Ostwald ripening

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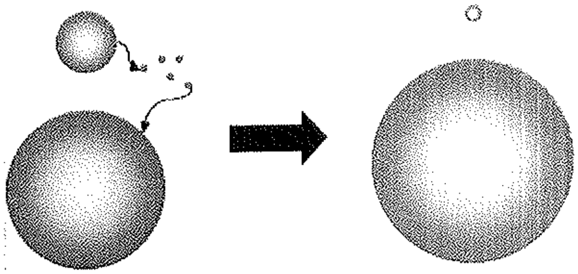


Basic schematic of the Ostwald ripening process

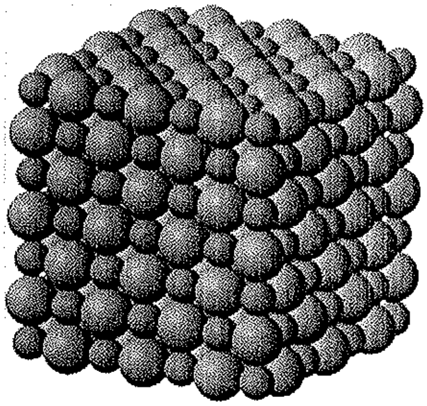
Ostwald ripening is an observed phenomenon in solid solutions or liquid sols which describes the change of an inhomogeneous structure over time. Over time, small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles.[1]

Dissolution of small crystals or sol particles and the redeposition of the dissolved species on the surfaces of larger crystals or sol particles was first described by Wilhelm Ostwald in 1896.[2] Ostwald ripening is generally found in water-in-oil emulsions, while flocculation is found in oil-in-water emulsions.[3]

Contents

Mechanism

This thermodynamically-driven spontaneous process occurs because larger particles are more energetically favored than smaller particles.[4] This stems from the fact that molecules on the surface of a particle are energetically less stable than the ones in the interior.



Cubic crystal structure (sodium chloride)

Consider a cubic crystal of atoms: all the atoms inside are bonded to 6 neighbors and are quite stable, but atoms on the surface are only bonded to 5 neighbors or fewer, which makes these surface atoms less stable. Large particles are more energetically favorable since, continuing with this example, more atoms are bonded to 6 neighbors and fewer atoms are at the unfavorable surface. As the system tries to lower its overall energy, molecules on the surface of a small particle (energetically unfavorable, with only 3 or 4 or 5 bonded neighbors) will tend to detach from the particle, as per the Kelvin equation, and diffuse into the solution. When all small particles do this, it increases the concentration of free molecules in solution. When the free molecules in solution are supersaturated, the free molecules have a tendency to condense on the surface of larger particles.[4] Therefore, all smaller particles shrink, while larger particles grow, and overall the average size will increase. As time tends to infinity, the entire population of particles becomes one large spherical particle to minimize the total surface area.

In 1961, Lifshitz and Slyozov [5] performed a mathematical investigation of Ostwald ripening in the case where diffusion of material is the slowest process. They began by stating how a single particle grows in a solution. This equation describes where the boundary is between small, shrinking particles and large, growing particles. They finally conclude that the average radius of the particles $\langle R \rangle$, grows as follows:

$$\langle R \rangle^3 - \langle R \rangle_0^3 = \frac{8\gamma c_\infty v^2 D}{9 R_g T} t$$

where

$\langle R \rangle$ = average radius of all the particles
γ = particle surface tension or surface energy
c_∞ = solubility of the particle material
v = molar volume of the particle material
D = diffusion coefficient of the particle material
R_g = ideal gas constant
T = absolute temperature and
t = time.

Note that the quantity $\langle R \rangle^3$ is different from $\langle R^3 \rangle$, and only the latter one can be used to calculate average volume, and that the statement that $\langle R \rangle$ goes as $t^{1/3}$ relies on $\langle R \rangle_0$ being zero; but because nucleation is a separate process from growth, this places $\langle R \rangle_0$ outside the bounds of validity of the equation. In contexts where the actual value of $\langle R \rangle_0$ is irrelevant, an approach that respects the meanings of all terms is to take the time derivative of the equation to eliminate $\langle R \rangle_0$ and t. Another such approach is to change the $\langle R \rangle_0$ to $\langle R \rangle_i$ with the initial time i having a positive value.

Also contained in the Lifshitz and Slyozov derivation is an equation for the size distribution function f(R, t) of particles. For convenience, the radius of particles is divided by the average radius to form a new variable, $\rho = R(\langle R \rangle)^{-1}$.

$$f(R,t) = \frac{4}{9}\left(\frac{3}{3+\rho}\right)^{\frac{7}{3}}\left(\frac{1.5}{1.5-\rho}\right)^{\frac{11}{3}}\exp\left(-\frac{1.5}{1.5-\rho}\right)\rho < 1.5$$

At the same time that Lifshitz and Slyozov published their findings, Carl Wagner performed his own mathematical investigation of Ostwald ripening,[6] examining both systems where diffusion was slow and also where attachment and detachment at the particle surface was slow. Although his calculations and approach were different, Wagner came to the same conclusions as Lifshitz and Slyozov for slow-diffusion systems. This duplicate derivation went unnoticed for years because the two scientific papers were published on opposite sides of the Iron Curtain in 1961.[*citation needed*] It was not until 1975 that Kahlweit addressed the fact that the theories were identical[7] and combined them into the Lifshitz-Slyozov-Wagner or LSW Theory of Ostwald ripening. Many experiments and simulations have shown LSW theory to be robust and accurate. Even some systems that undergo spinodal decomposition have been shown to quantitatively obey LSW theory after initial stages of growth.[8]

Wagner derived that when attachment and detachment of molecules is slower than diffusion, then the growth rate becomes

$$\langle R\rangle^2 = \frac{64\gamma c_\infty v^2 k_s}{81 R_g T} t$$

where k_s is the reaction rate constant of attachment with units of length per time. Since the average radius is usually something that can be measured in experiments, it is fairly easy to tell if a system is obeying the slow-diffusion equation or the slow-attachment equation. If the experimental data obeys neither equation, then it is likely that another mechanism is taking place and Ostwald ripening is not occurring.

Although LSW theory and Ostwald ripening were intended for solids ripening in a fluid, Ostwald ripening is also observed in liquid-liquid systems, for example, in an oil-in-water emulsion polymerization.[3] In this case, Ostwald ripening causes the diffusion of monomers (i.e. individual molecules or atoms) from smaller droplets to larger droplets due to greater solubility of the single monomer molecules in the larger monomer droplets. The rate of this diffusion process is linked to the solubility of the monomer in the continuous (water) phase of the emulsion. This can lead to the destabilization of emulsions (for example, by creaming and sedimentation).[9]

Specific examples

An everyday example of Ostwald ripening is the re-crystallization of water within ice cream which gives old ice cream a gritty, crunchy texture. Larger ice crystals grow at the expense of smaller ones within the ice cream, creating a coarser texture.[10]

Another gastronomical example is in the ouzo effect, where the droplets in the cloudy microemulsion grow by Ostwald ripening.

In geology, it is the textural coarsening, aging or growth of phenocrysts and crystals in solid rock which is below the solidus temperature. It is often ascribed as a process in the formation of orthoclase megacrysts,[11] as an alternative to the physical processes governing crystal growth from nucleation and growth rate thermochemical limitations.

In chemistry, the term refers to the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones. In the process, many small crystals formed initially slowly disappear, except for a few that grow larger, at the expense of the small crystals. The smaller crystals act as fuel for the growth of bigger crystals. Limiting Ostwald ripening is fundamental in modern technology for the solution synthesis of quantum dots.[12] Ostwald ripening is also the key process in the digestion of precipitates, an important step in gravimetric analysis. The digested precipitate is generally purer, and easier to wash and filter.

Oil droplets in pastis mixed with water grow by Ostwald ripening.

Ostwald ripening can also occur in emulsion systems, with molecules diffusing from small droplets to large ones through the continuous phase. When a miniemulsion is desired, an extremely hydrophobic compound is added to stop this process from taking place.

See also

- Rock microstructure

Cahn–Hilliard equation

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The **Cahn–Hilliard equation** (after John W. Cahn and John E. Hilliard) is an equation of mathematical physics which describes the process of phase separation, by which the two components of a binary fluid spontaneously separate and form domains pure in each component. If c is the concentration of the fluid, with $c = \pm 1$ indicating domains, then the equation is written as

$$\frac{\partial c}{\partial t} = D\nabla^2\left(c^3 - c - \gamma\nabla^2 c\right),$$

where D is a diffusion coefficient with units of $\mathrm{Length}^2/\mathrm{Time}$ and $\sqrt{\gamma}$ gives the length of the transition regions between the domains. Here $\partial/\partial t$ is the partial time derivative and ∇^2 is the Laplacian in n dimensions. Additionally, the quantity $\mu = c^3 - c - \gamma\nabla^2 c$ is identified as a chemical potential.

Related to it is the Allen–Cahn equation, as well as the Stochastic Cahn–Hilliard Equation and the Stochastic Allen–Cahn equation.

Features and applications

Of interest to mathematicians is the existence of a unique solution to the Cahn–Hilliard equation, given smooth initial data. The proof relies essentially on the existence of a Lyapunov functional. Specifically, if we identify

$$F[c] = \int d^n x \left[\frac{1}{4}\left(c^2 - 1\right)^2 + \frac{\gamma}{2}\left|\nabla c\right|^2\right],$$

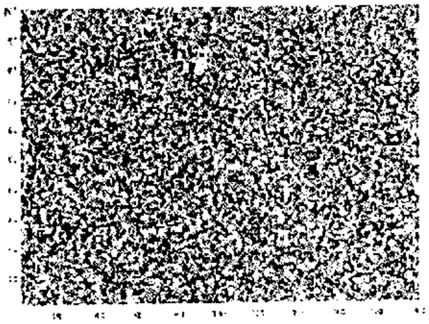
as a free energy functional, then

$$\frac{dF}{dt} = -\int d^n x \left|\nabla \mu\right|^2,$$

so that the free energy decays to zero. This also indicates segregation into domains is the asymptotic outcome of the evolution of this equation.

In real experiments, the segregation of an initially mixed binary fluid into domains is observed. The segregation is characterized by the following facts.

- There is a transition layer between the segregated domains, with a profile given by the function $c(x) = \tanh\left(\frac{x}{\sqrt{2\gamma}}\right)$, and hence a typical width $\sqrt{\gamma}$ because this function is an equilibrium solution of the Cahn–Hilliard equation.
- Of interest also is the fact that the segregated domains grow



Evolution of random initial data under the in time as a power law. That is, if $L(t)$ is a typical domain size, then $L(t) \propto t^{1/3}$. This is the Lifshitz–Slyozov law, and has been proved rigorously for the Cahn–Hilliard equation and observed in numerical simulations and real experiments on binary fluids.

- The Cahn–Hilliard equation has the form of a conservation law, $\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{j}(x)$, with $\mathbf{j}(x) = D\nabla\mu$. Thus the phase separation process conserves the total concentration $C = \int d^n x c(x,t)$, so that $\frac{dC}{dt} = 0$.
- When one phase is significantly more abundant, the Cahn–Hilliard equation can show the phenomenon known as Ostwald ripening, where the minority phase forms spherical droplets, and the smaller droplets are absorbed through diffusion into the larger ones.

The Cahn–Hilliard equations finds applications in diverse fields: in interfacial fluid flow, polymer science and in industrial applications. The solution of the Cahn–Hilliard equation for a binary mixture demonstrated to coincide well with the solution of a Stefan problem and the model of Thomas and Windle.[1] Of interest to researchers at present is the coupling of the phase separation of the Cahn–Hilliard equation to the Navier–Stokes equations of fluid flow.

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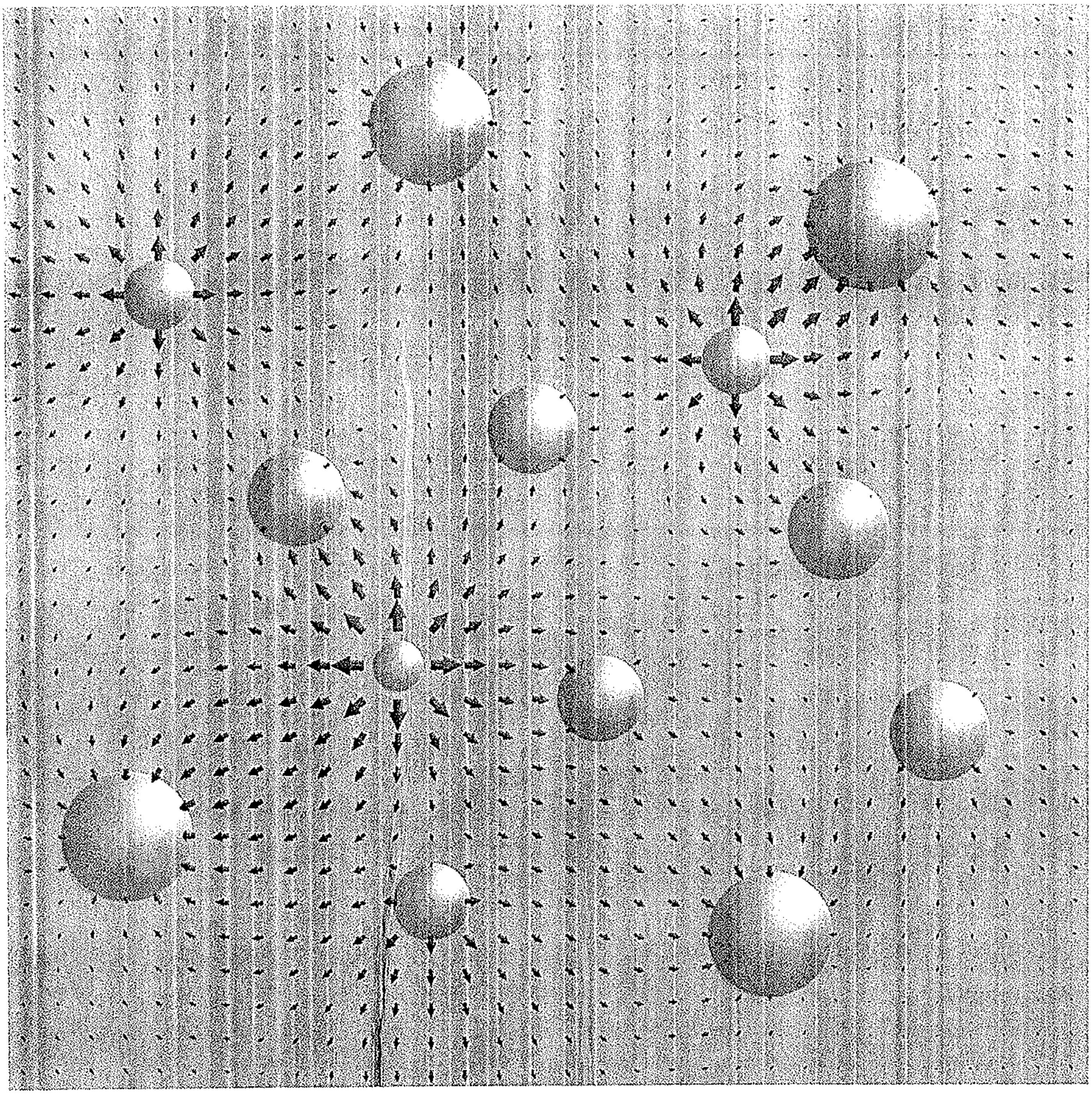


OSTWALD RIPENING: DROPLET PATTERNS

CAHN HILLIARD EQUATION

$$U_t = D\Delta\left[-\gamma\Delta U - U + U^3\right] \qquad \gamma = \varepsilon^2 \ll 1$$

$$U_n = 0,\ \partial_n \Delta U = 0 \quad \text{ON} \quad \partial\Omega.$$

NOW DEFINE

$$E(U) = \int_\Omega \left(\frac{\gamma}{2} |\nabla U|^2 + \frac{1}{4}\left(U^2 - 1\right)^2 \right) d\underline{x}.$$

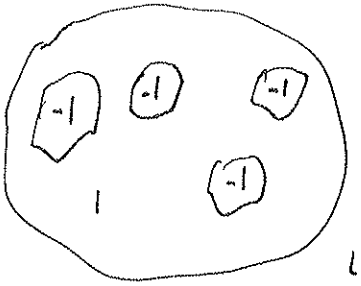
THEN ONE CAN SHOW THAT

$$\frac{dE}{dt} = -\int_\Omega |\nabla \mu|^2 \, d\underline{x} < 0.$$

WHERE $\mu = U^3 - U - \gamma \Delta U.$

THUS THE FREE ENERGY DECAYS AS $t \to \infty$

THE QUASI-EQUILIBRIUM STATES ARE ISLANDS OF $U \approx -1$ SEPARATING REGIONS WHERE $U \approx 1$ BY INTERFACES.



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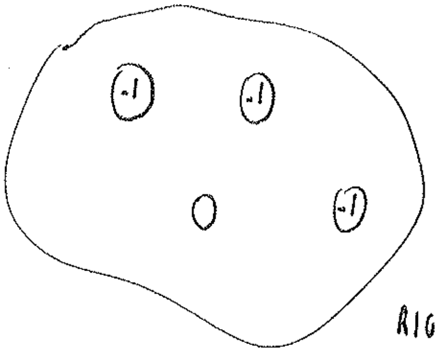


RIGHT

IF WE FIX THE MASS $M = \int_\Omega (U+1)\, d\underline{x}$ TO BE SMALL THEN WE OBTAIN A DROPLET PATTERN (RIGHT FIGURE) WITH ROUGHLY SPHERICAL SHAPED DROPLETS.

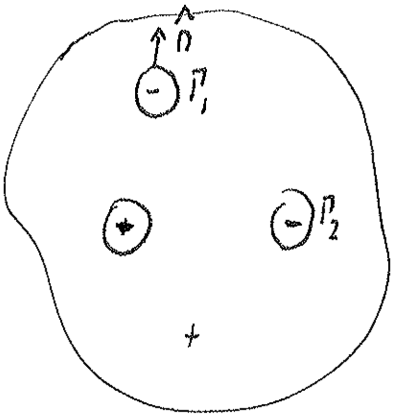
Q. WHAT IS DYNAMICS AS $t \gg 1$ OF SMALL DROPLET PATTERN?

IT CAN BE SHOWN

[SEE SECTION 5 OF "FRONT MIGRATION IN THE NONLINEAR CAHN-HILLIARD EQUATION", PROC. ROY. SOC. SERIES A VOL. 422, 1863, (1989), PP. 261-278)

THAT ON A SUITABLY LONG TIME SCALE AND FOR $\varepsilon \to 0$ THE CHEMICAL POTENTIAL U IS A SCALAR MULTIPLE OF THE SOLUTION TO THE FREE BOUNDARY MULLINS-SEKERKA PROBLEM

$$(*) \quad \begin{cases} \Delta U = 0 & \text{IN } \Omega \\ U = H_i & \text{ON } \Gamma(t) = \bigcup_{i=1}^{N} \Gamma_i(t) \\ V = -\left[\dfrac{\partial U}{\partial n} \right] & \text{ON } \Gamma(t) \\ \partial_n U = 0 & \text{ON } \partial\Omega. \end{cases}$$



- HERE H_i IS MEAN CURVATURE OF $\Gamma_i(t)$.
- $\left[\dfrac{\partial U}{\partial n} \right] = \dfrac{\partial U^+}{\partial n} - \dfrac{\partial U^-}{\partial n}$.
- $V > 0$ FOR A SHRINKING SPHERE (SIGN CONVENTION), IT IS THE OUTWARD NORMAL VELOCITY TO Γ_i.

Q1 CONSIDER A COLLECTION OF N SMALL-SPHERES $\Gamma_i : |\underline{x} - \underline{x}_i| = \varepsilon \rho_i$ WITH $\rho_i = \rho_i(t)$ AND $\varepsilon \ll 1$. WHAT IS THE DYNAMICS OF $\rho_i(t)$ FOR $i = 1, .., N$. DOES THIS SYSTEM EXHIBIT OSTWALD RIPENING?

FORMULATION FROM (*)

- LET $r_i = |x - x_i|$ BE RADIUS OF DROPLET.

  THEN $V = -dr_i/dt$

  BUT $r_i = \varepsilon \rho_i$. SO $V = -\varepsilon\, d\rho_i/dt$.

- NOW THE MEAN CURVATURE $H_i = 1/r_i$ SO $H_i = \frac{1}{\varepsilon \rho_i}$ ON Γ_i.

  NOW INSIDE THE DROP WE MUST HAVE $u_- = 1/\varepsilon\rho_i$ SO THAT $\partial_n u_- = 0$ ON Γ_i.

  THEN $\left[\frac{\partial u}{\partial n}\right] = \frac{\partial u}{\partial n}\Big|_+ - 0 = \frac{\partial u}{\partial r}\Big|_{r=r_i} = \frac{1}{\varepsilon}\frac{\partial u}{\partial \rho}\Big|_{\rho=\rho_i}$.

  CONSEQUENTLY, WE HAVE

$$-\varepsilon\, d\rho_i/dt = -\frac{1}{\varepsilon}\, \partial u/\partial\rho\Big|_{\rho=\rho_i}$$

  THIS GIVES

$$(2) \qquad \varepsilon^2\, d\rho_i/dt = \frac{\partial u}{\partial \rho}\Big|_{\rho=\rho_i} \quad \text{ON} \quad \rho = \rho_i .$$

- OUR PROBLEM THEN IS TO SOLVE THE FOLLOWING FOR $\rho_1, \dots, \rho_N$ GIVEN

$$(1) \qquad \left\{ \begin{array}{l} \Delta u = 0 \quad \text{IN} \quad \Omega \setminus \Gamma \\ u = 1/\varepsilon\rho_i \quad \text{ON} \quad \partial\Gamma_i = \{ |x - x_i| \leq \varepsilon \rho_i \} \\ \partial_n u = 0 \text{ ON } \partial\Omega \end{array} \right.$$

IN TERMS OF THE SOLUTION TO (1) WE THEN COMPUTE $dU/d\rho_i\big|_{\rho=\rho_i}$ AND OBTAIN AN ODE SYSTEM FOR $\rho_1,\dots,\rho_N$ FROM (2).

ASYMPTOTIC ANALYSIS

IN THE OUTER REGION WE PUT

$$U = U_0/\varepsilon + U_1 + \varepsilon U_2 + \dots$$

WHERE U_0 IS AN UNKNOWN CONSTANT. WE OBTAIN THAT FOR $i=1,2$

$$(3)\quad \begin{cases} \Delta U_i = 0 & \text{IN } \Omega \setminus \{\underline{x}_1,\dots,\underline{x}_N\} \\ \partial_n U_i = 0 & \text{ON } \partial\Omega \\ U_i \text{ SINGULAR AS } \underline{x} \to \underline{x}_j . \end{cases}$$

NOW IN THE INNER REGION NEAR $\underline{x} = \underline{x}_j$ WE PUT

$$\underline{y} = \varepsilon^{-1}(\underline{x} - \underline{x}_j)$$

AND WE EXPAND $\quad U = V_0/\varepsilon + V_1 + \dots$

SO THAT

$$(4)\quad \begin{cases} \Delta_y V_0 = 0 & y \notin \Gamma_j \qquad \rho = |\underline{y}| \\ V_0 = 1/\rho_j & \text{ON } \Gamma_j \\ V_0 \to U_0 & \text{AS } |y| \to \infty \end{cases}$$

AND

$$(5)\quad \begin{aligned} &\Delta_y V_1 = 0 && y \notin \Gamma_j \\ &V_1 = 0 && \text{ON } \Gamma_j \\ &V_1 \to \,? && \text{AS } |y| \to \infty \end{aligned}$$

THE SOLUTION TO (4) IS $V_0 = A + B/\rho$ FOR SOME A, B.

IN PARTICULAR WE OBTAIN

$$(6)\qquad V_0 = U_0 + (1 - \rho_j U_0)/\rho$$

THE MATCHING CONDITION IS, NEAR j^{th} "TRAP", THAT

$$(7)\qquad \underset{x \to x_j}{U_0/\varepsilon + U_1 + \varepsilon U_2} \sim \underset{|y| \to \infty}{\frac{V_0}{\varepsilon} + V_1 + \cdots}$$

THUS
$$U_0/\varepsilon + U_1 + \cdots \sim \frac{1}{\varepsilon}\left[U_0 + (1-\rho_j U_0)\frac{\varepsilon}{|\underline{x}-\underline{x}_j|} \right] + V_1 + \cdots \qquad (8)$$

WE CONCLUDE THAT

$$(9)\qquad U_1 \sim \frac{(1-\rho_j U_0)}{|\underline{x}-\underline{x}_j|} \quad \text{AS} \quad x \to x_j, \quad j = 1, \ldots, N$$

THE PROBLEM (3) WITH (9) FOR U_1 IS EQUIVALENT TO

$$(10)\qquad \left\{ \begin{array}{l} \Delta U_1 = -4\pi \sum_{j=1}^{N} (1-\rho_j U_0)\, \delta(\underline{x}-\underline{x}_j) \quad \text{IN} \quad \Omega \\ \partial_n U_1 = 0 \quad \text{ON} \quad \partial\Omega \end{array} \right.$$

THE SOLVABILITY CONDITION BY DIVERGENCE THEOREM IS

$$\sum_{j=1}^{N} (1-\rho_j U_0) = 0 \quad \longrightarrow \quad N = U_0 \sum_{j=1}^{N} \rho_j$$

THUS
$$U_0 = \frac{1}{\bar{\rho}} \quad \text{WITH} \quad \bar{\rho} = \sum_{j=1}^{N} \rho_j / N . \qquad (11)$$

NOW THE SOLUTION TO (10) IS WRITTEN AS

$$(12)\qquad U_1 = 4\pi \sum_{i=1}^{N} (1-\rho_i U_0)\, G(x; x_i) + \bar{U}_1 \quad \text{WHERE } \bar{U}_1 \text{ IS A CONSTANT.}$$

WHERE $G(\underline{x}; \underline{x}_i)$ IS NEUMANN G-FUNCTION

$$(13)\qquad \begin{array}{l} \Delta G = \dfrac{1}{|\Omega|} - \delta(\underline{x}-\underline{x}_i) \; ; \quad \partial_n G = 0 \quad \text{ON} \quad \partial\Omega \\ \displaystyle\int_\Omega G \, d\underline{x} = 0 , \quad G \sim \frac{1}{4\pi|\underline{x}-\underline{x}_i|} + R_{ii} + o(1) \quad \text{AS} \quad \underline{x} \to \underline{x}_i . \end{array}$$

BEFORE CONTINUING TO HIGHER-ORDER WE WILL OUTPUT THE LEADING ORDER ODE'S USING (2). FROM THE INNER EXPANSION $U = V_0/\varepsilon + V_1 + \cdots$, THEN (2) BECOMES

$$(14) \qquad \varepsilon^2 \frac{dp_j}{dt} = \frac{1}{\varepsilon} \frac{\partial V_0}{\partial p}\Big|_{p=p_j} + \frac{\partial V_1}{\partial p}\Big|_{p=p_j} + \cdots$$

BUT FROM (6), $\partial V_0/\partial p \big|_{p=p_j} = -\dfrac{(1-p_j U_0)}{p_j^2}$.

WE CONCLUDE THEN THAT

$$(15) \quad \left\{ \begin{aligned} &\varepsilon^3 \frac{dp_i}{dt} \cong -\frac{1}{p_j}\left[\frac{1}{p_j} - U_0 \right] \qquad j = 1, .., N \\ &\text{WHERE} \qquad U_0 = 1/\bar{p} \qquad \text{WITH} \qquad \bar{p} = \sum_{i=1}^{N} p_i \Big/ N . \end{aligned} \right.$$

<u>NOTE</u> : (15) IS AN ODE SYSTEM FOR $p_1, .., p_N$ UPON GIVING INITIAL DATA $p_1(0), .., p_N(0)$.

BEFORE CONSIDERING PROPERTIES OF (15) WE SHOW HOW TO GO TO ONE HIGHER ORDER IN THE CALCULATION.

FROM (12) WE EXPAND AS $\underline{x} \to \underline{x}_j$ TO GET

$$U_1 \sim 4\pi \sum_{i \neq j}^{N} (1 - p_i U_0) G_{ji} + \bar{U}_1 + 4\pi (1 - p_j U_0) \left[\frac{1}{4\pi |\underline{x} - \underline{x}_j|} + R_{jj} \right] \quad \text{AS } \underline{x} \to \underline{x}_j .$$

THUS

$$U_1 \sim \frac{(1 - p_j U_0)}{|\underline{x} - \underline{x}_j|} + B_j + \bar{U}_1 \qquad \text{AS } \underline{x} \to \underline{x}_j$$

$$G_{ji} \equiv G(\underline{x}_j ; \underline{x}_i)$$

WHERE WE DEFINE $\quad B_j \equiv 4\pi \sum_{i \neq j} (1 - p_i U_0) G_{ji} + 4\pi (1 - p_j U_0) R_{jj}$.

THEN THE MATCHING CONDITION GIVES

$$V_1 \sim B_j + \bar{U}_1 \quad \text{AS} \quad |y| \to \infty .$$

WE THEN HAVE THAT THE SOLUTION TO (5) WITH THIS BEHAVIOR IS

$$V_1 = (B_j + \bar{U}_1)\left(1 - \frac{\rho_j}{\rho}\right). \qquad (16)$$

WHERE $\bar{U}_1$ IS TO BE FOUND. THEN AT NEXT ORDER, WE OBTAIN FROM THE MATCHING CONDITION THAT

$$U_2 \sim -\frac{(B_j + \bar{U}_1)\rho_j}{|\underline{x} - \underline{x}_j|} \quad \text{AS} \quad \underline{x} \to \underline{x}_j .$$

THE PROBLEM FOR U_2 IS THEN

$$\Delta U_2 = 4\pi \sum_{j=1}^{N} (B_j + \bar{U}_1)\rho_j \, \delta(\underline{x} - \underline{x}_j) \quad \text{IN} \quad \Omega .$$

(17)

$$\partial_n U_2 = 0 \quad \text{ON} \quad \partial\Omega$$

FROM THE DIVERGENCE THEOREM WE GET THAT

$$\sum_{j=1}^{N} (B_j + \bar{U}_1)\rho_j = 0 .$$

THUS $$\bar{U}_1 \sum_{j=1}^{N} \rho_j = -\sum_{j=1}^{N} B_j \rho_j$$

WE CONCLUDE THAT

$$(18) \qquad \bar{U}_1 = -\frac{\sum_{j=1}^{N} B_j \rho_j}{N\bar{\rho}} \qquad \bar{\rho} = \frac{1}{N}\sum_{j=1}^{N} \rho_j .$$

NOW FROM (16),

$$\left.\frac{\partial v_1}{\partial \rho}\right|_{\rho=\rho_j} = \frac{1}{\rho_j}\left(B_j + \bar{u}_1 \right)$$

WE SUBSTITUTE THIS INTO THE ODE (14) TO OBTAIN

$$\varepsilon^3 \frac{d\rho_j}{dt} = -\frac{1}{\rho_j}\left(\frac{1}{\rho_j} - \frac{1}{\bar{\rho}}\right) + \frac{\varepsilon}{\rho_j}\left(B_j + \bar{u}_1 \right) \tag{19a}$$

WHERE
$$\left.\begin{aligned} \bar{u}_1 &= -\frac{1}{N\bar{\rho}} \sum_{j=1}^{N} B_j \rho_j \\ \text{AND} \quad B_j &= 4\pi \sum_{\substack{i=1 \\ i\neq j}}^{N} \left(1 - \frac{\rho_i}{\bar{\rho}}\right) G_{ji} + 4\pi\left(1 - \frac{\rho_j}{\bar{\rho}}\right) R_{jj} \end{aligned}\right\} \tag{19b}$$

WHERE $G_{ji} = G(\underline{x}_j; \underline{x}_i)$, R_{jj} FOUND FROM GREEN'S FUNCTION.

NOTICE THAT $B_j = B_j(\underline{x}_1, \ldots, \underline{x}_N)$ DEPENDS ON LOCATIONS OF DROPLETS.

PROPERTIES OF LEADING-ORDER SYSTEM

$$\varepsilon^3 \frac{d\rho_j}{dt} = -\frac{1}{\rho_j}\left(\frac{1}{\rho_j} - \frac{1}{\bar{\rho}}\right) \qquad j = 1, \ldots, N$$

WITH $\bar{\rho} = \frac{1}{N}(\rho_1 + \cdots + \rho_N)$.

WILL NOW BE DISCUSSED.

PROPERTIES :

(1) IF $p_i(0) < p_j(0)$ THEN $p_i(t) < p_j(t)$ ON COMMON DOMAIN OF EXISTENCE.

(2) $\sum_{i=1}^{N} p_i^3(t) = \sum_{i=1}^{N} [p_i(0)]^3$ (volume conservation)

(3) $\sum_{i=1}^{N} p_i^2(t)$ IS DECREASING. (surface area is decreasing)

(4) ASSUME $p_1(0) \leq \dots \leq p_N(0)$. THEN $\dot{p}_1 \leq 0$ AND $\dot{p}_N \geq 0$.

(5) ASSUME $p_1(0) \leq \dots \leq p_{N-1}(0) < p_N(0)$. THEN ALL EXCEPT THE N^{th} particle becomes extinct in finite times $T_1 \leq T_2 \leq \dots \leq T_{N-1}$.

PROOF (1) SUPPOSE $p_i(0) < p_j(0)$ BUT THAT $p_i(t^*) = p_j(t^*)$, FOR SOME $t^* > 0$. WE HAVE THAT $\varepsilon^3 \dot{p}_i = -\frac{1}{p_i}\left(\frac{1}{p_i} - \frac{1}{\bar{p}}\right)$ AND $\varepsilon^3 \dot{p}_j = -\frac{1}{p_j}\left(\frac{1}{p_j} - \frac{1}{\bar{p}}\right)$.

LET $d = p_j - p_i$. SOME ALGEBRA GIVES,

$$\varepsilon^3 d' = -d\,\chi_{ij} \qquad \chi_{ij} = \frac{1}{p_i^2 p_j^2}\left[\frac{1}{\bar{p}} p_j p_i - (p_j + p_i)\right]$$

$$d(t^*) = 0$$

THUS $d \equiv 0$, AND HENCE $p_i(0) = p_j(0)$, WHICH IS A CONTRADICTION.

(2) WE CALCULATE

$$\frac{d}{dt}\sum_{j=1}^{N} p_j^3 = 3\sum_{j=1}^{N} p_j^2 \dot{p}_j = 3\sum_{j=1}^{N} p_j\left(\frac{1}{\bar{p}} - \frac{1}{p_j}\right) = 3\left(\frac{N\bar{p}}{\bar{p}} - N\right) = 0.$$

(3) $$\frac{d}{dt}\sum_{i=1}^{N} p_i^2 = 2\sum_{i=1}^{N} p_i \dot{p}_i = 2\sum_{i=1}^{N}\left(\frac{1}{\bar{p}} - \frac{1}{p_i}\right) = \frac{N}{\bar{p}} - \sum_{i=1}^{N}\frac{1}{p_i} \leq 0$$

NOW SINCE $\bar{p} \geq \frac{1}{\left(\frac{1}{N}\sum_{i=1}^{N} 1/p_i\right)}$ (arithmetic mean ≥ harmonic mean) $\rightarrow \frac{d}{dt}\sum_{i=1}^{N} p_i^2 \leq 0$

(4) THIS IS IMMEDIATE SINCE $p_1(t) \leq \bar{p}(t) \leq p_N(t)$.

(5) WE LET T_1 BE THE TIME WHERE $\rho_1(T_1)=0$.

WE CLAIM THAT

$$\frac{1}{3}[\rho_1(0)]^3 \le T_1 \le \frac{1}{3}[\rho_1(0)]^3 \frac{N^{2/3}\left(\frac{3V}{4\pi}\right)^{1/3}}{\rho_N(0)-\rho_1(0)} \qquad V=\frac{4\pi}{3}\sum_{i=1}^{N}\rho_i^3(0).$$

TO PROVE THIS WE HAVE,

$$\dot{\rho}_1 = \frac{1}{\rho_1}\left(\frac{1}{\bar{\rho}}-\frac{1}{\rho_1}\right) \ge -\frac{1}{\rho_1^2}$$

integrating, we get

$$\rho_1^3(t) \ge -3t+\rho_1^3(0) \ge 0 \quad \text{FOR} \quad t \le \frac{1}{3}[\rho_1(0)]^3.$$

HENCE, THE COLLAPSE TIME T_1 SATISFIES $T_1 \ge \frac{1}{3}[\rho_1(0)]^3$.

NOW TO GET THE UPPER BOUND WE WRITE

$$\rho_1-\bar{\rho} = \frac{1}{N}\left[(\rho_1-\rho_2)+\cdots+(\rho_1-\rho_N)\right] \le \frac{1}{N}(\rho_1-\rho_N)$$

NOW

$$\dot{\rho}_1 = \frac{1}{\rho_1}\left(\frac{1}{\bar{\rho}}-\frac{1}{\rho_1}\right) = \frac{1}{\rho_1}\left(\frac{\rho_1-\bar{\rho}}{\rho_1\bar{\rho}}\right) \le \frac{1}{N\rho_1^2\bar{\rho}}(\rho_1-\rho_N)$$

THEREFORE,

$$\dot{\rho}_1 \le \frac{1}{N\rho_1^2}\,\frac{(\rho_1(0)-\rho_N(0))}{\frac{1}{N}\sum_{i=1}^{N}\rho_i} = -\frac{(\rho_N(0)-\rho_1(0))}{N\rho_i^2\left(\frac{1}{N}\sum\rho_i\right)} \qquad \text{WITH } \rho_N(0)-\rho_1(0)>0.$$

NOW WE HAVE A HOLDER ESTIMATE (RECALL $\sum_i |a_i b_i| \le \left(\sum_i |a_i|^p\right)^{1/p}\left(\sum_i |b_i|^q\right)^{1/q}$ FOR $1/p+1/q=1$)

$$\frac{1}{N}\sum_{i=1}^{N}\rho_i \le \left(\frac{1}{N}\sum_{i=1}^{N}\rho_i^3\right)^{1/3}, \longleftarrow \text{CONSTANT IN TIME.}$$

SINCE $\rho_1(0)-\rho_N(0)<0$, WE GET

$$\rho_1^2\,\dot{\rho}_1 \le \frac{\rho_1(0)-\rho_N(0)}{N^{2/3}\left(\frac{3V}{4\pi}\right)^{1/3}} \qquad \text{WITH} \qquad V=\frac{4\pi}{3}\sum_{i=1}^{N}\rho_i^3(0)$$

integrating we get

$$\frac{\rho_i^3}{3} \le \frac{[\rho_1(0)-\rho_N(0)]}{N^{2/3}\left(\frac{3V}{4\pi}\right)^{1/3}}\,t + \frac{\rho_i^3(0)}{3} \longrightarrow$$

this gives the estimate of the theorem.
