

AIChE MI

MODULAR INSTRUCTION

Series C: TRANSPORT
Volume 6: Transport Phenomena—
Special Topics



AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

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✓ TRANSPORT

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R. J. Gordon, Series Editor



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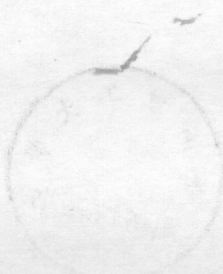
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INTRODUCTION

In 1975 a new venture in education by and for the chemical engineering community was initiated. Prepared by the CACHE Corporation (Computer Aids for Chemical Engineering Education) and under the sponsorship of the National Science Foundation (Grant HES 75-03911), a series of small self-study fundamental concept modules for various areas of chemical engineering were commissioned, Chemical Engineering Modular Instruction, CHEMI.

It has been found in recent studies that modular study is more effective than traditional instruction in both university and continuing education settings. This is due in large measure to the discrete focus of each module, which allows the student to tailor the speed and order of his or her study. In addition, since the modules have different authors, each writing in his or her area of special expertise, they can be produced more quickly, and students may be assured of timely information. Finally, these modules have been tested in the classroom prior to their publication.

The educational effect of modular study is to reduce, in general, the number of hours required to teach a given subject; it is expected that the decreased time and expense involved in engineering education, when aided by modular instruction, will attract a larger number of students to engineering, including those who have not traditionally chosen engineering. For the practicing engineer, the modules are intended to enhance or broaden the skills he or she has already acquired, and to make available new fields of expertise.

The modules were designed with a variety of applications in mind. They may be pursued in a number of contexts: as outside study, special projects, entire university courses (credit or non-credit), review courses, or correspondence courses; and they may be studied in a variety of modes: as supplements to course work, as independent study, in continuing education programs, and in the traditional student/teacher mode.

A module was defined as a self-contained set of learning materials that covers one or more topics. It should be sufficiently detailed that an outside evaluation could identify its educational objectives and determine a student's achievement of these objectives. A module should have the educational equivalent of a one to three hour lecture.

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Volume 1 of each series will appear in 1980; Volume 2 in 1981; and so forth. A tentative
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C6.1	Bubble Dynamics: An Illustration of Dynamically Coupled Rate Processes	T. G. Theofanous
C6.2	Miscible Dispersion	R. S. Subramanian
C6.3	Biomedical Examples of Transport Phenomena I—Coupled Diffusion Effects	R. H. Notter
C6.4	Biomedical Examples of Transport Phenomena II—Facilitated Diffusion	R. H. Notter
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Publication and dissemination of these modules is under the direction of Harold I. Abramson, Staff Director, Educational Activities, AIChE. Technical Editor is Lori S. Roth. Chemical engineers in industry or academia who are interested in submitting modules for publication should direct them to H. I. Abramson, Staff Director, Educational Activities, American Institute of Chemical Engineers, 345 East 47th Street, New York, N.Y. 10017.

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Solutions to the Homework Problems are available as a separate reprint from the AIChE Educational Services Dept., 345 East 46th St., New York, NY 10017. The cost is \$5.00.

Bubble Dynamics: An Illustration of Dynamically Coupled Rate Processes

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OBJECTIVES

At the completion of this module, the student should be able to:

1. Estimate vapor bubble growth rates in uniformly superheated liquids.
2. Identify the physical mechanism(s) that control the bubble growth process and those that, although present, can be neglected for the purposes of the calculation, for any given particular case of interest.
3. Evaluate the (heterogeneous and homogeneous) bubble nucleation characteristics.

PREREQUISITE MATHEMATICAL SKILLS

1. Elementary differential equations.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS

1. Equations of change.
2. Elementary thermodynamics of two-phase media.
3. Transient conduction.
4. Dimensional analysis.

solution for the heat and mass transfer rates. An important exception readers may already be familiar with is in the area of natural (free) convection. Here, temperature and concentration gradients give rise to body forces (buoyancy) that produce fluid motion. This motion, in turn, interacts with and affects the development of those gradients, so that a simultaneous solution (coupling) for both processes becomes necessary.

When the degree of coupling is a function of time, one may talk about dynamically coupled processes. Many examples of such processes may be found in the field of gas dynamics. The area of bubble dynamics, which is perhaps closer to the interests and practice of chemical engineering, provides numerous opportunities to investigate such processes. For the purposes of this presentation, the problem of vapor bubble growth has been selected for consideration. In very simple terms, the key interaction (coupling) here is between the liquid inertia, which must be "overcome" to initiate and develop the liquid motion, and the thermal conduction resistance in the liquid surrounding the vapor bubble, which must be overcome in order to maintain the heat supply equivalent to the latent heat requirements for the phase-change process that accompanies growth.

Having to deal with highly transient problems, it is reasonable to begin with a detailed consideration of the initial conditions. Thus, one learns about nucleation, which marks the inception of the bubble growth process. Then the module will continue with the physical interpretation of the individual transport processes that participate in the bubble growth phenomena and their mathematical formulation, emphasizing the simplifying assumptions incorporated in this formulation. There will then be a discussion on the methods and the nature of the solutions, and to conclude, a brief presentation of some more general situations of practical interest.

VAPOR BUBBLE NUCLEATION

Consider carrying out the following very simple experiment. In a clean test tube place a small quantity of Freon-11 and cover it with a thin layer of glycerol. Secure the tube inside a vacuum flask, such as those used for example by chemists for filtration. Replace the filter

INTRODUCTION

The primary purpose of this unit is to discuss the methodology for the study of dynamically *coupled* transport (rate) processes. The subject of "Bubble Dynamics" was selected as the vehicle for this study, not only because it provides a uniquely well suited area of application, but also because it will provide the opportunity to establish the fundamentals underlying the behavior of a very large number of naturally occurring and technologically important processes, not the least of which is the process of boiling.

In the majority of problems, the heat and mass transport rates depend upon the fluid mechanics, however, this dependence has been largely one-sided. That is, the problem could be solved in sequence, starting with the determination of the flow field and proceeding with the

assemblies with a stopcock equipped with a vacuum gauge (or even better a mercury manometer) and slowly apply vacuum through a respirator. You will observe that soon after the application of vacuum the tube contents "boil-off." It is very likely that during your first try, this "boil-off" process will be slow enough to see the nucleation of vapor bubble(s), which as they grow expell at least a portion of the tube contents and thus destroy the flask vacuum. Now repeat the experiment with a very carefully cleaned (cleaning solution: sodium chromate + concentrated sulphuric acid) and dried (distilled water, alcohol, and acetone in this order) test tube. You will observe a longer delay time and such a violent "boil-off" that although you will be able to *hear*, you will not be able to *see* the expulsion process itself.

All this behavior can be understood with the help of Figure 1. The initial state of the fluid in the test tube is indicated by point *O*, which for Freon-11 at room temperature and atmospheric pressure is slightly to the left of the vapor pressure curve indicated by the solid line (i.e., Freon-11 boils at 90°F). Since the liquid would have to be heated to its boiling point, $T^*(P_O)$, in order to achieve saturation, the state *O* is undersaturated (or subcooled) by the amount $T^*(P_O) - T_O$. As the pressure drops, the fluid state follows the trajectory *OAB*. Saturation is achieved at *A*. For pressures below the level P_A , the liquid is found in a metastable state; such states can only be achieved in the absence of any liquid-vapor interfaces which can sustain vaporization. At a system pressure P_B , the system is "superheated" by the amount $T_O - T^*(P_B)$, where $T^*(P_B)$ is the saturation temperature of the liquid at pressure P_B . When an opportunity for vaporization appears (nucleation event) somewhere inside the test tube, the *initial* rapid liquid vaporization is supplying vapor at a pressure P_A . Since the flask pressure is P_B , the resulting pressure differential will set the contents of the tube in motion. It is clear that this pressure driving

force increases with the amount of superheat present and thus, one can see qualitatively the reason for the violence of the event observed experimentally. For a closed system, like our flask, the path *BC* will be followed spontaneously, terminating at an intermediate state *C* on the saturation line. Next, let us consider the origin and characteristics of a "nucleation event."

For a system with no free, macroscopic liquid-vapor interfaces (like our system where the free surface of the Freon was "sealed" with a layer of glycerol, which has a much lower vapor pressure), nucleation must initiate from microscopic vapor or gas cavities. Such cavities are present on solid surfaces and may also form spontaneously in the liquid. The crucial aspect concerning the action of a particular cavity as a nucleation site is its size. The size, (radius R), determines the magnitude of the surface tension force, $2\sigma/R$, which is available to balance any difference between the cavity internal pressure (P_i) and ambient liquid pressure P_β . The equilibrium condition may be used to define the critical radius R_{cr} .

$$P_i = \frac{2\sigma}{R_{cr}} + P_\beta \quad (1)$$

It is easy to see that for cavities larger than the critical size, the force imbalance favors growth, and for cavities smaller than the critical size, the force imbalance favors collapse. Thus, any cavities that contain only vapor and are smaller than the critical size will vanish. However, on solid surfaces, especially in the presence, as is always the case, of small amounts of noncondensable gases, vapor and/or gas entrapment in microscopic cavities (surface imperfections) can occur in a fashion that leads to a spectrum of stable, microscopic nuclei. If the radius of curvature of the largest such nuclei is R_m , the maximum possible superheat would correspond to a pressure difference ΔP ,

$$\Delta P = \frac{2\sigma}{R_m} \quad (2)$$

For the example of our experiment, if cavity gas pressure is neglected, the minimum possible pressure level P_β would be given by:

$$P_\beta = P_i - \frac{2\sigma}{R_m} \approx P^*(T_O) - \frac{2\sigma}{R_m} \quad (3)$$

Since there is no direct way to control R_m the nucleation events are somewhat erratic. In a general way, the better the cleaning technique, the smaller is the size of R_m and thus, the larger the vacuum (superheat) achieved in the experiment. Further increases in superheat can be achieved by pressurizing the system, prior to the application of vacuum. This process is effective by forcing the cavities to a smaller size, thus decreasing R_m .

The mode of nucleation originating at pre-existing cavities is the most common one and is called heterogeneous nucleation. In most engineering systems there are enough dissolved gases and other impurities, and surface imperfections, that only very small superheats (a few degrees) become possible. For certain special laboratory condi-

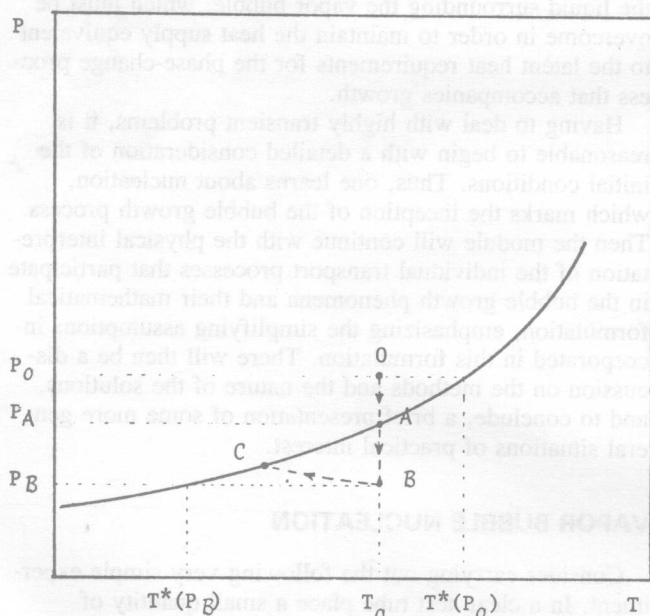


Figure 1. Metastable *O* liquid states in relation to its vapor pressure curve. Asteriks indicate saturation values, i.e., $P_A = P^*(T_O)$.

tions and solid/liquid pairs with good wetting properties, heterogeneous nucleation can sustain hundreds of degrees of superheat (for example, for the liquid sodium stainless steel pair, superheats up to 800°F have been measured). However, as long as the metastable liquid has any interfaces with solid surfaces, no matter what precautions have been taken, heterogeneous nucleation cannot be eliminated in practice. This type of nucleation can only be avoided by "sealing" the metastable liquid with another liquid of very low vapor pressure. For example, this can be accomplished by suspending (i.e., by mean of sound waves) a drop of the volatile liquid in a heated oil bath. Such a drop can be superheated well above the heterogeneous nucleation levels. In fact, it will always reach the same, *predictable*, level of superheat, known as the limit of superheat, and it will literally explode upon reaching this limit. This event is called spontaneous nucleation (or homogeneous nucleation) and it is due to thermal fluctuations of molecules in the liquid state, which can randomly achieve configurations such as to produce locally microscopic vapor cavities slightly larger than the "critical size." The rate of formation of such critical cavities, R_{cr} , may be calculated from the molecular thermodynamics of the liquid state and is given by:

$$J = A \exp \left\{ -\frac{10\pi\sigma^3}{3KT_l\Delta P^2} \right\} \quad (4)$$

where: $A \approx 10^{32} \text{ cm}^{-3} \text{ s}^{-1}$ and is known as the frequency factor, K is the Boltzman's constant, T_l is the temperature of the liquid and $\Delta P = P^*(R) - P_l$ is equivalent of the superheat present. This equation, due to its strong dependence on liquid temperature (notice that ΔP also depends strongly on T_l), has the character of a threshold equation. That is, up to the threshold temperature (T_{es}), the nucleation rate is extremely small, i.e., no nucleation is observed experimentally. When the temperature T_{es} is reached, however, and within a very small temperature interval, the nucleation rate increases dramatically, so as to clearly define a limit of superheat. At this limit, the rate of nuclei formation is so high that the drop will literally explode, i.e., the pressurization due to boiling is so great that shock waves are observed.

MATHEMATICAL FORMULATION

Attempting to develop simple mathematical solutions and through them, a first-order understanding of the bubble growth problem, one must identify for study the key physical phenomena that affect bubble growth in a generic fashion. A consideration of qualitative physical behavior may be helpful in that regard.

A vapor-filled critical cavity is depicted in Figure 2a. The cavity is immersed in a superheated liquid with temperature T_∞ and the system pressure is P_∞ . The vapor pressure in the cavity corresponds to the saturation pressure at the liquid temperature and since this pressure is balanced exactly by the surface tension force and the ambient pressure, there is no motion (bubble wall velocity is zero, $\dot{R} = 0$). A slight decrease in cavity size will yield monotonic cavity collapse, while a slight increase will yield monotonic growth. Hence the system is at unstable

equilibrium. Consider the case of growth. As R increases, the surface tension force decreases and the pressure imbalance across the liquid body increases, leading to its acceleration. On the other hand, bubble growth results in an expansion of its vapor contents and unless an equivalent amount of new vapor is supplied, the bubble internal pressure will decrease. Liquid vaporization, at the bubble wall, can provide the source for this vapor, however, the rate of vapor production is limited by the rate at which heat can be conducted to the bubble wall in order to satisfy the latent heat requirements. This situation is depicted in Figure 2b. The bubble wall velocity is positive (growth), the bubble wall temperature T_l and vapor pressure P_v have dropped from their initial values (cooling due to vaporization) and thus a driving force $T_\infty - T_l$ for heat transport has developed. The growth rate is determined by the pressure differential $P_l - P_\infty$, which is in turn determined by the opposing effects of bubble expansion and heat transport as previously discussed.

In real situations, the detailed manifestation of this physical phenomena can be quite complex. For example, the liquid phase temperatures may exhibit great temporal and spatial variations so that various portions of the bubble wall experience different temperature driving forces, possibly changing with time. An important example of this behavior is subcooled nucleate boiling, where as the bubble grows from the superheated wall region, it encounters subcooled liquid masses upon which condensation can take place. Thus portions of bubble wall could be evaporating while other portions could be condensing. This behavior, taking place at the microscopic level, could be important even for the nucleation process itself. Other difficulties exist. Bubbles growing rapidly on solid walls do not have time to rise, hence they obtain a hemispherical shape. Because of the non-slip condition on the wall as the bubble grows, a thin liquid film known as the microlayer is left behind (see Figure 3). This film can vaporize through its own superheat and by additional heating from the wall. Buoyancy forces also can play a role in promoting rise which affects bubble shape and mixing, complicating even further heat transport considerations. A large amount of literature is available for these and other problems.

A first step towards understanding the key physical interactions discussed in the two previous paragraph is to

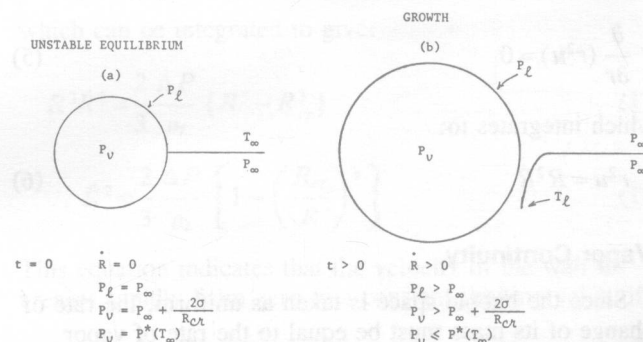


Figure 2. Qualitative illustration of vapor bubble growth from a cavity of critical size.

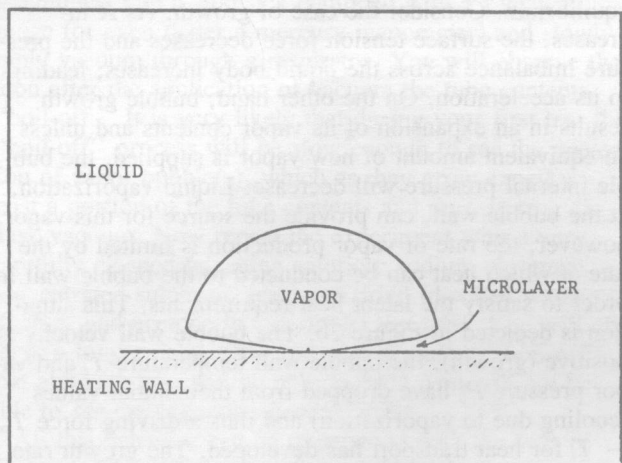


Figure 3. Illustration of microlayer geometry.

consider the problem of growth of a simple spherical vapor cavity, from its critical size, in a uniformly superheated incompressible liquid. Let us make the following not-so-restrictive assumptions:

- The bubble remains stationary with respect to the liquid, which is of infinite extent. In fact, because of the spherical divergence, the liquid velocities decrease rapidly away from the bubble so that any walls away by a few bubble diameters are not felt, i.e., a finite system behaves as if it was infinite.
- The bubble remains spherical throughout the growth period. This is basically a consequence of the previous assumption.
- The vapor in the bubble remains saturated at all times and it is in equilibrium with the bubble wall. In most cases of interest this is the case.
- Liquid viscosity is negligible. This is a good assumption except for some very high viscosity liquids.
- The vapor-to-liquid density ratio is much smaller than unity. This is true except near the thermodynamic critical point.

With these assumptions, let us proceed to the mathematical formulation of the growth problem (refer to Figure 4 for notation).

Liquid Continuity

$$\frac{\partial}{\partial r} (r^2 u) = 0 \quad (5)$$

which integrates to:

$$r^2 u = R^2 \dot{R} \quad (6)$$

Vapor Continuity

Since the bubble space is taken as uniform, the rate of change of its mass must be equal to the rate of vapor supply through vaporization. This rate of vaporization is obtained by converting the sensible heat supply to heat of

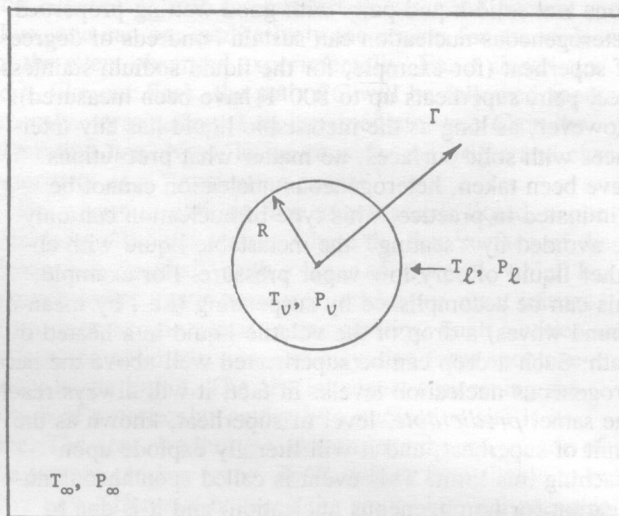


Figure 4. Notation for bubble growth formulation.

vaporization.

$$k_l \left. \frac{\partial T}{\partial r} \right|_R \frac{1}{\lambda} \quad (7)$$

where λ is the latent heat per unit mass. Hence:

$$\frac{d}{dt} \left(\frac{4}{3} \pi \rho_v R^3 \right) = 4\pi R^2 \left\{ k_l \left. \frac{\partial T}{\partial r} \right|_R \frac{1}{\lambda} \right\} \quad (8)$$

Liquid Momentum

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial r} = -\frac{1}{\rho_l} \frac{\partial p}{\partial r}$$

at $t > 0$

$$R < r < \infty \quad (9)$$

with

$$\begin{aligned} P(R, t) &= P_l \\ P(\infty, t) &= P_\infty \\ u(r, 0) &= 0 \\ R(0) &= R_{cr} \end{aligned}$$

The radial velocity at infinity is zero (see Equation 6), hence it is convenient to integrate this equation over the radial coordinate to obtain an equation for the bubble wall. First use Equation 6:

$$\frac{1}{r^2} \frac{d}{dt} (R^2 \dot{R}) + \frac{1}{2} \frac{\partial u^2}{\partial r} = -\frac{1}{\rho_l} \frac{\partial P}{\partial r} \quad (10)$$

Now integrate from R to ∞ .

$$\frac{1}{R} \frac{d}{dt} (R^2 \dot{R}) - \frac{1}{2} \dot{R}^2 = \frac{1}{\rho_l} (P_l - P_\infty) \quad (11)$$

Relate P_l to P_v by Equation 2 and rearrange:

$$R\ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho_l} (P_v - P_\infty) - \frac{2\sigma}{\rho_l R} \quad (12)$$

at $t > 0$ with

$$\dot{R}(0) = 0$$

$$R(0) = R_{cr}$$

Vapor Momentum

The need for this equation has been eliminated by assuming uniform vapor.

Liquid Energy

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial r} = \alpha_l \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial T}{\partial r} \right\}$$

$$t > 0$$

$$R < r < \infty \quad (13)$$

or making use of Equation 6,

$$\frac{\partial T}{\partial r} + \frac{R^2 \dot{R}}{r^2} \frac{\partial T}{\partial r} = \alpha_l \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial T}{\partial r} \right\} \quad (14)$$

with

$$T(r, 0) = T_\infty$$

$$T(R, t) = T^*(P_v)$$

$$T(\infty, t) = T_\infty$$

the second condition expresses assumption (c).

Vapor Energy

The need for this equation has been eliminated by assuming uniform, saturated vapor in equilibrium with the bubble wall.

System Coupling Discussion

Equations 12 and 14 are coupled through Equation 8. For a given P_v , Equations 12 and 14 can be solved for a small time increment for the acceleration (velocity and radius too) and temperature distribution in the liquid, respectively. These solutions can then be used in Equation 8 to find the resulting vapor density and thus, new vapor pressure (saturated vapor assumption). More elaborate models are possible, avoiding the assumptions of saturated vapor in equilibrium with the bubble wall, by making use of the vapor energy equation and a rate of vaporization expression based on the kinetic theory of gases; however, for most cases of interest these solutions indicate that this assumption is very nearly correct.

SOLUTIONS

Before considering the solution of the complete system of differential equations, it is instructive to consider certain limiting cases. These cases may be physically motivated and correspond to assigning total control to only one of the participating physical processes. For the case at hand, for example, one limit would correspond to negligible

heat transfer limitations. The temperature of the bubble wall would then be essentially equal to T_∞ and thus, the pressure of the vapor would remain constant and equal to its initial value $P^*(T_\infty)$. In this limit, Equation 12 is sufficient to solve for the growth rate. Since momentum effects play the primary role in this limit, this solution will be called the "momentum solution." The other extreme would correspond to the case where heat transfer is so limiting that the bubble wall cools quickly to the lowest possible temperature. Since in the complete process the pressure of the vapor starts at its maximum value, $P^*(T_\infty)$ and monotonically decreases towards P_∞ , the lowest possible vapor pressure is P_∞ and hence, the lowest possible wall temperature is $T^*(P_\infty)$. In this limit, the second boundary condition for Equation 14 is completely derived and thus a solution to Equation 14 can be obtained. Using this solution in Equation 8 the growth rate can be found. The solution at this limit will be called the "energy solution." The complete solution, discussed after the "momentum" and "energy" solutions, must encompass these two asymptotic limits and will provide quantitative criteria specifying the limits of their applicability.

Momentum Solution

The surface tension forces are important for the very initial (microscopic) stages of the growth process. The bubble growth process may be thought of to initiate from a small perturbation in any of the three quantities of the right-hand side of Equation 12, such as to produce a small positive result (initially the right-hand side is zero). According to Equation 12, an acceleration of the wall results, and this growth leads to a rapid decrease of the surface tension forces. Typically, critical radii are smaller than 10^{-3} cm, thus by the time the bubble is 10^{-1} cm the surface tension force has dropped to 1% of its initial value, i.e., can be considered negligible. Further, assuming that $P_v = P^*(T_\infty)$, and letting $\Delta P = P_v - P_\infty$, Equation 12 can be rearranged:

$$\frac{1}{2R^2 \dot{R}} \frac{d}{dt} \{ R^3 \dot{R}^2 \} = \frac{\Delta P}{\rho_l} \quad (15)$$

or

$$d \{ R^3 \dot{R}^2 \} = 2 \frac{\Delta P}{\rho_l} R^2 dR \quad (16)$$

which can be integrated to give:

$$R^3 \dot{R}^2 = \frac{2}{3} \frac{\Delta P}{\rho_l} \{ R^3 - R_{cr}^3 \} \quad (17)$$

$$\therefore \dot{R}^2 = \frac{2}{3} \frac{\Delta P}{\rho_l} \left\{ 1 - \left(\frac{R_{cr}}{R} \right)^3 \right\} \quad (18)$$

This equation indicates that the velocity of the wall increases rapidly from zero to a constant limiting value of

$$\dot{R} = \left\{ \frac{2}{3} \frac{\Delta P}{\rho_l} \right\}^{1/2} \quad (19)$$

which is essentially obtained by the time the bubble has grown to five times the critical size. This means that the wall acceleration may be neglected in Equation 12, and Equation 19 is applicable for the whole growth process. From Equation 19, the bubble radius (take $R_{cr} \sim 0$) may be obtained as:

$$R = \left\{ \frac{2}{3} \frac{\Delta P}{\rho_l} \right\}^{1/2} t \quad (20)$$

Energy Solution

Because of the nonlinearity present in the convective term of Equation 14, an analytical solution is rather involved. Let us proceed, therefore, with the help of a heuristic argument. The problem does have the character of transient conduction in an infinite media, hence expect that the thermal boundary layer will vary proportional to $\sqrt{\alpha_l t}$, and the approximate temperature gradient at the bubble wall will be:

$$\frac{\partial T}{\partial r} \Big|_R = \frac{T_\infty - T^*(P_\infty)}{\sqrt{\alpha_l t}} \quad (21)$$

Expanding the left-hand side of Equation 8 [using $\rho_v = \rho_v^*(P_\infty)$, which is constant] and utilizing Equation 21 gives:

$$4\pi\rho_v^*(P_\infty)R^2\dot{R} = 4\pi R^2 k_l \frac{T_\infty - T^*(P_\infty)}{\sqrt{\alpha_l t}} \frac{1}{\lambda} \quad (22)$$

or

$$\dot{R} = \frac{k_l(T_\infty - T^*(P_\infty))}{\lambda\rho_v^*(P_\infty)\sqrt{\alpha_l t}} \quad (23)$$

This equation in fact is within a constant of 0.98 from the exact solution of Equation 14. The solution for the radius (take $R_{cr} \sim 0$) is obtained by integration:

$$\begin{aligned} R &= 2 \frac{k_l[T_\infty - T^*(P_\infty)]}{\lambda\rho_v^*(P_\infty)\sqrt{\alpha_l}} \sqrt{t} \\ &= \frac{2\rho_l\hat{c}_l[T_\infty - T^*(P_\infty)]}{\lambda\rho_v^*(P_\infty)} \sqrt{\alpha_l t} \end{aligned} \quad (24)$$

Coupled Solution

Assume that Equations 19 and 23 are valid over the regime of combined momentum and energy control, provided that the "actual" driving forces are utilized:

$$\frac{dR}{dt} = \left\{ \frac{2}{3} \frac{P_v(t) - P_\infty}{P_l} \right\}^{1/2} \quad (25)$$

$$\frac{dR}{dt} = \sqrt{\alpha_l} \frac{\rho_l c_l [T_\infty - T_l(t)]}{\lambda\rho_v^*(T_v)} \frac{1}{\sqrt{t}} \quad (26)$$

Define

$$\phi^2 = \frac{T_v - T^*(P_\infty)}{T_\infty - T^*(P_\infty)} \quad (27)$$

and relate $P_v(t)$ and ρ_v to T_v by means of linear interpolation between the initial state $T_\infty, \rho_v^*(T_\infty)$ and the final state, $T^*(P_\infty), P_\infty$, that is

$$P_v - P_\infty = P_v^*(T_v) - P_\infty = [P_v^*(T_\infty) - P_\infty]\phi^2 \quad (28)$$

$$\begin{aligned} \rho_v - \rho_v^*(P_\infty) &= \rho_v^*(T_v) - \rho_v^*(P_\infty) \\ &= [\rho_v^*(T_\infty) - \rho_v^*(P_\infty)]\phi^2 \end{aligned} \quad (29)$$

Thus Equation 25 and 26 become:

$$\frac{dR}{dt} = A_* \phi \quad (30)$$

$$\frac{dR}{dt} = \frac{B}{2} \frac{(1 - \phi^2)}{[1 + (\Gamma - 1)\phi^2]} \frac{1}{\sqrt{t}} \quad (31)$$

where

$$A_*^2 = \frac{2}{3} \frac{P^*(T_\infty) - P_\infty}{\rho_l} \quad (32)$$

$$B^2 = 4\alpha_l \left\{ \frac{\rho_l c_l [T_\infty - T^*(P_\infty)]}{\lambda\rho_v^*(P_\infty)} \right\}^2 \quad (33)$$

and

$$\Gamma = \frac{\rho_v^*(T_\infty)}{\rho_v^*(P_\infty)} \quad (34)$$

The group A_* has dimensions length over time and the group B^2 has dimensions length square over time. They can be utilized, therefore, to define characteristic length and velocity scales, and thus nondimensionalize the system (Equations 30 and 31).

$$R^* = \frac{R}{(B^2/A_*)}$$

and

$$t^* = \frac{t}{(B^2/A_*^2)} \quad (35)$$

$$\therefore \frac{dR^*}{dt^*} = \phi \quad (36)$$

$$\frac{dR^*}{dt^*} = \frac{1 - \phi^2}{2[1 + (\Gamma - 1)\phi^2]} \frac{1}{\sqrt{t^*}} \quad (37)$$

From Equations 36 and 37, for ϕ :

$$\frac{\phi}{(1 - \phi^2)} [1 + (\Gamma - 1)\phi^2] = \frac{1}{2\sqrt{t^*}} \quad (38)$$

which can be solved for $\phi = \phi(t^*; \Gamma)$. Equation 36 can then be integrated to yield R^* as a function of t^* with Γ as a parameter, i.e., $R^* = R^*(t^*; \Gamma)$. The results are plotted in Figures 5 and 6. From these solutions, for $t^* < 10^{-2}$, a good approximation is $R^* = t^*$, which is the same as the momentum solution Equation 20; for $t^* >$

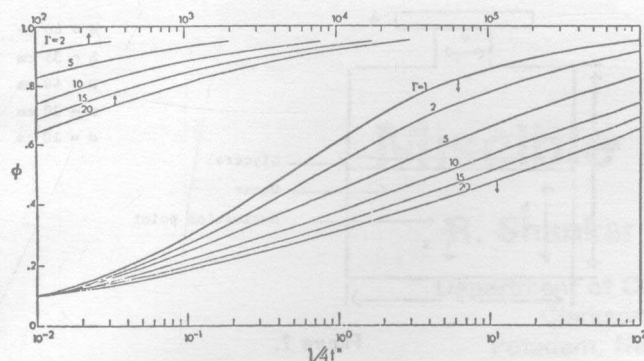


Figure 5. Solution to Equation 38.

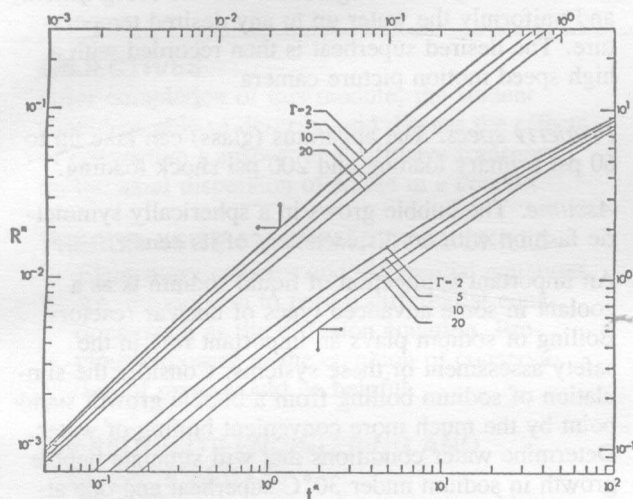


Figure 6. Universal plot of the bubble radius versus time.

10^2 , a good approximation is $R^* = \sqrt{t^*}$, which is the same as the energy solution Equation 24. For intermediate values of t^* , the process is controlled by both momentum and energy effects and the solution can be read off the graphs. This solution has been checked against experimental data as well as elaborate numerical simulations with excellent results.

For low values of the density ratio, ($\Gamma < 2$), the solution may be expressed analytically by:

$$R^* = \frac{2}{3B} \{ (B^2 t^* + 1)^{3/2} - B^2 t^* \} \quad (39)$$

where

$$B^2 = \frac{\lambda \rho_v^*(P_\infty)}{T^*(P_\infty)} \frac{T_\infty - T^*(P_\infty)}{P^*(T_\infty) - P_\infty} \quad (40)$$

NOMENCLATURE

A	= frequency factor, $10^{32} \text{ cm}^{-3} \text{ s}^{-1}$
A^*	= see Equation 32
B^*	= see Equation 33
\hat{c}	= heat capacity
J	= bubble nucleation rate
K	= Boltzman's constant
k	= thermal conductivity

P	= pressure
ΔP	= pressure difference
$P^*(T)$	= saturation pressure at T
R	= bubble radius
R^*	= dimensionless radius, see Equation 35
$\dot{R} = dR/dt$	= bubble wall velocity
$\ddot{R} = d^2R/dt^2$	= bubble wall acceleration
r	= radial coordinate
T	= temperature
$T^*(P)$	= saturation temperature at P
T_{es}	= spontaneous nucleation temperature
t	= time
t^*	= dimensionless time, see Equation 35
u	= radial liquid velocity

Greek Letters

α	= thermal diffusivity
λ	= latent heat of vaporization
Γ	= see Equation 34
ρ	= density
$\rho_v^*(P)$	= saturation vapor density at P
$\rho_v^*(T)$	= saturation velocity density at T
σ	= surface tension
ϕ^2	= see Equation 27

Subscripts

cr	= critical
i	= bubble internal
l	= liquid
m	= maximum
v	= vapor
∞	= condition at infinity

SUGGESTED COMPLIMENTARY READING

1. Dwyer, O. E., "Boiling Liquid-Metal Heat Transfer," Chapters 1-4, American Nuclear Society, Hinsdale, IL (1976).
2. Hsu, Y. Y., "Transport Processes in Boiling and Two-Phase Systems," Chapters 1 and 2, McGraw Hill, New York (1976).

STUDY PROBLEMS

1. In the absence of dissipation, the PdV work done by the vapor during bubble growth shows up as kinetic energy of the liquid. Utilize this idea to obtain an equation for the bubble wall motion. Now discuss the possibility of growth of a cylindrical or plane bubble in an infinity sea of liquid.
2. Consider the effects of viscosity on bubble growth rates.
 - (1) Should viscosity appear in the equation of motion, Equation 9? If so, in what form? If not, is the flow inviscid or irrotational?
 - (2) Modify Equation 12 to take into account viscous effects, by utilizing an augmented form of Equation 2 that equates the total radial stress in the liquid (at the wall) to $P_v - 2\sigma/R$.
 - (3) Consider the order of magnitude comparison of the various terms in the modified Equation 12, to obtain a criterion for judging the importance of viscous effects.

- Obtain approximate "energy solutions" for the bubble growth problem by neglecting appropriate terms in the thermal energy equation. Compare and discuss in physical terms the observed differences.
- Obtain an approximate "energy solution" for the bubble growth problem by means of the integral method. Utilize a quadratic temperature profile. Compare to the exact solution.

HOMEWORK PROBLEMS

- Calculate the size of the largest cavity present for a water system (at atmospheric pressure) that nucleates 50°C below its spontaneous nucleation limit. Estimate the resulting bubble growth rate, in miles per hour. At what time will the growth become controlled by thermal effects? At what time will 50% of the maximum possible driving force for heat transfer develop?
- A glass apparatus is being constructed for the study of nucleation and macroscopic growth of vapor bubbles in highly superheated liquids (Figure 7). You are asked to review the design and determine whether any safety problems exist. You'd also want to examine whether any operating limits can be specified to assure safety.

Intended Design and Operation: The apparatus consists of a cylindrical glass vessel as shown in the figure.

The nucleation point is approximately at the center of the flask. The flange A is used for the various penetrations such as vacuum give, pressure tap, etc. (not

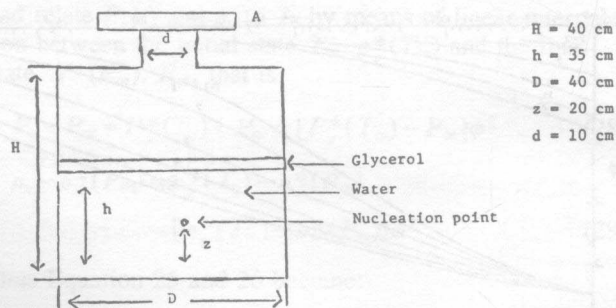


Figure 7.

shown). The glycerol is used to prevent premature nucleation. Infrared heating can be used to bring *quickly* and uniformly the water up to any desired temperature. The desired superheat is then recorded with a high speed motion picture camera.

Property specs: The apparatus (glass) can take up to 60 psi primary loading and 200 psi shock loading.

Assume: The bubble grows in a spherically symmetric fashion with no displacement of its center.

- An important application of liquid sodium is as a coolant in some advanced types of nuclear reactors. Boiling of sodium plays an important role in the safety assessment of these systems. Consider the simulation of sodium boiling from a bubble growth standpoint by the much more convenient boiling of water. Determine water conditions that will simulate bubble growth in sodium under 30°C superheat and one atmosphere pressure. Discuss the results in physical terms.

Miscible Dispersion

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OBJECTIVES

After completion of this module, the student should be able to describe and discuss the effects of convective transport and diffusive transport on the axial dispersion of solute in a conduit.

PREREQUISITE MATHEMATICAL SKILLS

1. Elementary calculus and differential equations.
2. An introduction to partial differential equations, such as the diffusion equation. Previous exposure to the equation of conservation of mass would be helpful.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS

1. Elementary modeling of transport problems, especially elementary concepts of convective and diffusive transport.

The list is by no means complete. New applications will, doubtless, be found in the future. Serious study of the subject was begun only about thirty years ago by G. I. Taylor in a classic paper (52), and new developments are being made even today.

In each of these examples, it might be seen that dispersion or mixing occurs due to two basic mechanisms. These are:

1. convective or bulk transport
2. diffusive or molecular transport

Simplistic as this might sound, the interactions between these two mechanisms lead to some very interesting consequences. Before proceeding further, it is important to distinguish between two basically different types of dispersion problems which emerge from the various applications.

In the first category, called "initial distribution problems," a certain finite amount of solute is introduced into a flow and permitted to disperse. There can be no non-trivial steady state in such a situation, and all phenomena of interest are transient. Elution chromatography is a good example of this problem. In generalized dispersion theory, such problems are handled by using an infinite series solution which satisfies the appropriate initial and boundary conditions. This series will be displayed later in this module.

A second category of dispersion problems is characterized by the example of a chimney emitting pollutant continuously into the atmosphere or a chemical plant discharging effluent continuously into a nearby stream. In such problems, one might imagine the fluid medium (atmosphere or river) to be initially devoid of solute. At time zero, the appropriate source of solute is turned on at the inlet. This type of problem may be termed an "inlet distribution problem." If the discharge rate is steady, a non-trivial steady state can be established at locations close to the system inlet after a while. This steady state will propagate down the flow as time goes on, carrying in front of it a transient region. One approach for handling this class of problems is to treat the continuous source as a series of pulses, each one of which can be handled using techniques suitable for initial distribution problems. This method is known as superposition (13) and its application to inlet distribution problems has been

INTRODUCTION

Miscible dispersion refers to the mixing phenomena which occur when two miscible fluids are brought together either when stationary or when they are in motion. This definition is very broad, and it is not possible to do justice to the wide range of topics it covers in one module. So, attention will be confined here to the phenomenon of dispersion which takes place when a solute is introduced into fluid flowing in a conduit. Specifically, no attempt will be made to treat mixing in agitated vessels, which also would be called "dispersion."

While dispersion phenomena are fascinating to study just from the point of view of scientific interest, there are practical reasons for developing a good understanding of such phenomena. Some applications are:

1. The distribution of tracers and drugs in the bloodstream.
2. Conventional chromatography.
3. Field flow fractionation or polarization chromatography.
4. The transient behavior of tubular reactors.
5. Pollutant transport in the atmosphere.
6. Material and thermal pollution of natural streams.

discussed by Gill and Sankarasubramanian* (25, 41), and Gill (26), and clarified by Subramanian (51). More recently, Smith (43-46) has used superposition innovatively to construct solutions to both classes of problems using his "delay-dispersion model."

In the rest of this module, attention is focused on "initial distribution problems" because of their relative simplicity.

THE PHYSICAL PROBLEM

The dispersion of a solute introduced into a fluid flowing into a conduit will be considered here. It is convenient to approach the complex problem in which a solute is dispersed due to the simultaneous action of convection and diffusion in the presence of a non-uniformly distributed velocity field, say in a circular tube, via simple, idealized, intermediate physical situations. These might be called "thought experiments."

Consider a slug of dilute solution, x_s units long and having a uniform concentration C_0 of a suitable solute held in an infinitely long circular tube as shown in Figure 1. This slug is separated from pure solvent on either side of it by suitable impermeable barriers. The axial coordinate x and the radial coordinate r are defined as shown in the figure. All the thought experiments will be performed on this system.

Experiment 1

At time zero, imagine the barriers on either side of the slug are removed without causing any disturbance in the fluid (this is very hard to do in practice, but easy to imagine). No pressure gradient is imposed on the fluid so that it remains completely stationary.

The solute will be observed to diffuse symmetrically on either side of the original slug. The velocity resulting from this diffusion is ignored by assuming the slug to be very dilute. There is no radial or angular variation of concentration in the system, since the slug is assumed to be initially uniform in concentration everywhere. This diffusion process can be described mathematically by the one-dimensional conservation equation for the local solute concentration, $C(t, x)$. For a derivation of the conservation equation, see Bird, et al (6).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

Here, t is time, and D is the molecular diffusivity of the solute in the fluid. The initial and boundary conditions on $C(t, x)$ for the system are:

$$\left. \begin{aligned} C(0, x) &= C_0, \quad |x| \leq \frac{1}{2} x_s \\ &= 0, \quad |x| > \frac{1}{2} x_s \end{aligned} \right\} \quad (2)$$

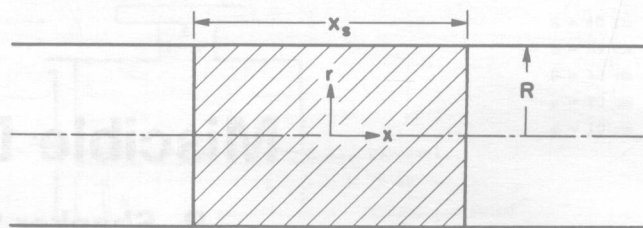


Figure 1. The system.

$$C(t, \pm \infty) = 0, \quad t \geq 0 \quad (3)$$

Equation 2 states that initially, the solute concentration is C_0 everywhere inside the slug and zero everywhere else. Equation 3 is characteristic of problems of this type, and indicates that solute never reaches axial stations infinitely far away from $x = 0$. The solution of Equations 1 to 3 for $C(t, x)$ is well-known and is given in Crank (14). Figure 2 shows the concentration distribution from this solution as a function of axial position for various values of time. In this simple thought experiment, there is no bulk (convective) transport. Figure 2 shows that symmetric axial spreading or dispersion of solute occurs due to molecular diffusion.

Experiment 2

Just as was done in the first experiment, imagine the barriers on either side of the slug are removed at time zero without causing any disturbance. However, this time, an axial pressure gradient is imposed on the fluid. This will result in bulk motion. This motion is assumed to be described by an idealized plug flow velocity profile. That is,

$$v_x = \text{constant} = v_m \quad (4)$$

Here, v_m is the cross-sectional average velocity defined by

$$v_m = \frac{\int_0^R v_x r \, dr}{\int_0^R r \, dr} = \frac{2}{R^2} \int_0^R v_x r \, dr \quad (5)$$

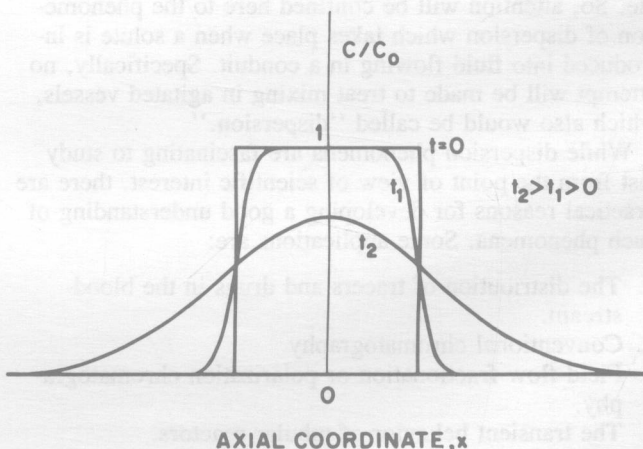


Figure 2. Concentration versus axial coordinate for the diffusion of a slug.

*R. Shankar Subramanian was formerly known as R. Sankarasubramanian.