smallest aggregate of atoms which can be still considered as a particle of the phase β and not a fluctuation in the matrix α . This problem will be discussed later in more detail. Equation (1) can be rewritten in the form:

$$\frac{\partial p}{\partial t} = - \frac{d \ln N_v}{dt} p - \frac{\partial(vp)}{\partial r} \quad (3)$$

From (2) it is obvious that

$$\int_{r_c}^{\infty} \frac{\partial f(r,t)}{\partial t} dr = \dot{N}_v = \frac{dN_v}{dt} \text{ and } \int_{r_c}^{\infty} \frac{\partial p(r,t)}{\partial t} dr = 0 \quad (4)$$

Integrating both sides of (3) we obtain:

$$\frac{d \ln N_v}{dt} = - \int_{r_c}^{\infty} \frac{\partial(vp)}{\partial r} dr = v(r_c)p(r_c) \quad (5)$$

RATE OF ENTROPY PRODUCTION

Turning now to the rate of entropy production, we note that there are three sources of entropy: the first, the configurational entropy due to the change of distribution of particle size of the system, the second is due to the concentration gradient caused by capillary forces acting near the particle interfaces, and the third, to the reduction of total surface energy of the system.

The entropy S_1 per unit volume due to particle distribution given by function p is:

$$S_1 = - N_v K \int_{r_c}^{\infty} p \ln p \, dr \quad (6)$$

and the rate of this entropy increases

$$\frac{dS_1}{dt} = - N_v k \int_{r_c}^{\infty} \frac{\partial p}{\partial t} (1 + \ln p) \, dr \quad (7)$$

which in view of the second equation (4) is

$$\frac{dS_1}{dt} = - N_v k \int_{r_c}^{\infty} \frac{\partial p}{\partial t} \ln p \, dr \quad (7')$$

The rate of entropy production due to the chemical potential μ gradient around one particle of radius r per unit volume⁴ is:

$$\frac{dS_r}{dt} = - \frac{1}{T} \int_r^{\infty} J \frac{\partial \mu}{\partial x} 4\pi x^2 \, dx \quad (8)$$

where J the diffusion flux is given by the familiar relation

$$J = - B \frac{\partial \mu}{\partial x} \quad (9)$$

and mobility $B = \frac{DC_0}{KT}$, where D is diffusion coefficient and C_0 the concentration expressed as the number of atoms or vacancies per unit volume, away from the

particle interface. Inserting (9) into (8) we obtain

$$\frac{dS_r}{dt} = 4\pi \frac{DC_o}{kT^2} \int_r^\infty \left(\frac{\partial \mu}{\partial x}\right)^2 x^2 dx \quad (10)$$

Chemical potential of a solution assumed to be ideal is:

$$\mu = \mu_o + kT \ln C \quad (11)$$

and

$$\frac{\partial \mu}{\partial x} = \frac{kT}{C} \frac{\partial C}{\partial x} \quad (11')$$

If the particle is a sphere then the steady state solution of the diffusion equation yields:

$$C = \frac{a}{x} + b \quad (12)$$

where constants a and b are determined from the boundary conditions

$$\begin{aligned} x = r, C &= C_o + \Delta C \\ x \rightarrow \infty, C &\rightarrow C_o \end{aligned} \quad (13)$$

Thus
$$C = C_o + \frac{r\Delta C}{x}$$

and
$$\frac{\partial C}{\partial x} = -\frac{a}{x^2} = -\frac{r\Delta C}{x^2} \quad (14)$$

where
$$\Delta C = \frac{2C_o \gamma \Omega}{kTr} \quad (15)$$

γ being the interface tension and Ω the atomic volume.

This relation is true when the radius of a particle is not too small.

For
$$\frac{2\gamma\Omega}{kTr} \gg 1$$

$$\Delta C = C_o \left[\exp\left(\frac{2\gamma r}{kTr}\right) - 1 \right] \quad (15')$$

For simplicity we shall use relation (15) throughout.

Introducing (14) first to (11') and then (11') into (10) and integrating,

we obtain

$$\frac{dS_r}{dt} = - \frac{4\pi DC_o r^2}{T} \left(\frac{\Delta C k T}{C_o} \right)^2 \left[\frac{1}{x} \right]_r^\infty = \frac{4\pi D r}{C_o} \frac{(\Delta C k T)^2}{T} \quad (16)$$

Replacing ΔC by expression (15) and rearranging

$$\frac{dS_r}{dt} = \frac{16\pi DC_o (\gamma \Omega)^2}{r T} \quad (17)$$

Therefore the rate of entropy production per unit volume due to the gradients near N_v particles is

$$\frac{dS_2}{dt} = N_v \int_{r_c}^{\infty} \frac{dS_r}{dt} dr = 16\pi N_v k DC_o \left(\frac{\gamma \Omega}{k T} \right)^2 \left(\frac{\bar{1}}{r} \right) \quad (18)$$

where a bar over a function signifies its mean value.

This equation is approximately true provided that N_v is not too large and the overlaps of concentration can be neglected.

Finally, the third source of entropy is the reduction of the total particle area. The rate of entropy production in this case can be calculated from the deDonder theorem,⁴

$$\frac{dS_3}{dt} = - \frac{1}{T} \frac{d\Delta G}{dt} \quad (19)$$

where ΔG is the Gibbs free energy of the system per unit volume. In our case $\Delta G = \gamma A$, where A is the total particle area per unit volume. Equation (19) can be rewritten in the form

$$\frac{dS_3}{dt} = - \frac{\gamma}{T} \frac{dA}{dt} \quad (20)$$

which with the help of A6 becomes

$$\frac{dS_3}{dt} = - \frac{2N_v \gamma}{T} \frac{\bar{1}}{rv} \quad (21)$$

The total rate of entropy production is obtained by adding (7'), (18) and (21)

$$\frac{dS}{dt} = \frac{dS_1}{dt_2} + \frac{dS_2}{dt} + \frac{dS_3}{dt} = - N_v k \left\{ \int_{r_c}^{\infty} \left(\frac{\partial p}{\partial t} \ln p - \frac{M}{r} + \frac{2\gamma}{kT} rv \right) p dr \right\} \quad (22)$$

where $M = 16\pi DC_o \left(\frac{\gamma\Omega}{kT} \right)^2$.

DERIVATION OF DISTRIBUTION FUNCTION

Now the function in equation (19) must be minimized with respect to all possible distribution functions, $p(r,t)$, subject however to certain conservation conditions, the first of which is that

$$\int_{r_c}^{\infty} p dr = 1. \quad (22)$$

One would be tempted to assume $\overline{r^2 v} = 0$ which means that the total volume of precipitates is conserved. However, as particles grow, the excess concentration around them decreases and in fact $\overline{r^2 v} > 0$. This problem is discussed in detail in Appendix B, where also it is shown that

$$\overline{r^2 v} = K_1 \left(\frac{\partial v}{\partial r} \right) \quad (B7)$$

where

$$K_1 = \frac{4\pi C_o \gamma \Omega L^2}{(C_1 - C_o) kT}$$

Therefore as the second conservation condition we have

$$\int_{r_c}^{\infty} \left(r^2 v - K_1 \frac{\partial v}{\partial r} \right) p dr = 0 \quad (23)$$

Finally we have to express the obvious fact that

$$\frac{d \ln N_v}{dt} < 0 \quad (24)$$

Let us take equation (3) and rewrite it in the form

$$\frac{\partial p}{\partial t} = - \frac{d \ln N_v}{dt} p - \frac{\partial v}{\partial r} p - v \frac{\partial p}{\partial r} \quad (3')$$

But the last term on the right side is simply $\frac{\partial p}{\partial t}$ because

$$v \frac{\partial p}{\partial r} = \frac{v}{\left(\frac{dr}{dt}\right)} \frac{\partial p}{\partial t} = \frac{\partial p}{\partial t} \quad (25)$$

Therefore

$$2 \frac{\partial p}{\partial t} = - \frac{d \ln N_v}{dt} p - \frac{\partial v}{\partial r} p. \quad (26)$$

Integrating both sides and taking into consideration (4) we obtain

$$\overline{\frac{\partial v}{\partial r}} = - \frac{d \ln N_v}{dt} \quad (27)$$

Hence $\left(\frac{\partial v}{\partial r}\right)$ is always positive.

Therefore another conservative condition is

$$\int_{r_c}^{\infty} \left(\frac{\partial v}{\partial r} - \overline{\frac{\partial v}{\partial r}} \right) p \, dr = 0 \quad (28)$$

To minimize function (22) variational calculus is used. First let us find a function I independent of conditions (2), (23) and (28). Using the method of Lagrange multipliers we multiply equation (2) by $(-N_v k \eta)$, (23) by $(-N_v k \beta)$ and (28) by $(-N_v k \lambda)$ and add the products to the function under the integral in equation (19). The desired function I has the form

$$I = \frac{\partial p}{\partial t} \ln p \cdot p + \eta p + \frac{2\gamma}{kT} r v - \beta K_1 \frac{\partial v}{\partial r} p - \lambda \overline{\frac{\partial v}{\partial r}} p + \beta^2 r^2 v p - \frac{M}{r} p + \lambda \frac{\partial v}{\partial r} p \quad (29)$$

or, using (3) and (27),

$$I = \left(\overline{\frac{\partial v}{\partial r}}\right) \ln p \cdot p - \frac{\partial v}{\partial r} \ln p \cdot p - v \ln p \frac{\partial p}{\partial r} + \eta p + \frac{2k}{kT} r v - \beta K_1 \frac{\partial v}{\partial r} p - \lambda \overline{\frac{\partial v}{\partial r}} p + \beta^2 r^2 v p - \frac{\mu}{r} p + \lambda \frac{\partial v}{\partial r} p. \quad (30)$$

The solution of the variational equation

$$\delta \int_{r_c}^{\infty} I \, dr = 0 \quad (31)$$

or, equivalently, Euler's equation

$$\frac{\partial I}{\partial p} - \frac{d}{dr} \left(\frac{\partial I}{\partial p_r} \right) = 0 \quad (32)$$

with $p_r = \frac{\partial p}{\partial r}$, should yield a distribution function $p(r,t)$ which minimizes the rate of entropy production given by equation (22);

$$\frac{\partial I}{\partial p} = \left(\frac{\partial v}{\partial r} \right) + \left(\frac{\partial v}{\partial r} \right) \ln p - \frac{\partial v}{\partial r} - \frac{\partial v}{\partial r} \ln p - v \frac{\partial \ln p}{\partial r} + \frac{2\gamma}{kT} rv +$$

$$\eta - \beta K_1 \frac{\partial v}{\partial r} - \lambda \left(\frac{\partial v}{\partial r} \right) + \beta r^2 v - \frac{M}{r} + \lambda \frac{\partial v}{\partial r}$$

$$\frac{\partial I}{\partial p_r} = -v \ln p \text{ and } -\frac{d}{dr} \left(\frac{\partial I}{\partial p_r} \right) = \frac{\partial v}{\partial r} \ln p + v \frac{\partial \ln p}{\partial r}$$

Euler's equation (32) becomes

$$\left(\frac{\partial v}{\partial r} \right) \ln p - (\lambda - 1) \left(\frac{\partial v}{\partial r} \right) + \eta + \beta r^2 v + \frac{2\gamma}{kT} rv - \frac{M}{r} + (\lambda - \beta K_1 - 1) \frac{\partial v}{\partial r} = 0$$

Yielding expression for $p(r,t)$ in the form

$$\left(\frac{\partial v}{\partial r} \right) \ln p = \eta + (\lambda - 1) \left(\frac{\partial v}{\partial r} \right) - \beta r^2 v - \frac{2\gamma}{kT} rv + \frac{M}{r} - (\lambda - \beta K_1 - 1) \frac{\partial v}{\partial r} \quad (33)$$

$\left(\frac{\partial v}{\partial r} \right) \ln p$ is always negative because $p(r,t) < 1$. For very large particles $p(r,t)$ should approach zero hence $\ln p \rightarrow -\infty$. Also for large particles $\frac{M}{r}$ and $\frac{\partial v}{\partial r}$ approach zero, hence $\beta r^2 v \rightarrow \infty$ and β must be positive.

For small particles as $r \rightarrow r_c$ only the last two terms on the right side of equation (30) count. The condition that the right side is negative is

$$-\frac{2\gamma}{kT} r_c v(r_c) + \frac{M}{r_c} - (\lambda - \beta K_1 - 1) \left(\frac{\partial v}{\partial r} \right)_{r_c} < 0 \quad (34)$$

and as $\left(\frac{\partial v}{\partial r} \right)_{r_c} > 0$

$$\lambda > 1 + \beta K_1 + \frac{M - \frac{2\gamma}{kT} r_c v(r_c)}{r_c \left(\frac{\partial v}{\partial r} \right)_{r_c}} \quad (34')$$

Summing up results obtained in this section one may say that the distribution function $p(r,t)$ for small r decreases to zero as an exponential function which can be approximated by an expression

$$p(r,t) \rightarrow \exp(-H(t)/r^n) \quad (35)$$

where $H(t)$ is a function of time only and n is a constant between 2 and 4. At large r , $p(r,t)$ has an exponential tail. In between there must be some maximum which, in principle, could be determined from (33), setting $\frac{d \ln p}{dr} = 0$. These properties of our distribution function are radically different from those obtained by Lifshitz and Slyozov² and Wagner³ whose functions decrease to zero as r^n and have rather sharp cutoff at large particle radii.

Appendix A

Mean Values

Evaluation of mean values of various functions introduced in the main text of this report is based on some simple theorems which now will be derived.

$$\overline{\frac{dr^n}{dt}} = \int_{r_c}^{\infty} r^n \frac{\partial p}{\partial t} dr \quad A1$$

which by equation (3) becomes

$$\begin{aligned} \overline{\frac{dr^n}{dt}} &= - \frac{d \ln N_v}{dt} \overline{r^n} - \int_{r_c}^{\infty} r^n \frac{\partial (vp)}{\partial r} dr \\ &= - \frac{d \ln N_v}{dt} \overline{r^n} + r_c^n v(r_c) p(r_c) + n \overline{r^{n-1} v} \end{aligned} \quad A2$$

Dividing this equation by $\overline{r^n}$ and using equations (5) we obtain

$$\frac{d \ln \overline{r^n}}{dt} = - \frac{d \ln N_v}{dt} \left(1 - \frac{r_c^n}{\overline{r^n}} \right) + n \frac{\overline{r^{n-1} v}}{\overline{r^n}} \quad A3$$

or as $r_c^n / \overline{r^n}$ is very small A3 can be written to good approximation

$$\frac{d \ln \overline{r^n}}{dt} = \frac{d \ln N_v}{dt} + n \frac{\overline{r^{n-1} v}}{\overline{r^n}} \quad A3'$$

This equation can be applied to obtain an expression for change of total area of particles per unit volume A with time. By definition

$$A = N_v \overline{r^2} \quad A4$$

Note that shape factor has been omitted. Converting A4 into logarithmic form and differentiating, we obtain

$$\frac{d \ln A}{dt} = \frac{d \ln N_v}{dt} + \frac{d \ln \bar{r}^2}{dt} \quad A5$$

Combining A5 with A3', equation A5 takes the form

$$\frac{d \ln A}{dt} = \frac{2 \bar{r} v}{\bar{r}^2} \quad A6$$

Next let us apply equation A3 to the evolution of total volume of precipitates or pores per unit volume in time. It is defined as

$$P = N_v \bar{r}^3 \quad A7$$

Again the shape factor is omitted. By the same mathematical manipulations as in the case of A given above we obtain

$$\frac{d \ln P}{dt} = \frac{3 \bar{r}^2 v}{\bar{r}^3} \quad A8$$

In case of precipitation of a second phase when total volume of molecules of that phase is conserved $\frac{d \ln P}{dt} = 0$ and we have

$$\bar{r}^2 v = 0 \quad A9$$

This condition is only an approximation because some of the molecules are in supersaturated solution due to the capillary forces at the interfaces of small particles and are released slightly increasing P, as the particles grow.

Finally using equation A3' or A3 it is easy to demonstrate that

$$\frac{d \bar{r}}{dt} - \bar{v} = - \frac{d \ln N_v \bar{r}}{dt} \quad A10$$

As $\frac{d \ln N_v}{dt} < 0$ we conclude that

$$\frac{d \bar{r}}{dt} > \bar{v} \quad A10'$$

the difference $\frac{d\bar{v}}{dt} - \frac{\partial \bar{v}}{\partial t}$ can be calculated as follows:

$$\frac{\partial \bar{v}}{\partial t} = \int_{r_c}^{\infty} \frac{\partial v}{\partial t} p \, dr = \int_{r_c}^{\infty} \frac{\partial v}{\partial r} \frac{dr}{dt} p \, dr = \int_{r_c}^{\infty} v \frac{\partial v}{\partial r} p \, dr = \overline{v \frac{\partial v}{\partial r}} \quad A11$$

and

$$\begin{aligned} \frac{d\bar{v}}{dt} &= \int_{r_c}^{\infty} v \frac{\partial p}{\partial t} \, dr = - \frac{d \ln N}{dt} \bar{v} - \int_{r_c}^{\infty} v \frac{\partial (vp)}{\partial r} \, dr \\ &= \frac{d \ln N}{dt} \bar{v} (v(r_c) - \bar{v}) + \overline{v \frac{\partial v}{\partial r}} \end{aligned} \quad A12$$

Hence from A12 and A11

$$\frac{d\bar{v}}{dt} - \frac{\partial \bar{v}}{\partial t} = \frac{d \ln N}{dt} \bar{v} (v(r_c) - \bar{v}) \quad A13$$

As $|v(r_c)| > |\bar{v}|$, we have $\frac{d\bar{v}}{dt} < \frac{\partial \bar{v}}{\partial t}$.

APPENDIX B

Average Particle Volume Change

It has been mentioned in the main text of this note that the relation $\overline{r^2 v}$ should not be equal to zero. Indeed, it means that the particle volume is not conserved. In reality the total number of atoms is conserved. If before separation into two phases, the number of B atoms per unit volume in homogeneous phase is C'_0 and after separation, C_0 in phase α and C_1 in β , then:

$$C'_0 = (1 - N_v \overline{r^3}) C_0 + C_1 N_v \overline{r^3} + \Delta N \quad (B1)$$

where ΔN is the excess number of atoms B per unit volume maintained in α (matrix) near the curved interfaces of the dispersed particles. Let us first estimate a number Δn of B atoms near one particle of radius r

$$\Delta n = 4\pi \int_r^L (C - C_0) x^2 dx \quad (B2)$$

where L is dimension of the specimen, $L \approx 1$. But $C - C_0$ by equation (14) is $r\Delta C/x$ where $\Delta C = \frac{2C_0\gamma\Omega}{kT}$. Therefore

$$\Delta n = \frac{4\pi C_0 \gamma \Omega (L^2 - r^2)}{kT} \quad (B3)$$

and

$$\Delta N = N_v \int_{r_c}^{\infty} \Delta n p dr \quad (B4)$$

As $L \gg r$

$$\Delta N = \frac{4\pi C_0 \gamma \Omega N_v L^2}{kT} \quad (B5)$$

Inserting this into B1, differentiating both sides of the equation with respect to t , and rearranging, we obtain

$$0 = \left(\frac{d \ln N_v}{dt} + \frac{d \ln \bar{r}^3}{dt} \right) N_v \bar{r}^3 (C_1 - C_0) + \frac{4\pi C_0 \gamma \Omega L^2 N_v}{kT} \frac{d \ln N_v}{dt} \quad (B6)$$

because obviously $dC'_0/dt = 0$.

But from A3' $\frac{d \ln N_v}{dt} + \frac{d \ln \bar{r}^3}{dt} = \frac{3 \bar{r}^3 \dot{v}}{\bar{r}^3}$; therefore B6 yields

$$3 \bar{r}^2 \dot{v} = - \frac{4\pi C_0 \gamma \Omega L^2}{(C_1 - C_0) kT} \frac{d \ln N_v}{dt} = \frac{4\pi C_0 \gamma \Omega L^2}{(C_1 - C_0) kT} \left(- \frac{\partial v}{\partial r} \right) \quad (B7)$$

and $\bar{r}^2 \dot{v} > 0$ as expected.

We may take this opportunity and show that v cannot be represented by a mean field approximation. For a diffusion controlled process in mean field approximation

$$v = \frac{\alpha}{r} \left(\frac{1}{r^*} - \frac{1}{r} \right) \quad (B8)$$

where α is a function of temperature only and $r^*(t)$ is the radius of the particles which, at time t , neither shrink nor expand. Inserting this expression in B7 after rather simple manipulations, we obtain

$$\frac{\bar{r}}{r^*} - 1 = K \left[2 \left(\frac{1}{r^3} \right) - \frac{1}{r^*} \left(\frac{1}{r^2} \right) \right] \quad (B9)$$

where $K = \frac{4\pi C_0 \gamma \Omega L^2}{3(C_1 - C_0) kT}$.

Solving equation B9 for r^* , we obtain

$$r^* = \frac{\bar{r} + K \left(\frac{1}{r} \right)}{1 + 2K \left(\frac{1}{r^3} \right)} \quad (B10)$$

As K is of the order of 10^{-6} and $\left(\frac{1}{r^2} \right)$ is much higher

$$r^* \approx \left(\frac{1}{r^2} \right) / 2 \left(\frac{1}{r^3} \right) \quad (B10')$$

From B8 we easily obtain

$$\frac{\partial v}{\partial r} = \frac{\alpha}{r^2} \left(\frac{2}{r} - \frac{1}{r^*} \right) \quad \text{B11}$$

and

$$\overline{\left(\frac{\partial v}{\partial r} \right)} = \alpha \left[2 \overline{\left(\frac{1}{r^3} \right)} - \overline{\left(\frac{1}{r^2} \right)} \frac{1}{r^*} \right] \quad \text{(B12)}$$

Inserting B10 into this expression, we obtain

$$\overline{\left(\frac{\partial v}{\partial r} \right)} = 0 \quad \text{(B13)}$$

which of course is impossible in our theory. Thus we have shown that the rate of particle radius change v is inadequately represented by mean field approximation.

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