

STATISTICAL BEHAVIOUR OF BUBBLES

IN LIQUIDS

A thesis submitted for the degree of
Doctor of Philosophy of the University of London

by

Christina Angelidou (Dipl.Eng., M.Sc.)

Department of Chemical Engineering and Chemical Technology,
Imperial College of Science and Technology,
London, SW7.

July 1978

To Michael

ABSTRACT

In this work the size distribution function of bubbles in thermodynamic equilibrium with the surrounding liquid was first derived in the absence of gravity. The derivation was based on the assumption that the gas is dispersed into bubbles in a completely random way with respect to the energies of the bubbles. The size distribution function of bubbles obtained when surface tension effects are neglected is of the same form as the empirical Nukiyama-Tanasawa distribution often applied to droplets. The derived size distribution functions agree well with the experimental size distributions of bubbles in water having been generated by an air entrainment process at the surface of the water or behind a ventilated body. The effect of gravity and coalescence on the size distribution function of bubbles in liquids was next investigated. The investigation resulted in a non-linear integro-differential equation for the distribution function of the radius and position of bubbles of sufficiently low concentration rising in their terminal velocities through a liquid. The effect of gravity, alone, showed that the distribution function derived in the absence of gravity (for bubbles at rest), describes as well locally, in steady state the size distribution function of bubbles rising in their terminal velocities through a liquid. In the case where the degree of coalescence of bubbles in the system is low,

the effect of gravity and coalescence on the bubble size distribution was shown by obtaining in steady state and neglecting surface tension forces, an approximate solution of the integro-differential equation.

ACKNOWLEDGEMENT

I would like to express my most sincere thanks to Dr. G.J. JAMESON for his encouragement and help during the years of my research at Imperial College.

One could not possibly thank EUCLID, NEWTON, MAXWELL, BOLTZMANN, GIBBS, LANDAU and the many other great scientists, but feels immensely grateful - and ecstatic - for the WORK they left behind them.

CONTENTS

Page

ABSTRACT

ACKNOWLEDGEMENT

CONTENTS

1.	INTRODUCTION	8
2.	SIZE DISTRIBUTION FUNCTIONS OF BUBBLES IN LIQUIDS IN THE ABSENCE OF GRAVITY	12
2.1	The distribution function of the bubble energy	12
2.2	The distribution function of the bubble radius	19
2.3	Comparison with experimental bubble size distributions	27
3.	EFFECT OF GRAVITY AND COALESCENCE ON THE SIZE DISTRIBUTION FUNCTION OF BUBBLES IN LIQUIDS	32
3.1	Continuity equation in the 4-dimensional ($\underline{x}, r_j$) space	32
3.2	Continuity equation in the 4-dimensional ($\underline{x}, r_j$) space, including coalescence of bubbles	38
3.3	Effect of gravity on the size distribution function of bubbles	46
3.4	Effect of gravity and coalescence on the size distribution function of bubbles	52
4.	CONCLUSIONS	63

	<u>Page</u>
NOTATION	66
REFERENCES	71
APPENDIX I	74
APPENDIX II	75

1. INTRODUCTION

Processes involving one phase dispersed in another are of great importance in the chemical and allied industries. Systems consisting of a gas dispersed in the form of bubbles in a liquid are often encountered in connection with mass and heat transfer processes, separation processes, and chemical reactions in gas-liquid reactors. Gas bubbles also exist at various depths in the interior of the sea. One of the most important properties of dispersions is the size distribution of the dispersed material. A knowledge of the size distribution of bubbles in liquids is necessary for the prediction of rates of heat and mass transfer, chemical reactions and separation processes. Information about the bubble size distribution at sea is of interest to a wide range of disciplines, including meteorology, chemical oceanography, marine biology and underwater acoustics.

The size distribution of bubbles dispersed in liquids depends not only on the condition and method of dispersion and the physical properties of gas and liquid but also on interaction processes like coalescence and break-up of bubbles. Although the mechanism of coalescence of bubbles has been extensively studied most of the information available is of a qualitative nature (De Vries 1972; Jackson 1964). The processes describing bubble coalescence are those of thinning and rupture of the liquid films separating the bubbles, and depend in general on a number of various parameters, the quantitative effect of which is still incompletely known.

Such parameters affecting the rates of thinning and rupture are surface tension gradients associated with temperature gradients and concentration gradients of adsorbed surfactants or dissolved components, double layer repulsions, viscosity, vibrations or shocks transmitted through the surrounding liquid. Evidently, bubble coalescence results in a decrease of the interfacial area in the system and in consequence in lower rates of heat and mass transfer and separation processes. Break-up of bubbles into smaller bubbles occurs only when the bubbles are sufficiently large, of radii about 2 to 3 cm. In that case the pressure variations in the liquid over the surface of a bubble exceed the capillary pressure and the bubble is deformed and finally breaks up (Levich 1962).

There have been no theoretical distributions for the size of bubbles in gas-liquid dispersions, although there have been a few for the size of droplets in liquid atomization processes. Filippov's (1961) stochastic analysis on the "decomposition" or splitting of particles into a finite number of other particles was used by Nakano and Tien (1970) to describe the disintegration of droplets during the secondary stage of a liquid atomization process. Usually the data on bubble size distributions are fitted to some empirical relationship such as the log-normal or normal distribution, or the distributions of Nukiyama and Tanasawa or Rosin and Rammler. While each of these relations has found favour with workers in specific fields none of them has any theoretical justification. Nukiyama and Tanasawa (1939, 1940) during their experimental studies on liquid atomization processes gave

empirical expressions for the average droplet diameter and the size distribution of droplets in sprays, whereas Rosin and Rammler (1933) proposed a size distribution function for application to powdered material such as coal.

In the case of systems of droplets of one liquid dispersed in another the effect of coalescence and break-up on the size distribution of droplets in homogeneous, continuous and batch agitated systems was investigated by Valentas and Amundson (1966). The droplet number population balance equation proposed by Valentas and Amundson was in fact based on the formulation made earlier by Hulburt and Katz (1964), of particle agglomeration. Hulburt and Katz (1964) were the first to apply the statistical mechanical approach to problems in particle technology. They wrote a conservation equation for the number of particles in phase space (with coordinates specifying the location of a particle as well as its quality) and applied that equation to describe a collisional agglomeration process for suspended particles.

In this work we find, in chapter 2, a theoretical size distribution function for bubbles in thermodynamic equilibrium with the surrounding liquid, in the absence of gravity. The derivation is based on the assumption that a gas dispersion forms in a completely random way with respect to the energies of the bubbles. A comparison with experimental bubble size distributions is made. In chapter 3 we investigate the effect of gravity and coalescence on the size distribution function of bubbles in liquids. We write an equation for the conservation of the number of bubbles of radii r_j in the 4-dimensional $(\underline{x}, r_j)$ space, and using Boltzmann's "Stosszahlansatz" or "molecular chaos" assumption (Boltzmann 1872) for the number

of collisions of bubbles, we obtain a non-linear integro-differential equation which describes how the number of bubbles in dx of radii r_j rising in their terminal velocities through a liquid, changes with time due to the streaming in the (x, r_j) space and due to the coalescences with other bubbles. The effect of gravity and coalescence on the size distribution function derived in chapter 2, is particularly investigated neglecting surface tension forces and assuming steady state.

2. SIZE DISTRIBUTION FUNCTIONS OF BUBBLES IN LIQUIDS IN THE ABSENCE OF GRAVITY

ἄει ὁ θεός γεωμετρεῖ

Plato

2.1 The distribution function of the bubble energy

Let us consider a very large volume of liquid, at rest, having a free surface. In the interior of the liquid, at some large depth there are small bubbles of various sizes, having been generated, for example, by an air entrainment process at the surface of the liquid.

In what follows we shall neglect gravity and assume that the temperature T of the liquid is everywhere the same and equal to the temperature of the surrounding atmosphere. We shall also regard liquid as an incompressible fluid.

Let N be the number of bubbles contained in a volume V of the system. We suppose that the bubbles are in thermodynamic equilibrium with the surrounding liquid and in consequence the temperatures and chemical potentials in the two phases are equal and constant (Landau and Lifshitz 1968). The equilibrium shape of the bubbles, neglecting gravity, is of course that of a sphere. Assuming no interaction whatever between the bubbles and themselves their total energy E_t is equal to the sum of the individual energies E_j , $j = 1, 2, \dots, N$ of the bubbles :

$$E_t = \sum_{j=1}^N E_j \quad (2.1.1)$$

Since we know that any perturbations at the surface of the liquid affect the interior less and less at greater and

greater depths, we can always say that the liquid surrounding the bubbles is at rest and, having neglected gravity, so are the bubbles. Therefore the energies E_j , $j = 1, 2, \dots, N$ of the bubbles in eqn. (2.1.1) are internal energies. However, with a view to other applications as well, we may assume that if the liquid is in a steady, uniform, potential flow the bubbles are wholly carried along with it, i.e. there is no relative velocity between the bubbles and the liquid. Because of the latter assumption the energies of the bubbles in eqn. (2.1.1) are again internal energies since we can always choose a reference system of co-ordinates in which the total two-phase system of the bubbles and the liquid is at rest.

We shall now proceed to calculate a distribution function for the energies E_j , $j = 1, 2, \dots, N$ of the bubbles, which will in turn lead to a distribution function for the radii r_j , $j = 1, 2, \dots, N$ of the bubbles.

We can see that in an orthogonal N -dimensional Cartesian space the system of the bubbles described by eqn. (2.1.1) can be represented by the point $(E_1, E_2, \dots, E_N)$ on the surface of an $N-1$ -dimensional hyperplane S_{N-1} , which cuts each axis j at a point E_t from the origin. The hyperplane S_{N-1} is the energy surface E_t for the system of bubbles; each point on the surface S_{N-1} gives a different configuration for the individual energies E'_j , $0 \leq E'_j \leq E_t$, $j = 1, 2, \dots, N$ of bubbles of the same total energy E_t .

We know that an air entrainment or gas dispersion process resulting in the formation of bubbles in a liquid, leads to a statistical distribution function for the bubble sizes (and

the bubble energies). We argue now that there is no reason whatever why the system of the bubbles should be given by a certain point on the surface S_{N-1} of total energy E_t and not by any other point of that surface. In other words we say that the probability that the system of bubbles is to be found anywhere on the energy surface S_{N-1} is constant, or equivalently that the way the gas is dispersed into bubbles is completely random with respect to the energies of the bubbles[†]. Therefore the probability $\mathcal{P}(s)$ that the system of bubbles is within a region s of the surface S_{N-1} defined by:

$$E_t = \sum_{j=1}^N E'_j, \quad 0 \leq E'_j \leq E_t, \quad j = 1, 2, \dots, N \quad (2.1.2)$$

is proportional to the Lebesgue measure $\mathcal{L}(s)$ (or "surface area") of this region, i.e.

$$\mathcal{P}(s) = \int_s \mathcal{P}(ds) \propto \mathcal{L}(s)$$

and using the normalisation condition for the probability $\mathcal{P}(s)$:

$$\int_{S_{N-1}} \mathcal{P}(ds) = 1,$$

we have:

$$\mathcal{P}(s) = \frac{\mathcal{L}(s)}{\mathcal{L}(S_{N-1})} \quad (2.1.3)$$

[†] i.e. all possible configurations of the bubble energies $E_1, E_2, \dots, E_N$ are equiprobable.

The above argument leading to the relation (2.1.3) is reminiscent of the principle of "equal a priori probabilities", if applied to the energy surface S_{N-1} of the bubbles (Gibbs 1902).

We are interested in the event $[E_j - dE_j/2 \leq E'_j < E_j + dE_j/2]$ which defines a set on the surface S_{N-1} , namely a differential hyperzone $dS_{N-1}(E_j)$ confined between two $N-1$ -dimensional planes, one defined by $E'_j = E_j - dE_j/2$ and the other by $E'_j = E_j + dE_j/2$. From eqn. (2.1.3) above, the probability of the set of interest $[E_j - dE_j/2 \leq E'_j < E_j + dE_j/2]$ is:

$$\mathcal{P}[E_j - dE_j/2 \leq E'_j < E_j + dE_j/2] \equiv f(E_j)dE_j = \frac{\mathcal{L}[dS_{N-1}(E_j)]}{\mathcal{L}(S_{N-1})} \quad (2.1.4)$$

where $f(E_j)$ is the distribution function (probability density) of the bubble energy regarded as a random variable E'_j .

Thus the problem of calculating the probability $\mathcal{P}[E_j - dE_j/2 \leq E'_j < E_j + dE_j/2]$ has been reduced to a geometrical calculation of the ratio of the surface area of the hyperzone $dS_{N-1}(E_j)$ over the surface area of the hyperplane S_{N-1} .

The Lebesgue measure $\mathcal{L}[dS_{N-1}(E_j)]$ of the hyperzone $dS_{N-1}(E_j)$ can be expressed as:

$$\mathcal{L}[dS_{N-1}(E_j)] = \mathcal{L}[S_{N-2}(E_j)] \cdot dH(E_j) \quad (2.1.5)$$

and the Lebesgue measure $\mathcal{L}(S_{N-1})$ of the hyperplane S_{N-1} , using eqn. (2.1.5) can be written, in the form of a Stieltjes

integral, as:

$$\mathcal{L}(S_{N-1}) = - \int_{E_j=0}^{E_j=E_t} \mathcal{L}[S_{N-2}(E_j)] dH(E_j) \quad (2.1.6)$$

where $S_{N-2}(E_j)$ is the $N-2$ -dimensional hyperplane resulting from the intersection of the $N-1$ -dimensional hyperplane $E'_j = E_j$ with the hyperplane S_{N-1} ; $H(E_j)$ is the minimum distance from the point $E'_j = E_t$ to the $N-2$ -dimensional hyperplane $S_{N-2} = S_{N-2}(E'_j = 0)$ resulting from the intersection of the $N-1$ -dimensional hyperplane $E'_j = 0$ with the hyperplane S_{N-1} ; $H(E_j)$ is the minimum distance from the point $E'_j = E_t$ to the hyperplane $S_{N-2}(E_j)$; H can be regarded as a generalisation of the altitude of a triangle.

From Euclidean geometry we have:

$$\frac{H(E_j)}{H} = \frac{E_t - E_j}{E_t} = 1 - \frac{E_j}{E_t} \quad (2.1.7)$$

and

$$dH(E_j) = - \frac{H}{E_t} dE_j \quad (2.1.8)$$

Also

$$\left(\frac{H(E_j)}{H} \right)^{N-2} = \frac{\mathcal{L}[S_{N-2}(E_j)]}{\mathcal{L}(S_{N-2})} \quad (2.1.9)$$

Eqn. (2.1.9) in combination with eqn. (2.1.7) gives:

$$\mathcal{L}[S_{N-2}(E_j)] = \left(1 - \frac{E_j}{E_t} \right)^{N-2} \mathcal{L}(S_{N-2}) \quad (2.1.10)$$

Substituting eqns. (2.1.8) and (2.1.10) into eqn. (2.1.5) we obtain:

$$\mathcal{L}[dS_{N-1}(E_j)] = -\frac{H}{E_t} \left(1 - \frac{E_j}{E_t}\right)^{N-2} \mathcal{L}(S_{N-2}) dE_j \quad (2.1.11)$$

and eqn. (2.1.6) becomes:

$$\mathcal{L}(S_{N-1}) = \frac{H}{E_t} \mathcal{L}(S_{N-2}) \int_{E_j=0}^{E_j=E_t} \left(1 - \frac{E_j}{E_t}\right)^{N-2} dE_j \quad (2.1.12)$$

Substitution of eqns. (2.1.11) and (2.1.12) into eqn. (2.1.4) gives for the distribution function $f(E_j)$:

$$f(E_j) = \frac{\left(1 - \frac{E_j}{E_t}\right)^{N-2}}{\int_0^{E_t} \left(1 - \frac{E_j}{E_t}\right)^{N-2} dE_j} \quad (2.1.13)$$

We have also:

$$\langle E \rangle = \mathcal{E} E_j' = \frac{E_t}{N} \quad (2.1.14)$$

where $\langle E \rangle = \mathcal{E} E_j'$ is the expectation (or average value) of E_j' .

It is natural to assume that $\langle E \rangle$ is independent of N , so that in the limit $N \rightarrow \infty$ also $E_t \rightarrow \infty$ as N , and distribution (2.1.13) becomes:

$$f(E_j) = \frac{1}{\langle E \rangle} \exp\left(-\frac{E_j}{\langle E \rangle}\right) \quad (2.1.15)$$

The standard deviation $\sigma_{E_j'}$ of E_j' can be easily calculated from the definition formula of the variance $\sigma_{E_j'}^2$:

$$\sigma_{E_j'}^2 = \mathcal{E} (E_j' - \langle E \rangle)^2 = \int_0^{\infty} (E_j - \langle E \rangle)^2 f(E_j) dE_j$$

If we substitute distribution (2.1.15) for $f(E_j)$, we find:

$$\sigma_{E_j'} = \langle E \rangle \quad (2.1.16)$$

We should probably note here that in deriving distribution (2.1.15) we made no use of properties peculiar to bubbles. Therefore, distribution (2.1.15) should give the energy distribution function of droplets in dispersions, provided of course that the same assumptions are valid, i.e. the liquid has been dispersed into droplets in a completely random way with respect to the energies of the droplets, the droplets are in thermal equilibrium with the dispersing phase, and gravity is neglected.

2.2 The distribution function of the bubble radius

From the distribution function (2.1.15) of the bubble energy found in the preceding section we can calculate the distribution function $f(r_j)$ of the bubble radius regarded too as a random variable r'_j .

The bubble energy E_j , taking into account surface tension forces, can be written as the sum of a "volume" part E_{vj} and a "surface" part E_{sj} :

$$E_j = E_{vj} + E_{sj} \quad (2.2.1)$$

The surface energy E_{sj} of the bubble is (Landau and Lifshitz 1968):

$$E_{sj} = F_{sj} + TS_{sj} = \left(\gamma - T \frac{d\gamma}{dT} \right) s_j \quad (2.2.2)$$

where F_{sj} is the surface free energy of the bubble; S_{sj} is the surface entropy of the bubble; T is the temperature constant in the two phases; s_j is the surface area of the bubble; γ is the surface tension between liquid and gas and is constant since the temperature and chemical potentials in the two phases are constant. Generally, the surface tension at the interface between two isotropic phases decreases with increasing temperature and becomes zero at the critical point. The law governing the dependence on the temperature of surface tension is not yet known. However, there are some empirical formulae like the Eötvös, Katayama and others (Adamson 1960) as well as experimental data (International Critical Tables 1928). For the surface tension γ between water and air, as for many other liquids, $d\gamma/dT$ is

very nearly constant at low temperatures, and as such we shall consider it.

The volume part E_{vj} of the bubble energy E_j can be calculated by means of a canonical or a grand canonical distribution function (the Gibbs distributions) for the molecules of the gas in the bubble. The internal energy of each bubble in eqns. (2.1.1) and (2.2.1) is in fact an average energy over an ensemble describing the microscopic (quantum) state of the gas in the bubble; this average energy is just what is meant by the term "energy" in thermodynamics (Landau and Lifshitz 1968). Any of the ensembles can be used to determine the thermodynamic properties of a body. The energy E_{vj} can be calculated using a canonical distribution function for the gas of the bubble and, to simplify matters, regarding the gas as a monatomic, ideal gas (Hill 1960):

$$E_{vj} = \frac{3}{2} P_j V_j \quad (2.2.3)$$

where P_j is the pressure within the bubble; V_j is the volume of the bubble. Substitution of eqns. (2.2.2) and (2.2.3) into eqn. (2.2.1) gives for the bubble energy E_j :

$$E_j = \frac{3}{2} P_j V_j + \left(\gamma - T \frac{d\gamma}{dT} \right) s_j \quad (2.2.4)$$

Since the bubbles and the liquid are in thermodynamic equilibrium the pressure P_j within the bubble is given by Laplace's formula as:

$$P_j = P + \frac{2\gamma}{r_j} \quad (2.2.5)$$

where P is the pressure of the liquid surrounding the bubble.

Substituting eqn. (2.2.5) into eqn. (2.2.4) and expressing the volume V_j and surface s_j of the bubble in terms of the bubble radius r_j we obtain the energy of the bubble as a function of the radius r_j :

$$E_j = 2\pi P r_j^3 + 4\pi(2\gamma - T \frac{d\gamma}{dT}) r_j^2 \quad (2.2.6)$$

and

$$\langle E \rangle = 2\pi P \langle r_j^3 \rangle + 4\pi(2\gamma - T \frac{d\gamma}{dT}) \langle r_j^2 \rangle \quad (2.2.7)$$

The distribution function $f(r_j)$ of the bubble radius can be calculated from the distribution function $f(E_j)$ of the bubble energy given by eqn. (2.2.6), as follows. Since the function $E_j(r_j)$ given by eqn. (2.2.6), is one-to-one for $r_j > 0$, we have:

$$f(E_j) dE_j = f(r_j) dr_j \quad (2.2.8)$$

Differentiating eqn. (2.2.6) with respect to r_j we find:

$$\frac{dE_j}{dr_j} = 6\pi P r_j^2 + 8\pi(2\gamma - T \frac{d\gamma}{dT}) r_j \quad (2.2.9)$$

From eqns. (2.2.8) and (2.2.9) and distribution (2.1.15) after substitution in the latter of E_j and $\langle E \rangle$ as given by eqns. (2.2.6) and (2.2.7) respectively, we obtain for the distribution function $f(r_j)$ the formula:

$$f(r_j) = \left(\frac{3Pr_j^2 + 4(2\gamma - Td\gamma/dT)r_j}{P\langle r^3 \rangle + 2(2\gamma - Td\gamma/dT)\langle r^2 \rangle} \right) \exp \left(- \frac{Pr_j^3 + 2(2\gamma - Td\gamma/dT)r_j^2}{P\langle r^3 \rangle + 2(2\gamma - Td\gamma/dT)\langle r^2 \rangle} \right) \quad (2.2.10)$$

The corresponding distribution function $f(d_j)$ of the bubble diameter is easily obtained from the distribution (2.2.10) using the relations:

$$f(d_j) d(d_j) = f(r_j) d(r_j) ; \quad d(d_j) = 2(dr_j)$$

so that

$$f(d_j) = \left(\frac{3Pd_j^2 + 8(2\gamma - Td\gamma/dT)d_j}{P\langle d^3 \rangle + 4(2\gamma - Td\gamma/dT)\langle d^2 \rangle} \right) \exp \left(- \frac{Pd_j^3 + 4(2\gamma - Td\gamma/dT)d_j^2}{P\langle d^3 \rangle + 4(2\gamma - Td\gamma/dT)\langle d^2 \rangle} \right) \quad (2.2.11)$$

The average bubble radius $\langle r \rangle$ can be calculated from its definition formula:

$$\langle r \rangle = \int_0^\infty r_j f(r_j) dr_j \quad (2.2.12)$$

if we substitute distribution (2.2.10) for $f(r_j)$. The resulting integral however cannot be evaluated analytically.

If we neglect surface tension forces the distribution function (2.2.10) of the bubble radius becomes much more simple:

$$f(r_j) = 3 \frac{r_j^2}{\langle r^3 \rangle} \exp \left(- \frac{r_j^3}{\langle r^3 \rangle} \right) \quad (2.2.13)$$

also

$$f(d_j) = 3 \frac{d_j^2}{\langle d^3 \rangle} \exp \left(- \frac{d_j^3}{\langle d^3 \rangle} \right) \quad (2.2.14)$$

The average bubble radius $\langle r \rangle$ can now be calculated analytically from formula (2.2.12) as:

$$\begin{aligned} \langle r \rangle &= \frac{3}{\langle r^3 \rangle} \int_0^\infty r_j^3 \exp \left(- \frac{r_j^3}{\langle r^3 \rangle} \right) dr_j = \Gamma(4/3) \langle r^3 \rangle^{1/3} \\ &= 0.893 \langle r^3 \rangle^{1/3} \end{aligned} \quad (2.2.15)$$

and the average bubble diameter $\langle d \rangle$ is obviously:

$$\langle d \rangle = 0.893 \langle d^3 \rangle^{1/3} \quad (2.2.16)$$

Using eqn. (2.2.15) the distribution function (2.2.13) of the bubble radius can be written also in the form:

$$f(r_j) = 3 \left(\frac{\Gamma(4/3)}{\langle r \rangle} \right)^3 r_j^2 \exp \left(- \frac{\Gamma(4/3) r_j}{\langle r \rangle} \right)^3 \quad (2.2.17)$$

The variance $\sigma_{r_j}^2$ of r_j is calculated from its definition

formula as:

$$\sigma_{r_j}^2 = \frac{3}{\langle r^3 \rangle} \int_0^\infty (r_j - \langle r \rangle)^2 \exp\left(-\frac{r_j^3}{\langle r^3 \rangle}\right) dr_j = \left\{ \Gamma(5/3) - \frac{[\Gamma(4/3)]^2}{\langle r^3 \rangle^{2/3}} \right\}$$

and the standard deviation σ_{r_j} of r_j is:

$$\sigma_{r_j} = \left\{ \Gamma(5/3) - [\Gamma(4/3)]^2 \right\}^{1/2} \langle r^3 \rangle^{1/3} = 0.322 \langle r^3 \rangle^{1/3} \quad (2.2.18)$$

or in terms of $\langle r \rangle$:

$$\sigma_{r_j} = \left\{ \frac{\Gamma(5/3)}{[\Gamma(4/3)]^2} - 1 \right\}^{1/2} \langle r \rangle = 0.360 \langle r \rangle \quad (2.2.18a)$$

The standard deviation σ_{d_j} of the bubble diameter is obviously given by the same formulae (2.2.18) and (2.2.18a), with $\langle d^3 \rangle$ and $\langle d \rangle$ in place of $\langle r^3 \rangle$ and $\langle r \rangle$ respectively. Neglecting surface tension forces, the distribution fraction $f(V_j)$ of the bubble volume can be easily obtained from distribution (2.2.13) using the relations:

$$f(V_j) d(V_j) = f(r_j) d(r_j) \quad ; \quad dV_j = 4\pi r_j^2 \quad ,$$

so that

$$f(V_j) = \frac{1}{\langle V \rangle} \exp\left(-\frac{V_j}{\langle V \rangle}\right) \quad (2.2.19)$$

Distribution (2.2.19) being of exactly the same form as the distribution function (2.1.15) of the bubble energy, shows that when surface tension effects are neglected, the way an ideal gas is dispersed into bubbles is, clearly, not only random with respect to the energies of the bubbles, as assumed, but is also random with respect to the volumes of the bubbles.

Distribution (2.2.14) is of the same form as the empirical Nukiyama-Tanasawa distribution (Nukiyama and Tanasawa 1940) often applied to droplets:

$$\frac{dn}{d(d_j)} = B d_j^2 \exp(-c d_j^\delta) \quad (2.2.20)$$

where B , c and δ are constants and dn is the number fraction of droplets with diameters in the interval $d(d_j)$.

Evaluation of the constant B from the normalisation condition:

$$\int_0^\infty \frac{dn}{d(d_j)} d(d_j) = B \int_0^\infty d_j^2 \exp(-c d_j^\delta) d(d_j) = 1$$

gives for B :

$$B = \frac{\delta c^{3/\delta}}{\Gamma(3/\delta)} \quad (2.2.21)$$

and with $\delta = 3$ and $c = 1/\langle d^3 \rangle$ the Nukiyama-Tanasawa distribution (2.2.20) becomes identical to our result as expressed by distribution (2.2.14). It would be interesting to note that in the case of droplets in dispersions the distribution function of the diameter of droplets is given by distribution (2.2.14) if one assumes that the dispersed liquid is an incompressible

fluid and that the way it has been dispersed into droplets is completely random with respect to the volumes of the droplets (irrespective of their energies). For a system of N droplets consisting of an incompressible liquid in dispersion we have:

$$V_t = \sum_{j=1}^N V_j \quad (2.2.22)$$

where V_j is now the volume of the j th droplet and V_t the total volume of the dispersed liquid. Such a system described by eqn. (2.2.22) can be represented in an orthogonal N -dimensional cartesian space by the point $(V_1, V_2, \dots, V_N)$ on the surface of $N-1$ -dimensional hyperplane which cuts each axis j at a distance V_t from the origin. Therefore if one assumes that the liquid has been dispersed into droplets in a completely random way with respect to the volumes of the droplets then an analysis similar to that made in section 2.1 for the energies leads to distribution (2.2.19) as the distribution function of the droplet volume and in consequence to distribution (2.2.14) as the distribution function of the droplet diameter.

We should probably make clear at this point that distributions (2.1.15) and (2.2.10) or (2.2.13) according to the "weak law of large numbers" in Probability Theory (Van der Waerden 1969), differ only slightly from frequencies in the limit $N \rightarrow \infty$, i.e. the number fraction dn of bubbles or droplets with radii in the interval dr_j converges to $f(r_j) dr_j$ as the number of bubbles or droplets becomes large. In fact the possibility of estimating distributions (2.2.10) or (2.2.13) experimentally rests on this law. Inevitably, distributions (2.2.10) and (2.2.13) or (2.2.17) involve the parameters $\langle r^3 \rangle$, $\langle r^2 \rangle$ or $\langle r \rangle$ which can only be obtained from the particular experimental data to which the aforementioned distributions are to be applied.

2.3 Comparison with experimental bubble size distributions

Bubbles in the sea: We have applied distributions (2.2.11) and (2.2.14) to the experimental data (histogram of Fig. 2.3.1) of Glotov et al. (Glotov et al. 1962) who simulated sea conditions in a laboratory sea water-filled tank and determined both acoustically and photographically the size distribution of air bubbles generated in the interior of the water (at a depth of 1.5 m from the surface) by artificial wind-driven waves. Distribution (2.2.11) very little differed from distribution (2.2.14) ($\pm 0.20 \text{ mm}^{-1}$ being the maximum difference occurring) and in the scale used for illustration the distributions coincided and are represented by the curve of Fig. 2.3.1. Taking into account the inevitable inaccuracy of the measurements when concerned with very small bubbles, we see from Fig. 2.3.1 that the theoretical distributions provide a good fitting to the experimental histogram. Also, the theoretical average diameter calculated from formula (2.2.16) is equal to 0.151 mm compared with the experimental average diameter which is equal to 0.155 mm. Glotov et al. approximated the histogram of Fig. 2.3.1 with three separate, limiting theoretical curves each corresponding to a different range of bubble diameters (one curve for the small-size bubbles, one for the medium-size bubbles and another for the large-size bubbles). Distributions (2.2.11) or (2.2.14) applied to the whole histogram give an equally good approximation. Furthermore, the conclusions of Glotov et al. about the stability of the bubble size distribution and its independence of the wind strength are consistent with the

assumptions made in deriving distribution (2.1.15).

Medwin (Medwin 1977) conducted in situ acoustic measurements of the bubbles in ocean waters but the way his experimental data are presented made it impossible for a reliable reproduction and in turn a comparison with the present theory.

Bubbles far behind a ventilated body: The size distribution of bubbles far behind an air ventilated body kept stationary in a water flow of velocity 2.1 m/s, was obtained photographically. The body, a streamlined hydrofoil, was tested in the rectangular, vertical test section of a closed-jet, recirculating water tunnel, a schematic representation of which is given in Fig. 2.3.2, and which was built especially for experiments conducted on the purpose of the Production of Small Gas Bubbles in Liquids with Low Consumption of Power (S.R.C.-sponsored research). The ventilation was natural and the air flowrate into the system at the time the photographs of the bubbles were taken was 10 lt/min (0.008 of the water flowrate), whereas the pressure of the water surrounding the bubbles was 85 kN/m^2 . Averaging of the data resulting from the analysis of two photographs of the bubbles gave the histogram of Fig. 2.3.3. Again distribution (2.2.11) coincided with distribution (2.2.14) in Fig. 2.3.3, and as we can see there is a very good agreement between the experimental and theoretical distributions. Also, the theoretical average diameter calculated from formula (2.2.16) is equal to 1.29 mm against the experimental value of 1.28 mm.

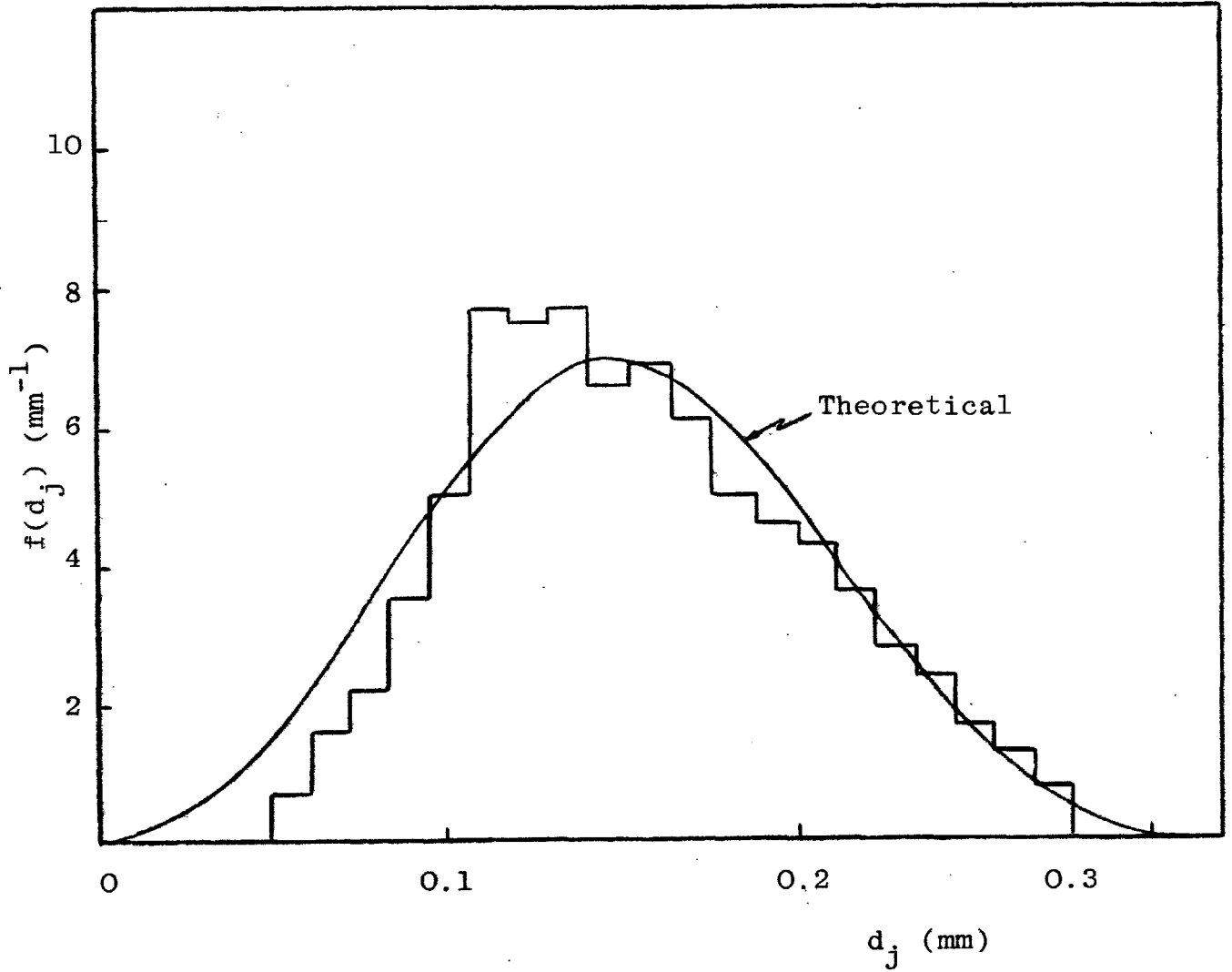


Fig. 2.3.1: Bubbles in the sea: theoretical and experimental (Glotov et al. 1962) size distributions.

$$\langle d \rangle_{\text{exp}} = 0.155 \text{ mm}; \quad \langle d \rangle_{\text{theor.}} = 0.151 \text{ mm}$$

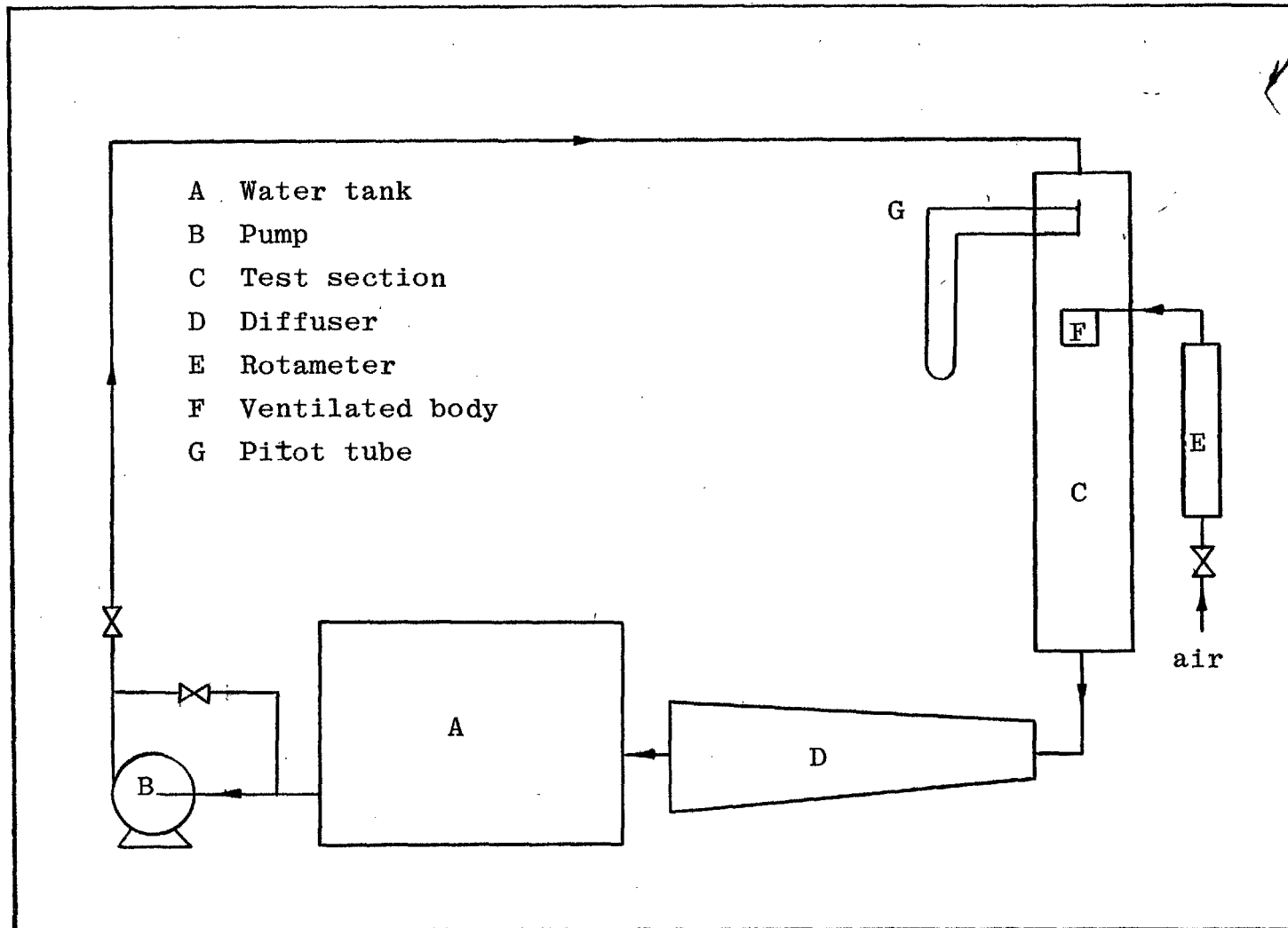


Fig. 2.3.2: Flow scheme of the ventilation system.

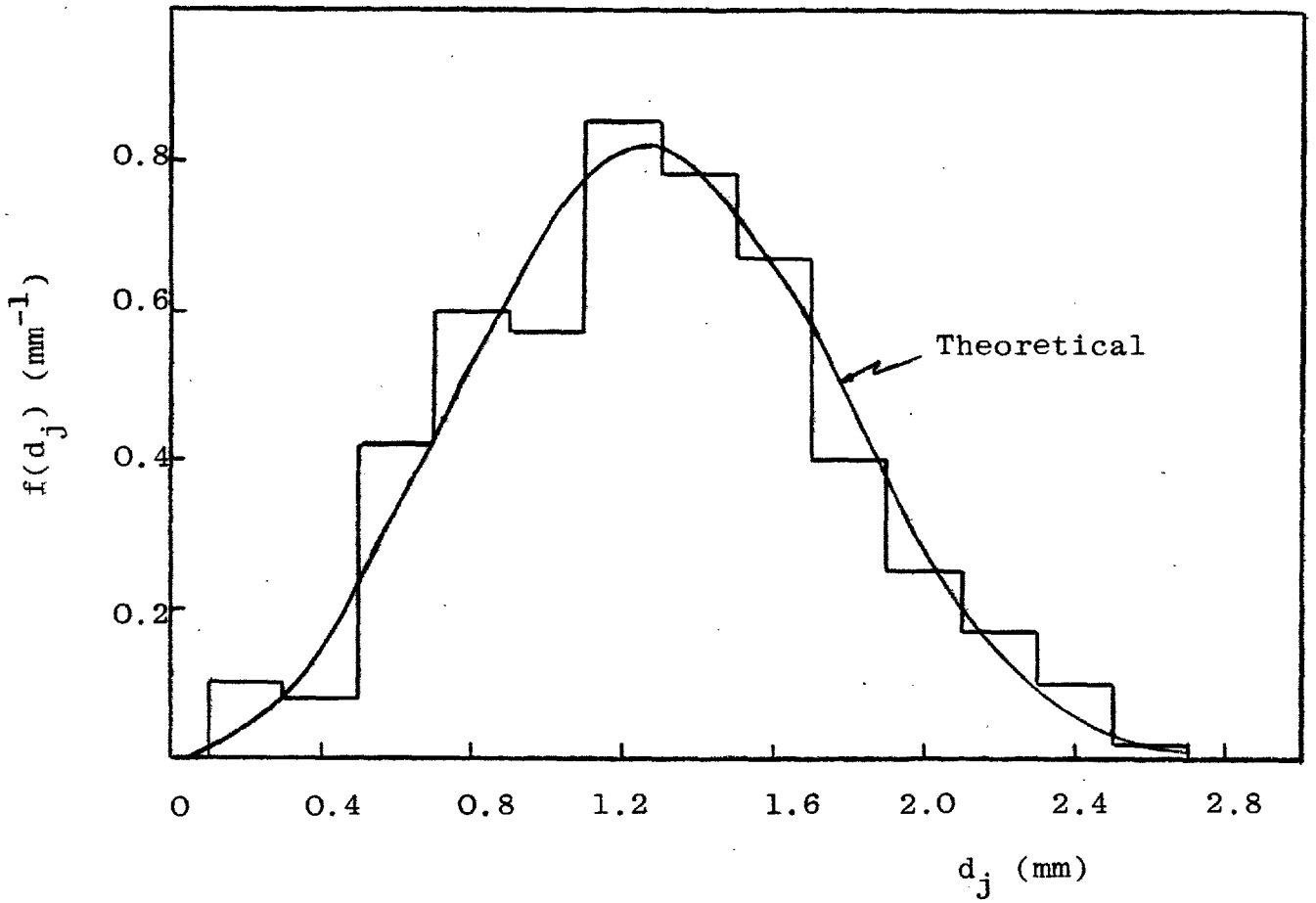


Fig. 2.3.3: Bubbles far behind a ventilated body:
theoretical and experimental size
distributions.

$$\langle d \rangle_{\text{exp}} = 1.29 \text{ mm}; \quad \langle d \rangle_{\text{theor.}} = 1.28 \text{ mm}$$

3. EFFECT OF GRAVITY AND COALESCENCE ON THE SIZE DISTRIBUTION FUNCTION OF BUBBLES IN LIQUIDS

3.1. Continuity equation in the 4-dimensional ($\underline{x}, \underline{r}_j$) space

Let us now consider a two-phase system consisting of small gas bubbles rising under the action of gravity alone, through a viscous, incompressible liquid which is otherwise at rest. Such a system being in the gravitational field is not homogeneous.

The bubbles considered are so small (of radii up to about 0.5 mm in pure water) that (a) variations of pressure in the liquid over the surface of the bubbles do not affect their sphericity, (b) the terminal velocities of the bubbles are functions of their radius, and (c) break-up of bubbles is highly improbable to occur.

Let $\varrho(\underline{x}, \underline{r}_j; t) d\underline{x} d\underline{r}_j$ denote the average (ensemble average) number of bubbles located at time t in a differential volume $d\underline{x}$ around the point $\underline{x}$ in physical space, and having radii in the range $[r_j - dr_j/2, r_j + dr_j/2]$. Clearly $d\underline{x} \int_0^\infty \varrho d\underline{r}_j \equiv d\underline{x} C$ denotes the average number of bubbles within $d\underline{x}$ at time t , $C = C(\underline{x}, t) \equiv \int_0^\infty \varrho d\underline{r}_j$ being the average, number concentration of bubbles in $d\underline{x}$ at time t , and $\int \varrho d\underline{x} d\underline{r}_j \equiv N(t)$ is the average total number of bubbles in the system at time t . The number density $\varrho(\underline{x}, \underline{r}_j; t)$ is in fact the distribution function at time t of the bubble position $\underline{x}'$ and radius r_j' , and when normalised becomes a probability density $f(\underline{x}, \underline{r}_j; t)$.

As the bubbles rise through the liquid, they inevitably collide with each other; some of the collisions may result in coalescences. If we neglect coalescence of bubbles we can write a simple equation for the conservation of the number of bubbles of radii r_j in the element $dx dr_j$ of the 4-dimensional $(\underline{x}, r_j)$ space:

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \underline{V}_j) = 0 \quad (3.1.1)$$

where the "velocity" $\underline{V}_j$ is the vector $\underline{V}_j = (v_{jx}, v_{jy}, v_{jz}, \frac{dr_j}{dt})$, v_{jx}, v_{jy}, v_{jz} being the x, y, z components respectively of the velocity $\underline{v}_j$ of the bubble of radius r_j .

Equation (3.1.1) is the equation of continuity in the $(\underline{x}, r_j)$ space and can be written, after expansion of the divergence term, as:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \rho \left[\frac{\partial v_{jx}}{\partial x} + \frac{\partial v_{jy}}{\partial y} + \frac{\partial v_{jz}}{\partial z} + \frac{\partial}{\partial r_j} \left(\frac{dr_j}{dt} \right) \right] + v_{jx} \frac{\partial \rho}{\partial x} + v_{jy} \frac{\partial \rho}{\partial y} + \\ v_{jz} \frac{\partial \rho}{\partial z} + \frac{dr_j}{dt} \frac{\partial \rho}{\partial r_j} = 0 \end{aligned} \quad (3.1.1a)$$

We can now assume that the dispersion of gas in the liquid is a dilute one, i.e.

$$\langle r \rangle \ll \lambda \quad (3.1.2)$$

where λ is the average interbubble distance in dx at time t , defined by:

$$\lambda = \left(\frac{1}{C}\right)^{1/3} ; \quad (3.1.3)$$

$\langle r \rangle \equiv \frac{1}{C} \int_0^\infty r_j \varrho dr_j$ is the average bubble radius in $d\tilde{x}$ at time t .

We also assume that the differential time dt involved in the derivation of eqn. (3.1.1) is such that:

$$\tau_c , \tau \ll dt \ll \tau_r \quad (3.1.4)$$

where τ_c is the average duration of a collision taking place between bubbles of radii r_j and r_i , as they move in $d\tilde{x}$; τ is the average time (Appendix I) needed for bubbles in $d\tilde{x}$ of any velocities to reach their terminal velocities, and τ_r is the average time between two successive collisions of bubbles.

The consequences of assumption (3.1.2) are that (a) the free motion of a bubble in $d\tilde{x}$ or equivalently the terminal velocity of a bubble in $d\tilde{x}$ is not affected by the presence of any other nearby bubbles and (b) the average time τ_r is large (collisions between bubbles are not frequent) and dt can be chosen in agreement with (3.1.4). On the other hand condition (3.1.4) ensures that any change in the distribution function ϱ in $d\tilde{x}$ during time dt due to collisions between the bubbles is negligible (since $dt \ll \tau_r$), and also that any deviation in the velocity of a bubble in $d\tilde{x}$ from its terminal value, due either to instantaneous collisions between the bubbles or a variation in the radius of the bubble, does not reflect in eqn. (3.1.1a) (since $\tau_c, \tau \ll dt$). Therefore the velocity $\tilde{v}_j = (v_{jx}, v_{jy}, v_{jz})$ of each of the bubbles of radii r_j

in eqn. (3.1.1a) is the terminal velocity v_{jz} (the coordinate z being measured vertically upwards) of a single bubble of radius r_j rising through a liquid. In other words we established by conditions (3.1.2) and (3.1.4) that collisions between bubbles rising under gravity through a liquid do not appear in any way in the continuity eqn. (3.1.1a) which thereby expresses how in the element $d\mathbf{x} dr_j$ the number $\rho d\mathbf{x} dr_j$ of bubbles of sufficiently low concentration ($C \ll 1/\langle r \rangle^3$) rising in their terminal velocities, changes with time due to the streaming in the 4-dimensional $(\mathbf{x}, r_j)$ space. With $v_x = v_y = 0$ and also $\frac{\partial v_z}{\partial z} = 0$ (since $v_{jz} = v_{jz}(r_j)$ and r_j, z are independent variables) eqn. (3.1.1a) becomes:

$$\frac{\partial \rho}{\partial t} + v_{jz} \frac{\partial \rho}{\partial z} + \frac{dr_j}{dt} \frac{\partial \rho}{\partial r_j} + \rho \frac{\partial}{\partial r_j} \left(\frac{dr_j}{dt} \right) = 0 \quad (3.1.5)$$

The terminal velocity v_{jz} (Levich 1962; Batchelor 1967) of a small spherical bubble of radius r_j rising freely through a liquid of density ρ and viscosity μ can be written as:

$$v_{jz} = K \frac{\rho g}{\mu} r_j^2 \quad (3.1.6)$$

where the coefficient $K = 1/3$ for Reynolds numbers $Re \ll 1$ in liquids free from surface-active impurities (bubbles of radii $r_j \ll 0.05$ mm in pure water).

= 2/9 for Reynolds numbers

$Re \ll 1$ in liquids not purified from surface-active agents
(bubbles of radii $r_j < 0.06$ mm in water)

= 1/9 for Reynolds numbers

$Re > 1$ in liquids free from surface-active impurities (bubbles of radii up to about 0.5 mm in pure water).

Assuming the gas in the bubbles to be an ideal gas we have for a bubble of radius r_j consisting of N_j molecules of gas:

$$P_j \left(\frac{4}{3} \pi r_j^3 \right) = N_j kT \quad (3.1.7)$$

The bubbles are supposed to be in thermal equilibrium with the surrounding liquid, i.e. the temperature T of the gas in the bubbles is constant and equal to the temperature of the liquid. Also, the temperature of the liquid is assumed to be the same everywhere. As we have already mentioned the bubbles considered are regarded as spherical, since, owing to their very small size the effect of gravity or pressure variations on their shape is entirely negligible (Landau and Lifshitz 1959). Therefore the pressure P_j within the bubble is given by Laplace's formula (2.2.5), and eliminating P_j from eqn. (3.1.7) using eqn. (2.2.5) we have:

$$Pr_j^3 + 2\gamma r_j^2 = \frac{3kT}{4\pi} N_j \quad (3.1.8)$$

Differentiating eqn. (3.1.8) with respect to time t we find:

$$\frac{dr_j}{dt} = - \left(\frac{r_j^2}{3Pr_j + 4\gamma} \right) \frac{dP}{dt} \quad (3.1.9)$$

The undisturbed pressure P of the liquid is known from Hydrostatics to be:

$$P = P_h + \rho g (h-z) \quad (3.1.10)$$

where h is the height of the liquid through which the bubbles rise; P_h is the pressure at the surface $z = h$ of the liquid.

Differentiating eqn. (3.1.10) with respect to time t we have:

$$\frac{dP}{dt} = - \rho g \frac{dz}{dt} = - \rho g v_{jz} \quad (3.1.11)$$

Now substituting eqn. (3.1.11), with v_{jz} as given by eqn. (3.1.6), into eqn. (3.1.9) we obtain:

$$\frac{dr_j}{dt} = \left(\frac{K\rho g}{\mu} \right) \left(\frac{r_j^4}{3(P_h/\rho g + h-z)r_j + 4\gamma} \right) \quad (3.1.12)$$

and differentiating eqn. (3.1.12) with respect to the radius r_j we find:

$$\frac{\partial}{\partial r_j} \left(\frac{dr_j}{dt} \right) = \left(\frac{K\rho g}{\mu} \right) \left(\frac{9(P_h/\rho g + h-z)r_j^4 + 16\gamma r_j^3}{[3(P_h/\rho g + h-z)r_j + 4\gamma]^2} \right) \quad (3.1.13)$$

Substitution of eqns. (3.1.6), (3.1.12) and (3.1.13) into eqn. (3.1.5) gives:

$$\begin{aligned} \frac{\partial e}{\partial t} + \frac{K\rho g}{\mu} \left\{ r_j^2 \frac{\partial e}{\partial z} + \left(\frac{r_j^4}{3(P_h/\rho g + h-z)r_j + 4\gamma} \right) \frac{\partial e}{\partial r_j} + \right. \\ \left. \left(\frac{9(P_h/\rho g + h-z)r_j^4 + 16\gamma r_j^3}{[3(P_h/\rho g + h-z)r_j + 4\gamma]^2} \right) e \right\} = 0 \end{aligned} \quad (3.1.14)$$

which is the equation of continuity in the 4-dimensional (x, r_j) space.

3.2 Continuity equation in the 4-dimensional $(\underline{x}, r_j)$ space, including coalescence of bubbles

In writing the equation of continuity (3.1.1) in $(\underline{x}, r_j)$ space we neglected coalescence of bubbles. As the bubbles rise through the liquid they inevitably collide with each other; some of the collisions result in coalescences. If coalescence of bubbles is taken into account then the continuity eqn. (3.1.1) is modified. Coalescences affect the rate of change of the distribution function $\varrho(\underline{x}, r_j; t)$ in two ways. First, among the set of bubbles in $d\underline{x}$ having radii r_j at time t , some undergo, during time dt , coalescences with other bubbles, say of radii r_i . These bubbles "disappear" from the set mentioned above; such coalescences represent a "loss" to $\varrho(\underline{x}, r_j; t)$. On the other hand, during time dt there are in $d\underline{x}$ coalescences between bubbles of different radii, say r_k and r_n , such that the radius of the resulting bubble is r_j . These coalescences obviously represent a "gain" to $\varrho(\underline{x}, r_j; t)$. The net effect of the coalescences is therefore given by the balance G-L of gains and losses, which combined with eqn. (3.1.1) gives:

$$\frac{\partial \varrho}{\partial t} + \text{div}(\varrho \underline{V}_j) = G - L \quad (3.2.1)$$

where $G d\underline{x} dr_j dt$ denotes the number of bubbles of radii in dr_j produced in $d\underline{x}$ during time dt , due to coalescences; $L d\underline{x} dr_j dt$ denotes the number of bubbles of radii in dr_j disappearing from $d\underline{x}$ during time dt , due to coalescences.

We now proceed to evaluate the terms G and L .

Assumptions (3.1.2) and (3.1.4) and their consequences still hold. We further assume that the differential volume $d\underline{x}$ is such that:

$$\lambda \ll (\underline{dx})^{1/3}$$

and

(3.2.2)

$$v_z dt \ll (\underline{dx})^{1/3}$$

where $v_z \equiv \frac{1}{C} \int_0^\infty |v_{jz} - \langle v_z \rangle| \varrho(\underline{x}, v_{jz}; t) dv_{jz}$ is the average peculiar speed of the bubbles in $\underline{dx}$ at time t , $\langle v_z \rangle \equiv \frac{1}{C} \int_0^\infty v_{jz} \varrho(\underline{x}, v_{jz}; t) dv_{jz}$ being the average velocity of the bubbles in $\underline{dx}$ at time t . Condition (3.2.2) ensures that the dispersion is homogeneous in $\underline{dx}$ as well as over a range of distances travelled by a bubble of speed v_z during time dt . A bubble of radius r_j in $\underline{dx}$, at time t , is generally surrounded by bubbles of various radii, greater, equal to or smaller than the radius r_j . We assume that any electrical interactions between the bubbles are entirely negligible, and no correlations (due, for example, to the effect of streaming in the liquid) exist at any time between the bubbles; the bubbles in the liquid are assumed to behave independently. Let us consider the collisions taking place in $\underline{dx}$ ($\underline{dx}$ such as given by inequalities (3.2.2)), during time dt (dt such as given by inequalities (3.1.4)), between bubbles of radii r_j and bubbles of radii r_i . Because of assumption (3.1.2) the collisions are only binary. We shall treat collisions of bubbles in a similar way to that used by Boltzmann (Boltzmann 1872) in deriving in 1872 his famous equation in the kinetic theory of gases, (Boltzmann's equation), which is used to describe the statistical motion of different particles or pseudo-particles (neutrons, electrons, ions, phonons, motor

cars) apart from the atoms and molecules originally considered by Boltzmann. Let a bubble of radius r_j , velocity v_{jz} (v_{jz} being measured in a laboratory system of reference κ), be in dx at time t . With respect to a system of reference κ' moving with this bubble, the bubbles of radii r_i (velocities v_{iz} in κ) have now velocities $v_{jz} - v_{iz}$. The number of collisions in κ' taking place in dx during time dt , between the bubbles of radii r_i and the bubble of radius r_j is equal to the number of centres of bubbles contained in a cylindrical shell of radii b and $b + db$ and height $|v_{jz} - v_{iz}|dt$, (Fig. 3.2.1), where $b = \sin\theta(r_j + r_i)$ is the minimum distance between the centres of the stationary bubble and a moving bubble. The number of such collisions (which is of course the same with respect to the laboratory system of reference κ) is:

$$\varrho(\underline{x}, r_i; t) dr_i 2\pi b db |v_{jz} - v_{iz}| dt \quad (3.2.3)$$

and since there are $\varrho(\underline{x}, r_j; t) d\underline{x} dr_j$ bubbles in $d\underline{x}$ of radii r_j at time t , the number of collisions in $d\underline{x}$ during dt between the bubbles of radii r_i and collision parameters b , and all the bubbles of radii r_j , is

$$\varrho(\underline{x}, r_j; t) d\underline{x} dr_j \varrho(\underline{x}, r_i; t) dr_i 2\pi b db |v_{jz} - v_{iz}| dt \quad (3.2.4)$$

Now some of the collisions (3.2.4) result in coalescence of bubbles. If $\mathcal{P}_c$ denotes the probability that two bubbles of radii, say r_j and r_i , will coalesce given that they collided, then it is reasonable to expect that $\mathcal{P}_c$ will generally depend

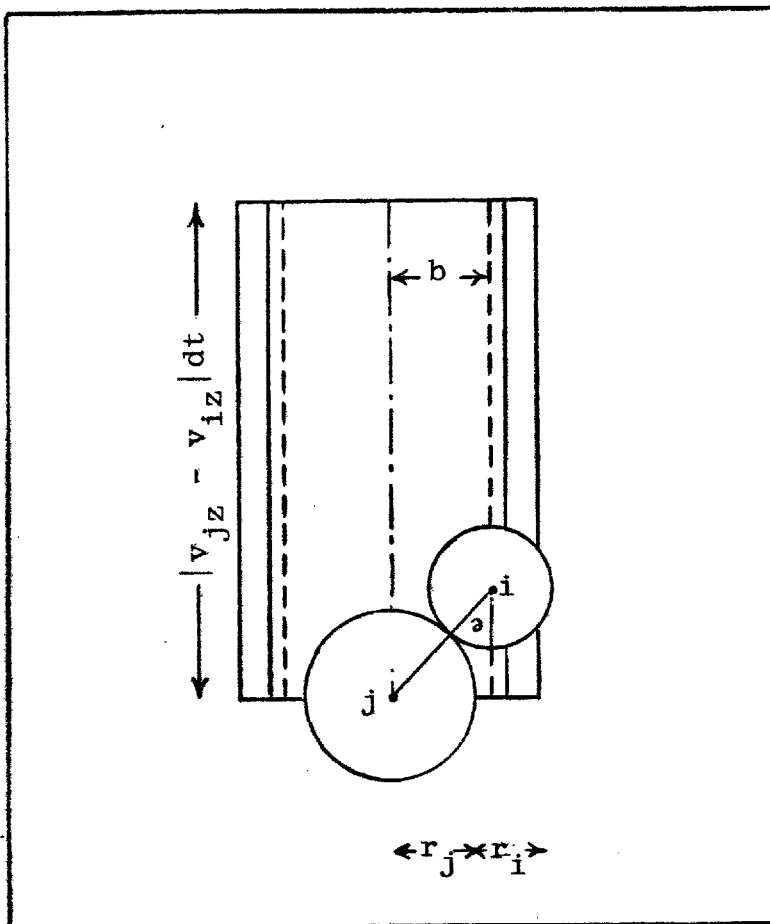


Fig. 3.2.1: Counting of the collisions of bubbles

on b , r_j , r_i as well as on the physical chemical properties of the bubbles in the liquid. Therefore the number of coalescences taking place in dx during time dt , between the bubbles of radii r_i and collision parameters b , and the bubbles of radii r_j , is:

$$\mathcal{P}_c(b, r_j, r_i) \varrho(x, r_j; t) dx dr_j \varrho(x, r_i; t) dr_i 2\pi b db |v_{jz} - v_{iz}| dt \quad (3.2.5)$$

Substituting, v_{jz}, v_{iz} as given by eqn. (3.1.6) into (3.2.5), and integrating over the total range $[0, r_j + r_i]$ of the distance b and the total range $[0, \infty]$ of the radius r_i , we obtain the total number of coalescences taking place in dx during time dt , involving bubbles of radii r_j :

$$\frac{2K\rho g\pi}{\mu} dx dr_j dt \int \mathcal{P}_c(b, r_j; r_i) \varrho(x, r_j; t) \varrho(x, r_i; t) |r_j^2 - r_i^2| b db dr_i \quad (3.2.6)$$

which clearly, divided by $(dx dr_j dt)$, represents the loss term L in eqn. (3.2.1):

$$L = \frac{2K\rho g\pi}{\mu} \int \mathcal{P}_c(b, r_j, r_i) \varrho(x, r_j; t) \varrho(x, r_i; t) |r_j^2 - r_i^2| b db dr_i \quad (3.2.7)$$

In the same way we can calculate the gain term G of eqn. (3.2.1). By repeating the previous argument leading to (3.2.5) we find that the number of coalescences taking place in dx during time dt , between the bubbles of radii r_n and collision parameters b , and the bubbles of radii r_k , is:

$$\mathcal{P}_c(b, r_k, r_n) \varrho(\underline{x}, r_k; t) d\underline{x} dr_k \varrho(\underline{x}, r_n; t) dr_n 2\pi b db |v_{kz} - v_{nz}| dt \quad (3.2.8)$$

We are interested only in the coalescences which result in bubbles of radii r_j , and if we assume that there is no diffusion or flow of gas into the liquid when a coalescence takes place, then the radius r_j of the resulting bubbles must satisfy the equation:

$$P_k \left(\frac{4}{3} \pi r_k^3 \right) + P_n \left(\frac{4}{3} \pi r_n^3 \right) = P_j \left(\frac{4}{3} \pi r_j^3 \right) \quad (3.2.9)$$

which after substitution of P_k , P_n and P_j given by eqn. (2.2.5), becomes:

$$Pr_j^3 + 2\gamma r_j^2 - [P(r_k^3 + r_n^3) + 2\gamma (r_k^2 + r_n^2)] = 0 \quad (3.2.10)$$

so that

$$r_j = F(r_k, r_n) \quad (3.2.11)$$

is the solution of eqn. (3.2.10).

If we now multiply (3.2.8) by $\delta\{r_j - F(r_k, r_n)\} dr_j$, δ being the Dirac δ -function, substitute v_{kz} , v_{nz} as given by eqn. (3.1.6), integrate over the total range $[0, r_k + r_n]$ of the distance b and the range $[0, r_j]$ of each of the radii r_k , r_n and divide the result by 2 (since by integrating with respect to both radii r_k , r_n we obviously consider a pair of values (r_k, r_n) twice), we obtain the total number of coalescences taking place in $d\underline{x}$ during time dt and resulting

in bubbles of radii r_j :

$$\frac{K_0 g \pi}{\mu} dx dr_j dt \int \mathcal{D}_c(b, r_k, r_n) \mathcal{C}(\tilde{x}, r_k; t) \mathcal{C}(\tilde{x}, r_n; t) \delta\{r_j - F(r_k, r_n)\}$$

$$|r_k^2 - r_n^2| b db dr_k dr_n$$

(3.2.12)

The above result (3.2.12), when divided by (dx, dr_j, dt) , represents the gain term G in eqn. (3.2.1):

$$G = \frac{K_0 g \pi}{\mu} \int \mathcal{D}_c(b, r_k, r_n) \mathcal{C}(\tilde{x}, r_k; t) \mathcal{C}(\tilde{x}, r_n; t) \delta\{r_j - F(r_k, r_n)\}$$

$$|r_k^2 - r_n^2| b db dr_k dr_n$$

(3.2.13)

where $F(r_k, r_n) = r_j$ is the solution of eqn. (3.2.10).

Eqn. (3.2.1) combined with eqn. (3.1.14), can be written more explicitly as:

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{C}(\tilde{x}, r_j; t) + \frac{K_0 g}{\mu} \left\{ r_j^2 \frac{\partial}{\partial z} \mathcal{C}(\tilde{x}, r_j; t) + \left(\frac{r_j^4}{3(P_h / \rho g + h - z) r_j^{+4\gamma}} \right) \frac{\partial}{\partial r_j} \mathcal{C}(\tilde{x}, r_j; t) \right. \\ \left. + \left(\frac{9(P_h / \rho g + h - z) r_j^4 + 16 r_j^3}{[3(P_h / \rho g + h - z) r_j^{+4\gamma}]^2} \right) \mathcal{C}(\tilde{x}, r_j; t) \right\} = G - L \end{aligned} \quad (3.2.14)$$

with G, L given by eqns. (3.2.13) and (3.2.7) respectively.

Eqn. (3.2.14) is the continuity equation in the 4-dimensional $(\underline{x}, r_j)$ space, including coalescence of bubbles; it expresses how in the element $d\underline{x} dr_j$ the number $\varrho d\underline{x} dr_j$ of bubbles of sufficiently low concentration ($C \ll 1/\langle r \rangle^3$) rising in their terminal velocities through a liquid, changes with time due to the streaming in $(\underline{x}, r_j)$ space and due to the coalescences with other bubbles.

We should probably discuss now in more detail the consequences of conditions (3.2.2) and (3.1.4) in connection with the derivation of the gain and loss terms (3.2.13) and (3.2.7) of eqn. (3.2.1). If condition (3.2.2) were not satisfied then the distribution function ϱ in (3.2.3) would have to be evaluated at the point the collision partner is coming from (and not at $\underline{x}$), and that would have resulted in a final equation, delocalised in space. On the other hand condition (3.1.4) ensures that the distribution function ϱ in $d\underline{x}$, does not change much as a result of the collisions and subsequent coalescences of bubbles taking place in $d\underline{x}$ during time dt (since $dt \ll \tau_r$). If condition (3.1.4) ($dt \ll \tau_r$), were not satisfied then the distribution function ϱ in (3.2.3) would have to be evaluated at an earlier time (and not at t), and that would have resulted in a final equation in which the rate of change of ϱ at time t would have depended not only on the instantaneous value of ϱ , but also on its previous history. Condition (3.1.4) therefore, ensures the Markovian character of the collision and coalescence processes.

3.3 Effect of gravity on the size distribution function of bubbles

If coalescence of bubbles is zero or negligible (either because the probability of coalescence $\mathcal{P}_c = 0$ or the concentration of bubbles in the liquid is so low that collisions between the bubbles are very rare), then eqn. (3.2.14) obviously reduces to eqn. (3.1.14). If, in turn, we neglect surface tension forces eqn. (3.1.14) becomes, in steady state ($\frac{\partial \varrho}{\partial t} = 0$), much more simple:

$$\frac{\partial \varrho}{\partial z} + \frac{r_j}{3(P_h/\rho g + h - z)} \frac{\partial \varrho}{\partial r_j} = - \frac{1}{P_h/\rho g + h - z} \varrho \quad (3.3.1)$$

At $z = 0$ the bubbles are always at rest. We assume that the distribution function (probability density) of the bubble radius in dx around $z = 0$, is given by distribution (2.2.13) derived in section 2.2. Then we have:

$$\varrho_0 \equiv \varrho(z = 0, r_j) = C_0 f(r_j) = 3C_0 \frac{r_j^2}{\langle r^3 \rangle_0} \exp\left(-\frac{r_j^3}{\langle r^3 \rangle_0}\right) \quad (3.3.2)$$

where $C_0 \equiv C(z = 0) = \int_0^\infty \varrho_0 dr_j$ is the average, number concentration of bubbles in dx around $z = 0$; $\langle r^3 \rangle_0 \equiv \frac{1}{C} \int_0^\infty r_j^3 \varrho_0 dr_j$ is the average of the cube of the bubble radius in dx around $z = 0$.

Eqn. (3.3.1) is a linear partial differential equation of first order in two independent variables z, r_j with initial condition given by eqn. (3.3.2), and can be solved as follows (Courant and Hilbert 1962): The system of ordinary differential equations defining in terms of a parameter η the characteristic

curves of the partial differential eqn. (3.3.1) is:

$$\frac{dz}{d\eta} = 1$$

$$\frac{dr_j}{d\eta} = \frac{r_j}{3(P_h/\rho g+h-z)} \quad (3.3.3)$$

$$\frac{d\varrho}{d\eta} = -\frac{\varrho}{(P_h/\rho g+h-z)}$$

Integration of the differential eqn. (3.3.1) is equivalent to integration of the system of differential eqns. (3.3.3). Solution of the system (3.3.3) gives the one-parameter family of the characteristic curves:

$$z = z_0 + \eta$$

$$r_j = r_{j0} \left(\frac{P_h/\rho g+h-z_0-\eta}{P_h/\rho g+h-z_0} \right)^{-1/3} \quad (3.3.4)$$

$$\varrho = \varrho_0 \left(\frac{P_h/\rho g+h-z_0-\eta}{P_h/\rho g+h-z_0} \right)$$

where z_0 , r_{j0} , ϱ_0 are the initial values (for $\eta = 0$) of z , r_j and ϱ respectively. To solve the initial value problem we prescribe z_0 , r_{j0} , ϱ_0 as functions of a parameter ξ :

$$\begin{aligned}
 z_0 &= 0 \\
 r_{j0} &= \xi \\
 \rho_0 &= 3C_0 \frac{\xi^2}{\langle r^3 \rangle_0} \exp\left(-\frac{\xi^3}{\langle r^3 \rangle_0}\right)
 \end{aligned} \tag{3.3.5}$$

The family of characteristics intersecting the initial curve (3.3.5) is given by:

$$\begin{aligned}
 z &= \eta \\
 r_j &= \xi \left(1 - \frac{\eta}{P_h/\rho g + h}\right)^{-1/3}
 \end{aligned} \tag{3.3.6}$$

$$\rho = \frac{3C_0}{\langle r^3 \rangle_0} \xi^2 \left(1 - \frac{\eta}{P_h/\rho g + h}\right) \exp\left(-\frac{\xi^3}{\langle r^3 \rangle_0}\right)$$

The determinant

$$\Delta(\eta, \xi) = \frac{\partial z}{\partial \eta} \frac{\partial r_j}{\partial \xi} - \frac{\partial z}{\partial \xi} \frac{\partial r_j}{\partial \eta} = \left(1 - \frac{\eta}{P_h/\rho g + h}\right)^{-1/3}$$

has on the initial curve (3.3.5) the value:

$$\Delta = \Delta(\eta = 0, \xi) = 1$$

which is different from zero. Therefore the parameters η and ξ can be eliminated from (3.3.6):

$$\eta = z ; \quad \xi = r_j \left(1 - \frac{z}{P_h/\rho g + h}\right)^{1/3}$$

and ϱ can now be expressed as a function of z and r_j :

$$\varrho = 3C_0 \frac{r_j^2}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right)^{5/3} \exp \left\{ - \frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right) \right\} \quad (3.3.7)$$

Eqn. (3.3.7) is the solution of the partial differential eqn. (3.3.1) with initial condition given by eqn. (3.3.2). If we integrate eqn. (3.3.7) over the total range, $[0, \infty]$, of the bubble radius r_j , we obtain the concentration C of the bubbles in dx around height z , as a function of z :

$$C \equiv \int_0^\infty \varrho \, dr_j = C_0 \left(1 - \frac{z}{P_h / \rho g + h}\right)^{2/3} \quad (3.3.8)$$

Distribution (3.3.7) can be normalised to become a probability density $f(z, r_j)$, as:

$$f(z, r_j) \equiv \frac{\varrho}{\int_0^\infty \varrho \, dr_j} = 3 \frac{r_j^2}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right) \exp \left\{ - \frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right) \right\} \quad (3.3.9)$$

The average bubble radius $\langle r \rangle_z$ in dx around height z can be calculated as a function of z from its definition formula:

$$\langle r \rangle_z = \int_0^\infty r_j f(z, r_j) \, dr_j, \quad (3.3.10)$$

if we substitute for $f(z, r_j)$ distribution (3.3.9) with $\langle r^3 \rangle_0$ expressed in terms of $\langle r \rangle_0$ from eqn. (2.2.15); we find:

$$\langle r \rangle_z = \langle r \rangle_0 \left(1 - \frac{z}{P_h / \rho g + h} \right)^{-1/3} \quad (3.3.11)$$

The average of the cube of the bubble radius $\langle r^3 \rangle_z$ in dx around z , calculated from its definition formula:

$$\langle r^3 \rangle_z = \int_0^\infty r_j^3 f(z, r_j) dr_j \quad (3.3.12)$$

with $f(z, r_j)$ given by distribution (3.3.9), is:

$$\langle r^3 \rangle_z = \langle r^3 \rangle_0 \left(1 - \frac{z}{P_h / \rho g + h} \right)^{-1} \quad (3.3.13)$$

and substituting $\langle r^3 \rangle_0$ as given by eqn. (3.3.13) into distribution (3.3.9) we come to the interesting result:

$$f(z, r_j) = 3 \frac{r_j^2}{\langle r^3 \rangle_z} \exp\left(- \frac{r_j^3}{\langle r^3 \rangle_z} \right) \quad (3.3.14)$$

which shows that distribution (2.2.13) derived in section 2.2 for bubbles at rest, describes as well, locally, in steady state, the size distribution of bubbles rising in their terminal velocities through a liquid.

Our result, as expressed by distribution (3.3.9), shows how the size distribution function of bubbles in a given system (of a given height h of liquid and a given pressure P_h at $z = h$), changes with height z from that at $z = 0$ given by distribution (2.2.13). Distribution (3.3.9) in fact depends on the ratio of the hydrostatic pressure at height z over that at $z = 0$, and as such, for a given pressure P_h , say, the atmospheric and a given height z , varies with the height h of liquid. In Fig. 3.3.1 it is illustrated how for a system of gas bubbles in pure water of height $h = 3\text{m}$ and pressure $P_h = 1\text{ atm.}$ at $z = 3\text{m}$, the size distribution function of bubbles changes with height z ; $\langle r^3 \rangle_0$ was taken to be 0.05 mm^3 .

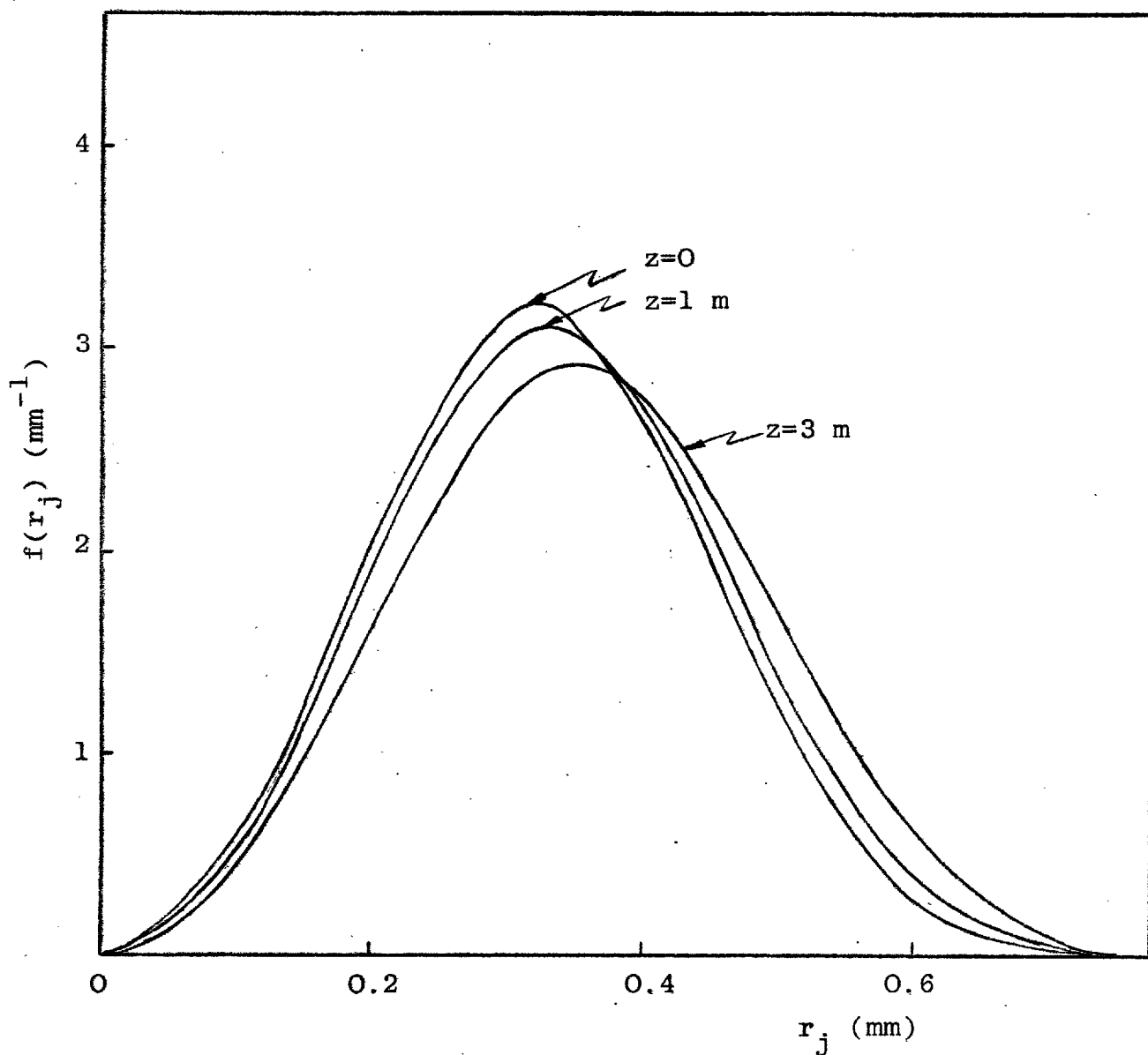


Fig. 3.3.1: Effect of gravity on the size distribution function of bubbles.

$$\langle r \rangle_0 = 0.329 \text{ mm} ; \langle r \rangle_{z=1 \text{ m}} = 0.338 \text{ mm} ;$$

$$\langle r \rangle_{z=3 \text{ m}} = 0.358 \text{ mm}$$

3.4 Effect of gravity and coalescence on the size distribution function of bubbles

If we neglect surface tension forces and assume that the initial condition is given by eqn. (3.3.2), eqn. (3.2.14) becomes in steady state:

$$r_j^2 \frac{\partial}{\partial z} \varrho(z, r_j) + \frac{r_j^3}{3(P_h/\rho g + h - z)} \frac{\partial}{\partial r_j} \varrho(z, r_j) + \frac{r_j^2}{P_h/\rho g + h - z} \varrho(z, r_j) = G' - L' \quad (3.4.1)$$

where

$$G' = \pi \int \mathcal{P}_c(b, r_k, r_n) \varrho(z, r_k) \varrho(z, r_n) \delta\{r_j - F(r_k, r_n)\} |r_k^2 - r_n^2| b db dr_k dr_n \quad (3.4.2)$$

with

$$F(r_k, r_n) = r_j = (r_k^3 + r_n^3)^{1/3} ; \quad (3.4.3)$$

$$L' = 2\pi \int \mathcal{P}_c(b, r_j, r_i) \varrho(z, r_j) \varrho(z, r_i) |r_j^2 - r_i^2| b db dr_i \quad (3.4.4)$$

Eqn. (3.4.1) is a non-linear integro-differential equation in two independent variables z, r_j , with initial condition given by eqn. (3.3.2). When coalescence of bubbles is zero or negligible, then eqn. (3.4.1) obviously reduces to eqn. (3.3.1) the solution of which is given by eqn. (3.3.7).

We shall assume that the probability of coalescence $\mathcal{P}_c$ is equal to unity, i.e. all collisions between the bubbles result in coalescences. We shall obtain an approximate solution

of eqn. (3.4.1) by putting solution (3.3.7) into the right-hand side of eqn. (3.4.1), performing the integrations and then solving the resulting partial differential equation. The solution thus obtained is of course an approximate solution of eqn. (3.4.1), valid when the degree of coalescence in the system is low either because the probability of coalescence $\mathcal{P}_c$ is low enough or because the concentration of bubbles in the liquid is very low. But since we assumed $\mathcal{P}_c = 1$, the solution obtained will be valid when the concentration of bubbles in the liquid is very low.

If we perform the integration in eqn. (3.4.2) with respect to b , with $\mathcal{P}_c = 1$, we obtain:

$$G' = \frac{\pi}{2} \int \varrho(z, r_k) \varrho(z, r_n) \delta\{r_j - F(r_k, r_n)\} |r_k^2 - r_n^2| (r_k + r_n)^2 dr_k dr_n \quad (3.4.5)$$

Elimination of the δ -function from eqn. (3.4.5) (Appendix II), gives:

$$G' = \frac{\pi}{2} r_j^2 \int_0^{r_j} \varrho\{z, (r_j^3 - r_n^3)^{1/3}\} \varrho(z, r_n) \left| 1 - \frac{r_n^2}{(r_j^3 - r_n^3)^{2/3}} \right| \left[(r_j^3 - r_n^3)^{1/3} + r_n \right]^2 dr_n \quad (3.4.6)$$

Substituting $\varrho\{z, (r_j^3 - r_n^3)^{1/3}\}$ and $\varrho(z, r_n)$ as given by eqn. (3.3.7) into eqn. (3.4.6), and performing the integration with respect to r_n we find:

$$G' = 1.1\pi \frac{C_o^2}{\langle r^3 \rangle_o^2} r_j^9 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{10/3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} \quad (3.4.7)$$

Integration of eqn. (3.4.4) with respect to b , with

$\mathcal{P}_c = 1$ gives:

$$L' = \pi \varrho(z, r_j) \int_0^\infty \varrho(z, r_i) |r_j^2 - r_i^2| (r_j + r_i)^2 dr_i \quad (3.4.8)$$

Substituting $\varrho(z, r_i)$ as given by eqn. (3.3.7) and performing the integration with respect to r_i we obtain:

$$\begin{aligned} L' = & \pi C_o \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} \varrho(z, r_j) \left\{ r_j^4 - \frac{2}{3} \Gamma(1/3) \langle r^3 \rangle_o^{1/3} \right. \\ & \left. \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} r_j^3 + \right. \\ & + 2 \langle r^3 \rangle_o \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1} r_j \left(\frac{10}{3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} - 1\right) + \\ & + \frac{4}{9} \Gamma(1/3) \langle r^3 \rangle_o^{4/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-4/3} + 4 \int_0^{r_j} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \right. \\ & \left. \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} dr_j \left[r_j^3 - \frac{2}{3} \langle r^3 \rangle_o \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1} \right] \Big\} \end{aligned} \quad (3.4.9)$$

If we approximate the integrand in eqn. (3.4.9) by:

$$\exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} \cong \left[1 - \frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right]$$

$$\theta\left\{\langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} - r_i\right\}$$

θ being the unit step function:

$$\theta\left\{\langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} - r_j\right\} = \begin{cases} 1; r_i < \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} \\ 0; r_i > \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} \end{cases},$$

then eqn. (3.4.9) becomes for $r_i < \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3}$:

$$\begin{aligned} L' = \pi C_o \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} \varrho(z, r_j) & \left\{ - \langle r^3 \rangle_o^{-1} \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^7 + \right. \\ & + \frac{17}{3} r_j^4 - \frac{2}{3} \Gamma(1/3) \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} r_j^3 + \frac{2}{3} \langle r^3 \rangle_o \\ & \left. \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1} r_j \left(10 \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} - 7\right) + \right. \\ & \left. + \frac{4}{9} \Gamma(1/3) \langle r^3 \rangle_o^{4/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-4/3} \right\} \quad (3.4.10) \end{aligned}$$

and for $r_j > \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3}$:

$$\begin{aligned}
L' = & \pi C_0 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} e(z, r_j) \left\{ \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^4 - \right. \\
& \left. \left(\frac{2}{3} \Gamma(1/3) - 3\right) \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} r_j^3 + \right. \\
& \left. 2 \langle r^3 \rangle_0 r_j \left(\frac{10}{3} \exp \left\{ -\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right) \right\} - 1\right) + \right. \\
& \left. \left(\frac{4}{9} \Gamma(1/3) - 2\right) \langle r^3 \rangle_0^{4/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1} \right\} \quad (3.4.11)
\end{aligned}$$

The resulting partial differential equation is:

$$\frac{\partial \mathcal{Q}}{\partial z} + \frac{r_j}{3(P_h/\rho g+h-z)} \frac{\partial \mathcal{Q}}{\partial r_j} = - e \left(\frac{1}{P_h/\rho g+h-z} + Q \right) + R \quad (3.4.12)$$

where

$$R \equiv \frac{G'}{r_j^2} = 1.1 \pi \frac{C_0^2}{\langle r^3 \rangle_0^2} r_j^7 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{10/3} \exp \left\{ -\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right) \right\} ; \quad (3.4.13)$$

$$\begin{aligned}
Q \equiv \frac{1}{e} \left(\frac{L'}{r_j^2} \right) = & \pi C_0 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} \left\{ - \langle r^3 \rangle_0^{-1} \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^5 + \right. \\
& \frac{17}{3} r_j^2 - \frac{2}{3} \Gamma(1/3) \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} r_j + \\
& \frac{2}{3} \langle r^3 \rangle_0 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1} r_j^{-1} \left(10 \exp \left\{ -\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right) \right\} - 7\right) + \\
& \left. \frac{4}{9} \Gamma(1/3) \langle r^3 \rangle_0^{4/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-4/3} r_j^{-2} \right\} \quad (3.4.14)
\end{aligned}$$

$$\text{for } r_j < \langle r \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} ;$$

$$Q = \pi C_o \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} \left\{ \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^2 - \left(\frac{2}{3} \Gamma(1/3) - 3\right) \langle r^3 \rangle_o^{1/3} \right.$$

$$\left. \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} r_j + 2 \langle r^3 \rangle_o r_j^{-1} \left(\frac{10}{3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_o} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} - 1\right) + \right.$$

$$\left. \left(\frac{4}{9} \Gamma(1/3) - 2\right) \langle r^3 \rangle_o^{4/3} \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^{-2} \right\} \quad (3.4.15)$$

$$\text{for } r_j > \langle r^3 \rangle_o^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{1/3} .$$

Eqn. (3.4.12) can be solved in the same way as eqn. (3.3.1)

in section 3.3, by integrating the system of ordinary differential eqns:

$$\frac{dz}{d\eta} = 1$$

$$\frac{dr_j}{d\eta} = \frac{r_j}{3(P_h/\rho g+h-z)} \quad (3.4.16)$$

$$\frac{d\varrho}{d\eta} = -\varrho \left(\frac{1}{P_h/\rho g+h-z} + Q \right) + R$$

with initial curve given by (3.3.5). We obtain the solution:

$$\varrho(z, r_j) = 3C_0 \frac{r_j^2}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{5/3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_0}\right\} \left(1 - \frac{z}{P_h/\rho g+h}\right) \left\{ \exp(-Qz) + \frac{0.36}{W} [1 - \exp(-Qz)] \right\} \quad (3.4.17)$$

where for $r_j < \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3}$, Q is given by eqn. (3.4.14), and

$$\begin{aligned} W = & \langle r^3 \rangle_0^2 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-2} \left[-\langle r^3 \rangle_0^{-2} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-2} + \right. \\ & \frac{17}{3} \langle r^3 \rangle_0^{-1} \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^{-3} - \frac{2}{3} \Gamma(1/3) \langle r^3 \rangle_0^{-2/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} r_j^{-4} \\ & + \frac{2}{3} r_j^{-6} \left(10 \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} - 7\right) + \\ & \left. \frac{4}{9} \Gamma(1/3) \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} r_j^{-7} \right] ; \quad (3.4.18) \end{aligned}$$

for $r_j > \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3}$ Q is given by eqn. (3.4.15),

and

$$\begin{aligned} W = & \langle r^3 \rangle_0^2 \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-2} \left[\langle r^3 \rangle_0^{-1} \left(1 - \frac{z}{P_h/\rho g+h}\right) r_j^{-3} - \left(\frac{2}{3} \Gamma(1/3) - 3\right) \right. \\ & \langle r^3 \rangle_0^{-2/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{2/3} r_j^{-4} + 2r_j^{-6} \left(\frac{10}{3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h/\rho g+h}\right)\right\} - \right. \\ & \left. \left. -1\right) + \left(\frac{4}{9} \Gamma(1/3) - 2\right) \langle r^3 \rangle_0^{1/3} \left(1 - \frac{z}{P_h/\rho g+h}\right)^{-1/3} r_j^{-7} \right] \quad (3.4.19) \end{aligned}$$

Eqn. (3.4.17) is an approximate solution of eqn. (3.4.1) when the probability of coalescence $\mathcal{P}_c = 1$ and the concentration of bubbles in the liquid is very low.

One could probably assume an independence between the factors (b, r_j, r_i) and any other physico-chemical factors governing the process of coalescence, thus expressing the probability of coalescence $\mathcal{P}_c$ as $\mathcal{P}_c = \mathcal{C} g(b, r_j, r_i)$, where $\mathcal{C}$ is independent of b , r_j and r_i . A purely mechanical model could then be employed to express $g(b, r_j, r_i)$ as a function of b , r_j and r_i . On the other hand, if we assume that $\mathcal{P}_c = \mathcal{C}$ i.e. the probability of coalescence is independent of b , r_j and r_i , then for low values of $\mathcal{C}$ and not necessarily very low concentrations of bubbles†, eqn. (3.4.17) (appropriately accommodated) is an approximate solution of eqn. (3.4.1):

$$\rho(z, r_j) = 3C_0 \frac{r_j^2}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right)^{5/3} \exp\left\{-\frac{r_j^3}{\langle r^3 \rangle_0} \left(1 - \frac{z}{P_h / \rho g + h}\right)\right\} \cdot$$

$$\left\{ \exp(-Q'z) + \frac{0.36}{W} [1 - \exp(-Q'z)] \right\} \quad (3.4.20)$$

where $Q' = \mathcal{C}Q$; Q as given by eqns. (3.4.14) and (3.4.15).

Our result as expressed by distribution (3.4.17) or (3.4.20) is illustrated in Fig. 3.4.1 and Fig. 3.4.2. For a system of liquid height $h = 2$ m, $P_h = 1$ atm. and bubble

†Note however that for eqn. (3.4.1) to be valid the

concentration of bubbles in the liquid has to be sufficiently low, i.e. $C_0 \ll 1/\langle r \rangle_0^3$.

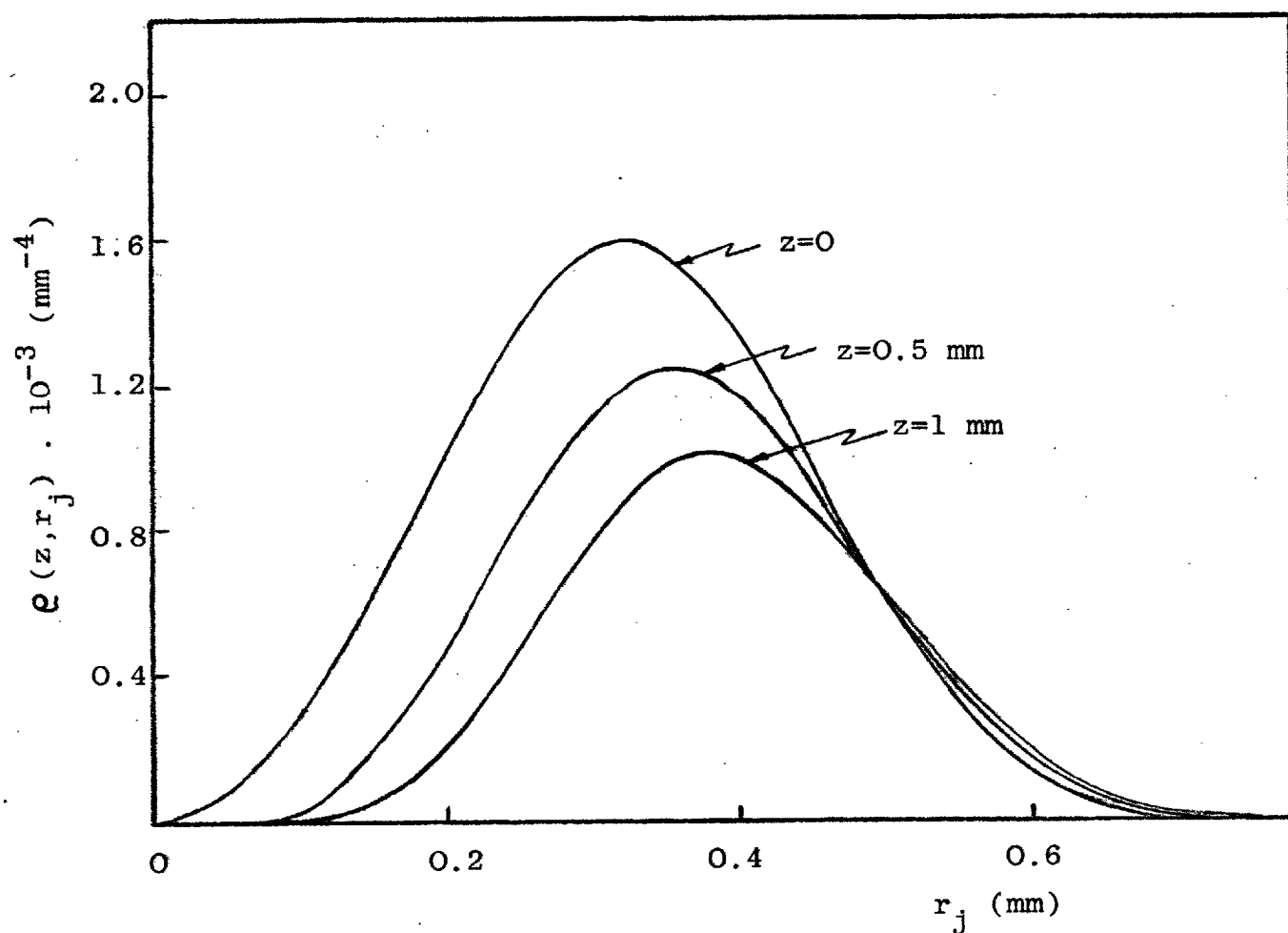


Fig. 3.4.1: Effect of gravity and coalescence on the size distribution function of bubbles.
 $\langle r \rangle_0 = 0.329 \text{ mm}$; $C_0 = 0.5 \cdot 10^{-3} \text{ mm}^{-3}$; $\mathcal{P}_c = 1$

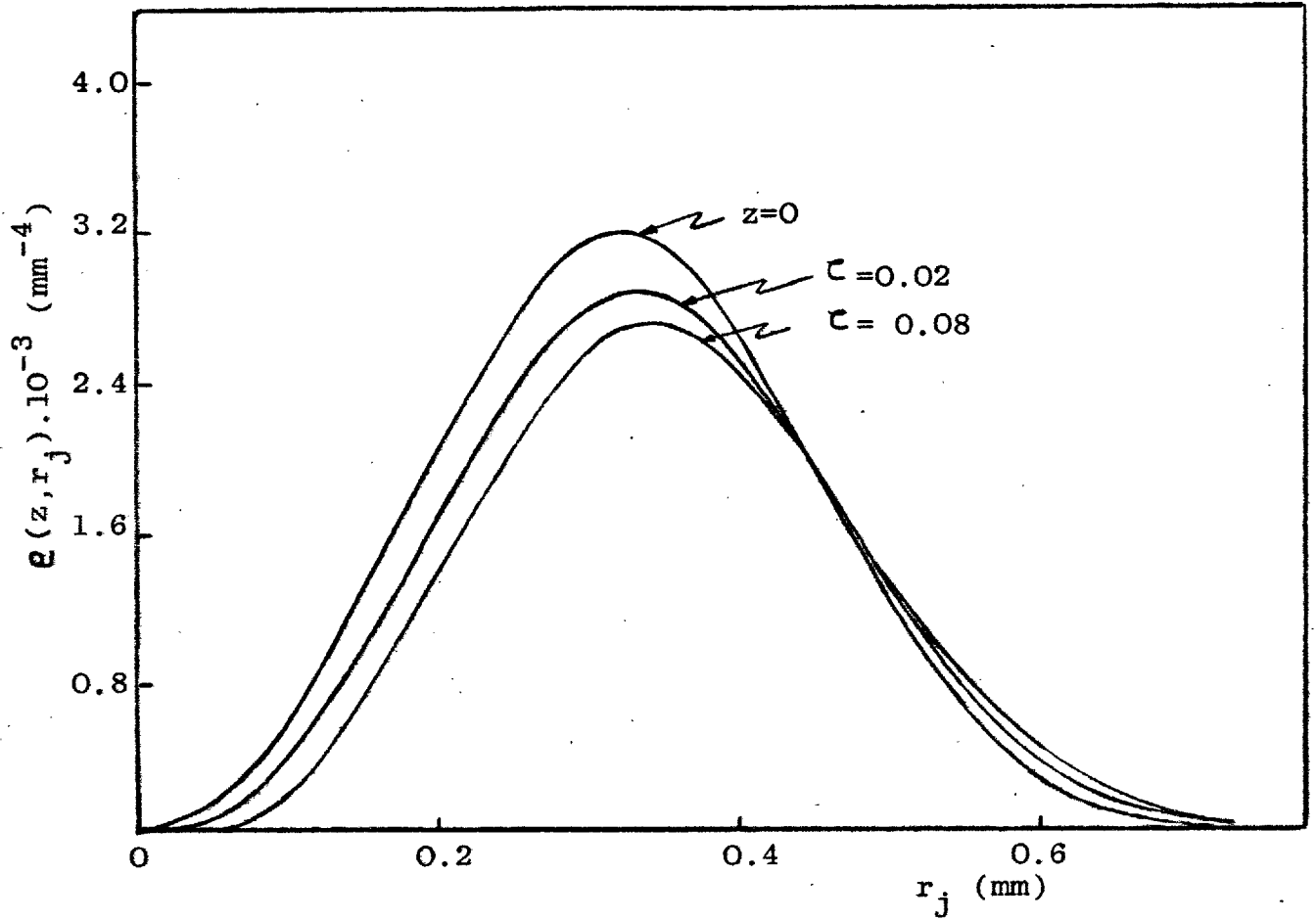


Fig. 3.4.2: Effect of gravity and coalescence on the size distribution function of bubbles.

$$\langle r \rangle_0 = 0.329 \text{ mm}; \quad C_0 = 1.10^{-3}; \quad z = 1 \text{ m}$$

concentration $C_0 = 0.5 \cdot 10^{-3} \text{ mm}^{-3}$ distribution (3.4.17) was plotted for various values of z in Fig. 3.4.1. The variation of the size distribution function of bubbles with height z as a result mainly of coalescences, is clear. In Fig. 3.4.2 distribution (3.4.20) was plotted at $z = 1 \text{ m}$ for different values $\mathcal{C}$ of the probability of coalescence; the bubble concentration C_0 was taken to be $C_0 = 1 \cdot 10^{-3} \text{ mm}^{-3}$.

4. CONCLUSIONS

In chapter 2 we made the assumption that a gas is dispersed in a liquid into bubbles in a completely random way with respect to the energies of the bubbles and we subsequently derived, for bubbles in thermal equilibrium with the surrounding liquid, in the absence of gravity (for bubbles either at rest or wholly carried along with the ambient liquid, in its potential flow), the distribution function (2.1.15) of the bubble energy. The distribution functions (2.2.10) and (2.2.13) or (2.2.11) and (2.2.14) of the bubble radius or diameter following from the distribution function (2.1.15) of the bubble energy agree well with the experimental size distribution of bubbles in water, generated by an air entrainment process at the surface of the water or behind a ventilated body. Inevitably distributions (2.2.10) and (2.2.13) or (2.2.17) involve the parameters $\langle r^3 \rangle$, $\langle r^2 \rangle$ or $\langle r \rangle$ which can only be obtained from the particular experimental data to which the aforementioned distributions are to be applied. The experimental cases considered here showed that distribution (2.2.11) very little differs from distribution (2.2.14). This is hardly surprising, since for a certain volume, say $\pi \langle d \rangle^3 / 6$ of air in water, the surface energy is much less than the volume energy and surface effects are negligible compared with volume effects. Therefore, distribution (2.2.14) or (2.2.13), owing to its much more simple form alone, can be applied to describe the size distribution of the bubbles in liquids. Distribution (2.2.14) is of the same form as the empirical Nukiyama-Tanasama

distribution often applied to droplets. It would be interesting to note that distribution (2.2.14) gives also the size distribution function of droplets of an incompressible liquid if the way the liquid is dispersed into droplets is assumed to be completely random with respect to the volumes of the droplets (irrespective of the energies of the droplets).

In chapter 3 we investigated the effect of gravity and coalescence on the size distribution function of sufficiently small bubbles. The investigation resulted in eqn. (3.2.14) which is a non-linear integro-differential equation for the distribution function at time t of the position and radius of bubbles of sufficiently low concentration, rising in their terminal velocities through a liquid which is otherwise at rest. The effect of gravity, alone, on the distribution function (2.2.13) was obtained in steady state, and is given by distribution (3.3.9) and illustrated in Fig. 3.3.1. The result expressed in the form of distribution (3.3.14) shows that distribution (2.2.13) derived in the absence of gravity (for bubbles at rest), describes as well locally, in steady state the size distribution function of bubbles rising in their terminal velocities through a liquid. The effect of gravity and coalescence on the bubble size distribution was obtained as an approximate solution of eqn. (3.2.14) in steady state, for the case where the degree of coalescence of bubbles in the system is low, and is given by distribution (3.4.17) or (3.4.20). In obtaining distribution (3.4.17) or (3.4.20) the probability of coalescence was assumed to be

equal to unity or generally independent of the bubble radii and collision parameter. The variation, due mainly to coalescence, of the size distribution function of bubbles with height z , and probability of coalescence $\bar{C}$ is shown in Figs.3.4.1 and 3.4.2. Our approach in investigating the effect of coalescence on the size distribution function of bubbles rising in their terminal velocities through a liquid is of course not a realistic one: We assumed statistical independence for the bubbles in the liquid and probability of coalescence independent of the bubble radii. Theoretical determination of the probability of coalescence in terms of the bubble radii as well as other parameters affecting the process of coalescence, would result in the prediction of bubble size distributions in liquids and further work in that direction would be suggested.

NOTATION

b	collision parameter
B	constant in distribution (2.2.20)
c	constant in distribution (2.2.20)
$\mathcal{C}$	coalescence coefficient
C	average, number concentration of bubbles in dx at time t
C_0	average, number concentration of bubbles in dx around $z = 0$
d_j	diameter of the j th bubble or droplet
$\langle d \rangle$	average bubble diameter
$\langle d^2 \rangle$	average of the square of the bubble diameter
$\langle d^3 \rangle$	average of the cube of the bubble diameter
$\xi E'_j$	expectation of E'_j
$\xi r'_j$	expectation of r'_j
E_j	internal energy of the j th bubble
E'_j	internal energy of the j th bubble regarded as a random variable
E_t	total energy of the bubbles
E_{sj}	surface part of the internal energy of the j th bubble
E_{vj}	volume part of the internal energy of the j th bubble
$\langle E \rangle$	average bubble energy

$f(d_j)$	distribution function (probability density) of the bubble diameter
$f(E_j)$	distribution function (probability density) of the bubble energy
$f(r_j)$	distribution function (probability density) of the bubble radius
$f(V_j)$	distribution function (probability density) of the bubble volume
$f(\tilde{x}, r_j ; t)$	distribution function (probability density) at time t , of the bubble position and radius
F	$\equiv F(r_k, r_n) = r_j$, solution of eqn. (3.2.10)
g	acceleration of gravity
G	"gain" term in eqn. (3.2.1)
h	height of liquid
H	minimum distance from the $E_j' = E_t$ to S_{N-2}
$H(E_j)$	minimum distance from the point $E_j' = E_t$ to the hyperplane $S_{N-2}(E_j)$
k	Boltzmann's constant
K	coefficient in eqn. (3.1.6)
ℓ	length on the curve $F(r_k, r_n) = r_j$
$\mathcal{L}(s)$	Lebesgue measure of s
$\mathcal{L}(S_{N-1})$	Lebesgue measure of S_{N-1}
$\mathcal{L}(S_{N-2})$	Lebesgue measure of S_{N-2}
$\mathcal{L}[dS_{N-1}(E_j)]$	Lebesgue measure of $dS_{N-1}(E_j)$
L	"loss" term in eqn. (3.2.1)
n	number fraction of droplets or bubbles with diameters $< d_j$

N	number of bubbles or droplets
N_j	number of gas molecules within the j th bubble
$\mathcal{P}(s)$	probability that the system of bubbles is within s
$\mathcal{P}_c$	probability that two bubbles will coalesce given that they collided
P	pressure of the liquid surrounding the bubbles
P_h	pressure at the surface $z = h$ of the liquid
P_j	pressure within the j th bubble
r_j	radius of the j th bubble or droplet
r'_j	radius of the j th bubble regarded as a random variable
$\langle r \rangle$	average bubble radius
$\langle r^2 \rangle$	average of the square of the bubble radius
$\langle r^3 \rangle$	average of the cube of the bubble radius
$\langle r^3 \rangle_z$	average of the cube of the bubble radius in dx around z
$\langle r^3 \rangle_0$	average of the cube of the bubble radius in dx around $z = 0$
R_e	Reynold's number $= 2\rho v_{jz} r_j / \mu$
s	a region of the surface S_{N-1}
s_j	surface area of the j th bubble

S_{N-1}	N-1-dimensional hyperplane in an N-dimensional Cartesian space, cutting each coordinate at a point E_t from the origin
S_{N-2}	N-2-dimensional hyperplane resulting from the intersection of the N-1-dimensional hyperplane $E'_j = 0$ with the hyperplane S_{N-1}
$S_{N-2}(E_j)$	N-2-dimensional hyperplane resulting from the intersection of the N-1-dimensional hyperplane $E'_j = E_j$ with the hyperplane S_{N-1}
S_{sj}	surface entropy of the jth bubble
T	temperature of the dispersed gas and the liquid
v_j	velocity of the jth bubble
v_z	average peculiar speed of the bubbles in dx , at time t
v_{jz}	terminal velocity of the jth bubble
$\langle v_z \rangle$	average velocity of the bubbles in dx , at time t
V_j	volume of the jth bubble or droplet
V_t	total volume of the dispersed liquid
$\langle V \rangle$	average bubble or droplet volume

Greek letters

γ	surface tension between the gas of the bubbles and the surrounding liquid
Γ	Gamma function
δ	constant in distribution (2.2.20)
η	parameter
κ	laboratory system of reference
κ'	system of reference moving with the j th bubble
λ	average interbubble distance in $d\tilde{x}$ at time t
μ	viscosity of liquid
ξ	parameter
$\mathcal{Q}(\tilde{x}, r_j; t)$	distribution function (not normalised) at time t , of the bubble position and radius
ρ	density of liquid
ρ_g	density of gas
$\sigma_{E'_j}$	standard deviation of E'_j
$\sigma_{E'_j}^2$	variance of E'_j
$\sigma_{r'_j}$	standard deviation of r'_j
$\sigma_{r'_j}^2$	variance of r'_j
τ	average time needed for bubbles in $d\tilde{x}$ of any velocities to reach their terminal velocities
τ_c	average duration of a collision between the bubbles in $d\tilde{x}$
τ_r	average time between two successive collisions of bubbles in $d\tilde{x}$

REFERENCES

- Adamson, A.W. 1960 Physical Chemistry of Surfaces.
Interscience.
- Batchelor, G.K. 1967 An Introduction to Fluid Dynamics.
Cambridge University Press.
- Boltzmann, L. 1872 Lectures on Gas Theory. University of
California Press, 1964.
- Courant, R. and Hilbert, D. 1962 Methods of Mathematical
Physics, vol. II. Interscience.
- De Vries, A.J. 1972 Adsorptive Bubble Separation
Techniques (ed. R. Lemlich), p.7. Academic Press.
- Filippov, A.F. 1961 Theory Prob. Applications U.S.S.R.
6 275.
- Gibbs, J.W. 1902 Elementary Principles in Statistical
Mechanics. Yale University Press.
- Glotov, V.P., Kalobaev, P.A. and Neuimin G.G. 1962 Sov.
Phys. Acoust. 7 341.
- Hill, T.L. 1960 An Introduction to Statistical
Thermodynamics. Addison-Wesley, U.S.A.
- Hulburt, H.M. and Katz. S. 1964 Chem. Eng. Sci.
19 555.
- International Critical Tables 1929. McGraw-Hill,
New York.
- Jackson, R. 1964 Chem. Engr. 107.

Kreyszig, E. 1972 Advanced Engineering Mathematics.
John Wiley.

Landau, L.D. and Lifshitz, E.M. 1959 Fluid Mechanics.
Pergamon Press.

Landau, L.D. and Lifshitz, E.M. 1968 Statistical
Physics. Pergamon Press.

Levich, V.G. 1962 Psysico-chemical Hydrodynamics.
Prentice-Hall.

Medwin, H. 1977 J. Geophys. Res. 82 971.

Nakano, Y. and Tien, C. 1970 Ind. Eng. Chem. Fundl. 9 98.

Nukiyama, S. and Tanasawa, Y. 1939 Trans. Soc. Mech. Engrs.
(Japan) 5 68.

Nukiyama, S. and Tanasawa, Y. 1940 Trans. Soc. Mech.
Engrs. (Japan) 6 63.

Rosin, P. and Rammler, E. 1933 J. Inst. Fuel 7 29.

Valentas, K.J. and Amundson, N.R. 1966 Ind. Eng. Chem.
Fundl. 5 533.

Van der Waerden, B.L. 1969 Mathematical Statistics.
Springer-Verlag, Berlin.

APPENDICES

APPENDIX I

The average time τ needed for bubbles in dx of any velocities to reach their terminal velocities is of the order of $\sim 10^{-5}$ s. for bubbles of radii up to about 0.5 mm in pure water. The equation of motion of a bubble of radius r_j , density ρ_g , is for, say, $Re > 1$:

$$\left(\frac{4}{3} \pi r_j^3\right) \rho_g \frac{dv_{jz}}{dt} + 12 \pi \mu r_j v_{jz} = \left(\frac{4}{3} \pi r_j^3\right) g \rho \quad (I.1)$$

Eqn. I.1 is an ordinary differential equation, the solution of which is (Kreyszig 1972):

$$v_{jz} = \frac{\rho g r_j^2}{9\mu} + \left(v_{jo} - \frac{\rho g r_j^2}{9\mu}\right) \exp\left(-\frac{3\mu}{\rho_g r_j^2} t\right) \quad (I.2)$$

where v_{jo} is the bubble velocity at time $t = 0$. If we approximate

$$\exp\left(-\frac{3\mu}{\rho_g r_j^2} t\right) \cong 1 - \frac{3\mu}{\rho_g r_j^2} t$$

then eqn. (I.1) becomes:

$$v_{jz} \cong \frac{\rho g r_j^2}{9\mu} + \left(v_{jo} - \frac{\rho g r_j^2}{9\mu}\right) \left(1 - \frac{3\mu}{\rho_g r_j^2} t\right)$$

and

$$\tau \cong \frac{\rho_g}{3\mu} \langle r^2 \rangle \sim 10^{-5} \text{ s}$$

APPENDIX II

The δ -function $\delta\{r_j - F(r_k, r_n)\}$ can be eliminated from eqn. (3.4.5) as follows: The solution $F(r_k, r_n) = r_j$ of eqn. (3.2.10) is defined on the subset $A = \{(r_k, r_n) \mid 0 \leq r_k < \infty \text{ and } 0 \leq r_n < \infty\}$ of a 2-dimensional space $\mathbb{R}^2$, spanned by an orthogonal, Cartesian system of coordinates r_k and r_n . We can make the "1-1" transformation: $(r_k, r_n) \rightarrow (F, \ell)$ i.e. we can assign to each element (r_k, r_n) of A a distinct image (F, ℓ) , where $F \equiv F(r_k, r_n)$ and ℓ is the length of the curve $F(r_k, r_n) = r_j$, measured from a certain point, say, $(r_j, 0)$ to the point (r_k, r_n) . A differential element $dr_k dr_n$ of the domain A of transformation is connected with a differential element $dF d\ell$ of the range of transformation through the formula:

$$dr_k dr_n = \frac{dF d\ell}{\left| \frac{\partial(F, \ell)}{\partial(r_k, r_n)} \right|} \quad (\text{II.1})$$

where $\left| \frac{\partial(F, \ell)}{\partial(r_k, r_n)} \right|$ is the absolute value of the Jacobian $\frac{\partial(F, \ell)}{\partial(r_k, r_n)}$ of the transformation, defined by:

$$\frac{\partial(F, \ell)}{\partial(r_k, r_n)} = \begin{vmatrix} \frac{\partial F}{\partial r_k} & \frac{\partial F}{\partial r_n} \\ \frac{\partial \ell}{\partial r_k} & \frac{\partial \ell}{\partial r_n} \end{vmatrix} = \frac{\partial F}{\partial r_k} \frac{\partial \ell}{\partial r_n} - \frac{\partial F}{\partial r_n} \frac{\partial \ell}{\partial r_k} \quad (\text{II.2})$$

We also have:

$$d\ell = \left| \frac{\partial \ell}{\partial r_k} dr_k + \frac{\partial \ell}{\partial r_n} dr_n \right| = (dr_k^2 + dr_n^2)^{\frac{1}{2}} \quad (\text{II.3})$$

On the curve $F \equiv F(r_k, r_n) = r_j$ the differentials dr_k, dr_n satisfy the relation:

$$\frac{\partial F}{\partial r_k} dr_k + \frac{\partial F}{\partial r_n} dr_n = 0$$

or

$$\frac{dr_k}{dr_n} = - \frac{\partial F / \partial r_k}{\partial F / \partial r_n} \quad (\text{II.4})$$

Substituting eqn. (II.4) into eqn. (II.3) we obtain:

$$\left| \frac{\partial F}{\partial r_k} \frac{\partial \ell}{\partial r_n} - \frac{\partial F}{\partial r_n} \frac{\partial \ell}{\partial r_k} \right| = \left[\left(\frac{\partial F}{\partial r_k} \right)^2 + \left(\frac{\partial F}{\partial r_n} \right)^2 \right]^{\frac{1}{2}} = \|\text{grad } F\| \quad (\text{II.5})$$

From eqns. (II.5) and (II.2) we have:

$$\left| \frac{\partial(F, \ell)}{\partial(r_k, r_n)} \right| = \|\text{grad } F\| \quad (\text{II.6})$$

and eqn. (II.1) becomes:

$$dr_k dr_n = \frac{dF d\ell}{\|\text{grad } F\|} \quad (\text{II.7})$$

Substitution of eqn. (II.7) into eqn. (3.4.5) gives:

$$G' = \frac{\pi}{2} \int_{F=0}^{F=\infty} dF \int_{C(F)} e^{\{z, r_k(F, \ell)\}} e^{\{z, r_n(F, \ell)\}} \delta(r_j - F) \left[r_k(F, \ell) \right]^2 -$$

$$\left[r_n(F, \ell) \right]^2 \left[r_k(F, \ell) + r_n(F, \ell) \right]^2 d\ell / \|\text{grad } F(F, \ell)\|$$

$$\begin{aligned}
&= \frac{\pi}{2} \int_{C(r_j)} e^{\{z, r_k(r_j, \ell)\}} e^{\{z, r_n(r_j, \ell)\}} \left| [r_k(r_j, \ell)]^2 - \right. \\
&\quad \left. [r_n(r_j, \ell)]^2 \right| [r_k(r_j, \ell) + r_n(r_j, \ell)]^2 \\
&\quad d\ell / \|\text{grad } F(r_j, \ell)\|
\end{aligned}$$

(II.8)

Neglecting surface tension forces, $F \equiv F(r_k, r_n)$ is given by eqn. (3.4.3), and $d\ell / \|\text{grad } F\|$ is calculated, in terms of r_j as:

$$d\ell / \|\text{grad } F\| = dr_n (r_j^3 - r_n^3)^{-2/3} r_j^2 \quad (\text{II.9})$$

Substitution of eqn. (II.9) and r_k as given by eqn. (3.4.3) into eqn. (II.8) gives eqn. (3.4.6).