A Course in

THERMODYNAMICS: THEORY WITH APPLICATIONS

ROBERT C. REID
and
MICHAEL MODELL
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

To many students, thermodynamics is a stagnant field and a boring subject; articles on thermodynamics courses usually reinforce such opinions. If we had less enthusiasm for our course, even the writing of this article would itself be a chore. However, over the years of evolving our course, we have enjoyed it more each year; on occasion, our enthusiasm even infects some of the students and we reap the ultimate reward of a teacher.

To describe our first year graduate course in thermodynamics, we have divided this article into four brief sections. We describe the approach, then summarize the content, and then discuss both the problems used and type of presentation.

APPROACH

THE SCOPE OF THE COURSE is limited to the theory and application of classical thermodynamics. Although it is presumed that all graduate students have had at least one undergraduate course in thermodynamics, the backgrounds are so varied that we have found it essential to start at the fundamental level of basic concepts.

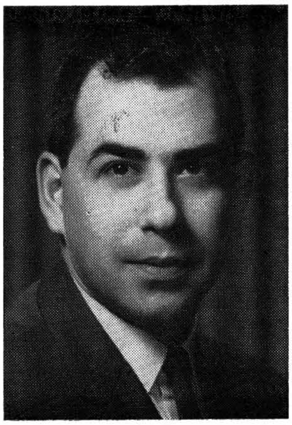
Most approaches to classical thermodynamics follow one of two extremes: the historical approach, which parallels closely the chronological developments of concepts (and misconceptions); or the postulatory approach, in which axioms that cannot be proved from first principles are stated. There are merits and draw-backs in each extreme.

Advocates of the historical approach contend that if we are to expect our students to evolve new concepts and theories in their lifetime, we must expose them to the historical development of existing theories. On the other hand, existing postulatory approaches make no reference to historical developments. The basis for the laws of thermodynamics are impersonally stated in a small number of postulates which cannot be proved and can only be disproved by showing that consequences derived from them are in conflict with experimentally verified facts. The postulates tend to be mathematical and abstract, but from them, the laws of thermodynamics are derivable. Many students are not impressed because little insight is provided for the necessity for defining new concepts or properties.

We have attempted to blend the salient features of the two extremes. We assume the state of knowledge which existed in 1600 and proceed to evolve the laws and concepts in a manner parallel to the historical development, but using hindsight to avoid the misconceptions and confusion which existed in the preclassical period. We clearly identify those principles which our ancestors learned to accept without proof; these are stated as postulates, but in a form which could be understood by Black, Lavoisier, Kelvin, or Carnot.

If we are to develop a set of fundamental laws of nature with few preconceived notions, we must first develop the facility of conducting experiments; that is, we need tools which are sensitive to changes in a system so that we can quantify our experiments. A sealed liquid thermometer is one such tool and we associate an arbitrary θ-temperature scale with this device. Using this thermometer, we should be able to show experimentally that certain containers are very effective in thermally isolating systems from their environment. By a logical extension of this reasoning, we are led to our first idealized concept—the adiabatic wall. Historically, this concept paved the way to calorimetry and the appreciation that matter possesses unique properties such as specific and latent heats. (It also led to a metaphysical interpretation in the form of the Caloric Theory and the conservation-conversion dilemma, which was not completely resolved until the mid 1800's.)

With this type of background, we introduce the first two postulates (see Table I) to establish the concept of the *state of equilibrium* and the methodology required to quantify it. The third



R. C. Reid is a Professor of Chemical Engineering at Massachusetts Institute of Technology and Editor of the AIChE Journal. He received a B.S. in Mechanical Engineering from Kings Point, and in Chemical Engineering received a B.S. and M.S. from Purdue and a Sc.D. from M.I.T. He is a registered professional engineer in Massachusetts. His fields of specialization are cryogenics, thermodynamics, and properties of materials. In addition to having authored a number of articles in professional journals, he is co-author with T. K. Sherwood of "The Properties of Gases and Liquids, Their Estimation and Correlation." He is currently a Council Member of the AIChE. (Left.)

Michael Modell is an Associate Professor of Chemical Engineering at the Massachusetts Institute of Technology. He received the B.S., M.S., and Sc.D. degrees in Chemical Engineering from M.I.T. His areas of specialization are heterogeneous catalysis and thermodynamics.

Postulate I

For closed simple systems with given internal restraints, there exist stable equilibrium states which can be characterized completely by two independently variable properties in addition to the masses of the particular chemical species initially charged.

Postulate II

In processes for which there is no net effect on the environment, all systems (simple and composite) with given internal restraints will change in such a way as to approach one and only one stable equilibrium state for each simple subsystem. In the limiting condition, the entire system is said to be at equilibrium.

Postulate III

For any equilibrium states, (1) and (2), for a closed system the change of state represented by (1) → (2) and/or the reverse (2) → (1) can occur by at least one adiabatic process and the adiabatic work interaction between this system and its surroundings is determined uniquely by specifying the end states (1) and (2).

Postulate IV

If the sets of systems A, B and A, C each have no heat interactions when connected across non-adiabatic walls, then there will be no heat interaction if systems B and C are also so connected.

TABLE II.
Subdivisions of Content

ENERGY; CONCEPTS AND CONSEQUENCES
REVERSIBILITY; CONCEPTS AND CONSEQUENCES
RELATIONSHIPS FOR SINGLE PHASE SIMPLE SYSTEMS
SINGLE PHASE SIMPLE SYSTEMS OF PURE MATERIALS
CRITERIA OF EQUILIBRIUM AND STABILITY
MULTICOMPONENT SINGLE PHASE SIMPLE SYSTEMS
PHASE EQUILIBRIA
CHEMICAL EQUILIBRIA
OPTIONAL TOPICS (SURFACE THERMODYNAMICS, EXTERNAL FORCE FIELDS, IONIC SOLUTIONS, ETC.)

postulate, which forms the basis of the *conservation of energy*, is stated in terms of the mechanical concept of work. The fourth postulate is the *Zeroth Law*; it is enlightening to today's student to find that it was not immediately obvious to the seventeenth century scientist.

CONTENT

FOLLOWING THE INTRODUCTION of the four basic postulates, the subject matter is subdivided into eight chapters of class notes, as shown in Table II. The theoretical basis of classical thermodynamics is established in the first three chapters, which represents about half of the term. (This is not to imply that the first half of the course is entirely theoretical. As described in the next section, most of the classroom time is devoted to working problems which illustrate the applications of the theory.)

The flow of concepts is illustrated approximately in Figure 1. The developments up to the introduction of the Fundamental Equation (F.E.) parallels the historical evolution.

The introduction of the formalism of the F.E. and Legendre transforms is a departure from traditional chemical engineering courses. (This route is becoming commonplace in physics and other engineering fields, but these are too often highly theoretical and devoid of applications.) The F.E. is introduced because we believe that it is of significant conceptual value in handling one of the central problems in engineering application: namely, what are the minimum data required to solve a given problem and how does one manipulate available data to more useful forms.

The F.E. (i.e., $U = f(S,V,N_1, , , , N_n)$ in the energy representation) contains all thermodynamic information for a given single phase sys-

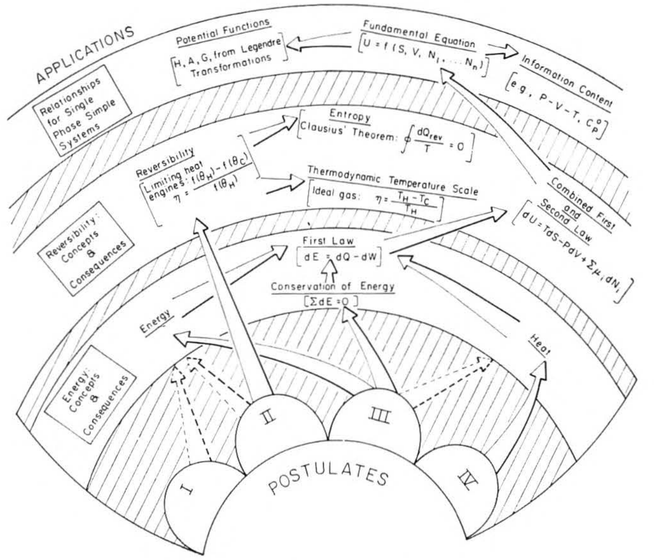


Fig. 1.—Flow of Concepts.

tem.* All other thermodynamic properties can be derived from it. Although we do not have available the F.E. for many materials, we can determine what other data sets have equivalent information content. Using Legendre transformations to preserve the information content, it is shown that $H = f(S,P,N_1, \ldots N_n)$ is also a F.E. and, thus, a Mollier diagram contains all thermodynamic information. Similarly, the F.E. of a pure material can be reconstructed given the equation of state and heat capacity. Thus, any problem can be solved using P-V-T and C_p data, i.e., if these data are available, we need not search for any other data.

The last half of the course focuses on the application of these principles to systems of increasing complexity (see Table II). Following a discussion of single phase systems of pure materials, the criteria of equilibrium and stability are introduced so as to set the stage for treating mixtures and phase equilibrium.

Single phase mixtures are synthesized from pure materials using the criteria of equilibrium to mix reversibly. Paralleling the pure material development, the type of data necessary to describe a mixture is discussed. The concept of ideal mixing is then appreciated as an idealization for which mixture properties can be synthesized from pure component data. Many common mixture properties (e.g., chemical potential, fugacity, activity coefficient) are explored as alternative methods of presenting similar information.

Phase equilibrium and chemical equilibrium are treated as progressively more complex applications of the building blocks covered previously. In these areas especially, it is stressed that thermodynamics is of little practical utility without sound engineering judgment. A phase diagram can only be constructed when there is prior knowledge of what phases do in fact exist and what properties (e.g., information equivalent to the F.E.) each phase exhibits. Similarly, the concept of chemical equilibria is of little use in the complex systems engineers generally face until there are data or insight into the kinetically feasible routes.

Through the class notes, solutions to problems are illustrated. These problems are similar in nature to those described in the following section.

PROBLEMS

PROBLEMS ARE GENERALLY formulated to help the student understand and apply principles. The better problems are ones which force students to analyze real and/or practical situations and which encompass new ideas that differ from their prior experience. Further, we have found that the way a problem is stated is very important. It is poor methodology to ask for an answer given some input data, e.g., what is the change in entropy during compression of isobutylene at . . . . Rather, the problem statement should pose a real situation wherein the student is motivated to use creativity in devising a solution.

The most instructive problems have an additional challenge. They are so conceived that there are multiple solutions depending upon how the real situation is modeled. A good case in point would be the following:

> **During emergency launch operations, to fill a missile with RP-4 (a kerosene-based fuel), the ullage volume of the fuel storage tank is pressurized with a gas and, after a predetermined level is attained, the fuel forced out of a bottom drain line to the missile. Normally, banks of high-pressure nitrogen cylinders supply the pressurizing gas. We have recently received a suggestion from our launch director to substitute air for nitrogen since the base has a large source of compressed air available at all times. Several of us are concerned about the safety of the operation should air be used, and we would appreciate a memorandum from you commenting upon this proposed change.**
>
> **We would still pressurize rapidly from atmospheric pressure to about 150 psia. The fuel storage tanks are horizontal and cylindrical in shape with an ullage volume of about 10 percent.**

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*Neglecting surface and body forces.

The introduction of the formalism of the Fundamental Equation and Legendre Transforms is a departure from traditional ChE courses.

Additional information can be provided in the problem statement regarding fuel tank dimensions, conditions in the compressed air supply, etc.

The problem is true-to-life in that the solution is not clean-cut. Various questions immediately plague the student in his quest for an answer. Would any significant heat transfer occur between the pressurized ullage gas and the liquid fuel tank walls? Would the ullage gases be well-mixed during pressurization or would there be a stratification with each incoming element of fresh gas compressing the gas already present (an unmixed case)? The solution for various limiting cases with an assessment of their probability must be made. For a completely-mixed case it can be demonstrated that the temperature rise of the air entering the tank is always less than a typical flash point of kerosene. On the other hand, for an unmixed case, the air adjacent to the fuel can heat to temperatures well in excess of the flash point (assuming no heat transfer to the liquid fuel). Thus, two physical models of the process lead to opposite recommendations. The many alternate possibilities force the student to separate the physics from the thermodynamics, i.e., such a problem illustrates one of the real weaknesses of thermodynamics in that the latter is only of value after the physical processes are clearly defined. The importance of considering fluid mechanics, mixing, and mass and heat transfer simultaneously with the thermodynamics is essential in most real problems.

Our graduate students gain confidence in their ability to analyze new applications of thermodynamics through such problems. As most of our problems originated in our consulting practice, they also provide a student with incentive to solve as homework what someone else actually got paid to handle!

Illustrative of other typical problems assigned in the past year or so, Table III was prepared. Note the attempt to involve the student emotionally in a real process—yet if these statements are dissected, it will be found that no esoteric analysis is necessary—just basic thermodynamics with a good dose of engineering judgment and common sense.

. . . most of our problems originated in our consulting practice . . .

PRESENTATION

UNDERLYING THE FORMULATION of this subject is our strong conviction that the application of thermodynamics to real situations is far more difficult to grasp than the theory. Thus, lectures in the ordinary sense are few and the usual class hour is devoted to a discussion of the assigned problem(s).

Although the manner of presentation is closely tied to the preference of the instructor, the kind of problems covered is particularly amenable to a dialogue-type presentation. As early as possible a first-name basis is established in the class; and, in a problem discussion, we act more as moderators or devil's advocates than as teachers. As one student flounders or hesitates we often immediately shift to someone else to continue—or we encourage spontaneous outbursts of indignation should another make a statement of fact or assume a point with which there is disagreement. Perhaps 10 or 15 students may be involved in setting up the solution of a problem, and even at the conclusion there still may be a minority objection. Such a class routine is difficult to describe and sounds as though bedlam exists! Sometimes this is so, and in such cases the role of the instructor is very important in leading the discussion to a conclusion (with help from the class) and showing that some avenues of approach are either incorrect or fruitless. Yet each student who proposes a path must be satisfied on an intellectual basis why his is not the optimum route.

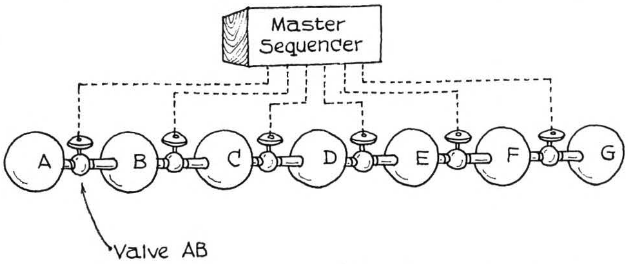
The ideal class period finishes with a general agreement regarding the approaches and models formulated and, minimizing all arithmetic, with the final answer (or answers!).

We feel that this type of approach is exciting and that student involvement soon unites the members of the class so that each begins to see and appreciate alternate approaches and ideas. Certainly, our stated objective in the course is to teach the basic concepts of thermodynamics, but equally important we must teach students to analyze new problems, recognize and evaluate alternate approaches, and arrive at conclusions based upon the best theory and data that are available. Our course is, as W.K. Lewis so often proposed and practiced, to encourage the students to initiate or follow a proposed solution, offer alternate approaches, and make logical decisions—in short, to *think*.

TABLE III. ILLUSTRATIVE PROBLEMS

1. Our old friend Rocky Jones has been tinkering in the laboratory and has produced an interesting device which he calls an "integral pulsed shock tube." As yet, we do not see a large commercial market. In fact, we are not sure what it actually does! Could you analyze this device and answer the brief questions given later?

A long, insulated tube is divided into chambers of equal volume by rigid, adiabatic partitions.



Each partition has a fast-operating valve to allow flow of gas between compartments when the valve in open. The operation of this device is a follows: Compartment A is initially filled with helium gas at 40°F and 64 atm. The rest of the compartments are evacuated to zero pressure. All valves are closed. At time zero, valve AB is quickly opened and gas flows from A to B. Just when the *pressures* are equalized in A and B, valve AB is shut and valve BC opens. As before, just at the time the pressures in B and C are equal, valve BC is shut and valve CD opened. This sequence is continued until gas enters the last compartment, G.

There is no axial heat conduction and no heat conduction across the valves or partitions. Helium is an ideal gas with a $C_p = 5$ cal/gmole—°K and $C_v = 3$ cal/gmole—°K.

a. When valve FG has just closed, what is the temperature and the pressure in compartment G?

b. When the sequencing is completed all valves are opened and the pressure allowed to equalize in all compartments. Slow axial conduction also equalizes the temperature in all compartments. What is the equilibrium temperature and pressure?

c. Rocky is a bit uncertain how much work it requires to prepare his integral pulsed shock tube for firing. Estimate the minimum work per mole of helium initially in compartment A. In this calculation, assume all compartments of the shock tube initially contain helium at 1 atm, 40°F. Any helium that is removed must be pumped into a large tank containing helium at a constant pressure of 2 atm, 40°F. Also any helium used to charge compartment A to 64 atm is to be taken from the same tank. If, in your calculations, any heat transfer occurs, assume you have a large heat sink or source at 40°F.

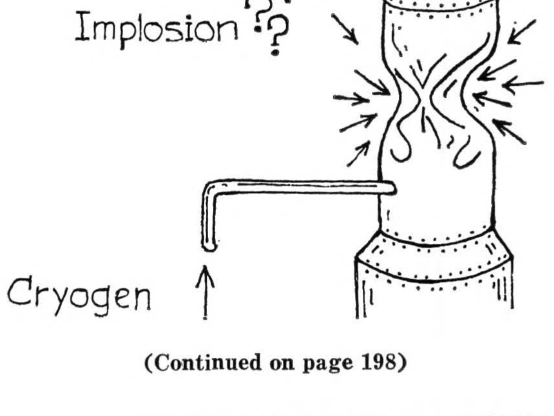
Problem statements should pose a real situation wherein the student is motivated to use creativity in devising a solution.

d. Can you suggest any use for Rocky's new device?

2. It appears to be an established fact that, on occasion, during rapid loading of liquid oxygen or liquid hydrogen into missile tanks, some tanks have imploded with catastrophic results. Such tanks are constructed to withstand an internal pressure somewhat above atmospheric, but they will collapse if the ambient pressure significantly exceeds the internal pressure.

Our information is that during this critical loading period, the cryogen may be all gas, a mixture of gas and liquid, or all liquid. The cryogen is pumped through a side port and has intimate contact with gas already in the tank at ambient temperature.

Please analyze this problem and submit a list of recommendations regarding steps to be taken to minimize the implosion hazards. Also, comment on the suggestion that there may exist a critical quality for the operation. This critical quality is defined as that fraction of vapor in the feed which, if exceeded, precludes any possible implosion.



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many of the programs in his class work, he would be able in the future to introduce these algorithms as subroutines into some of his other programs or use them for class work in other courses. It was this particular feature of the class that attracted many of the students into the course because, although there were other related courses being taught in other departments, the general level of applicability of the material in those other courses was quite small. Students felt that they were unable to solve real problems after having completed the other courses.

CONCLUSIONS FROM THE COURSE

THE COURSE SERVED a definite need in emphasizing the applications of the techniques associated with large scale optimization problems. Although the student was not trained to be a practitioner, he was able to obtain a firm grasp of the techniques available to solve real optimization problems. The course enabled the student to gain a broad mastery of nonlinear programming techniques through reading and practice. Furthermore, it fitted in well with the courses on linear and nonlinear programming, dynamic programming, control theory, network flow theory, queueing theory, and the other courses required to obtain a firm foundation in management science and operations research. The role played by the student in the exchange of information between students (and the instructor) seemed to provide considerable motivation for the course as did the provision of the computer routines and documentation.

APPENDIX A

The power consumption of a heated stirred vessel is given by the relation:

$$P = 2.63 \times 10^{-3} FsL^5 \left(\frac{n}{60}\right)^3$$

For Reynolds numbers (a dimensionless group encorporating the speed of rotation N and the diameter of the blade L) greater than 150, relation

$$F = \left(\frac{\mu}{3750\ snL^2}\right)^{0.05}$$

and for Reynolds numbers smaller than 150,

$$F = \frac{33.3}{\left(\frac{3750\ snL^2}{\mu}\right)^{0.75}}$$

find the lowest power consumption to mix a vessel containing 6000 gallons of a fluid for which $s = 0.8$ and $\mu = 200$.

Data: Assume for simplicity a 8 inch clearance between the impeller and the tank wall. The Reynolds number is defined as

$$Re = \frac{3750\ snL^2}{\mu}$$

The cost of the tank is \$100 per pound of metal, and the wall thinkness must be at least ¼″ up to a 6 foot height and ⅜″ for greater height. Assume capital charges per year of 0.25 of the cost of the tank and a power cost of \$0.01 per kwh. The operating hours are 600 per year.

NOTATION

F = empirical relation
L = impeller diameter, ft.
n = impeller speed, rpm
s = specific gravity, dimensionless
μ = viscosity, lb/(ft) (hr)

REID & MODELL (Continued from page 172)

Some relevant data are given below:
C_p(vapor) = 5.8 (H_2) ; 7.0 (O_2), Btu/lbmol—°R.
Assume ideal gases.

	Saturation Temperature at 37psia, °R	Heat of Vaporization Btu/lb
O_2	180	86
H_2	43.2	197

3. Our Advanced Technology Laboratory is still attempting to find ways to separate oxygen from air. One of their more recent ideas involves the trapping of oxygen with potassium oxides, i.e., K_2O would be reacted with oxygen to form K_2O_2 and KO_2. Then with a pressure- or temperature-swing cycle, oxygen gas would be released. We in the Engineering Division have been asked to comment upon this scheme and to prepare a preliminary flowsheet.

The data at our disposal are a bit fragmentary. Experiments were carried out to determine the equilibrium partial pressure of oxygen over molten potassium oxides. Samples of pure KO_2 were placed on a MgO boat in an evacuated tube. The tube was inserted into an oven at a sufficiently high temperature that the oxide melted. The pressure of the evolved oxygen was measured after equilibrium was attained. From this pressure measurement, the tube volume, and oven temperature, the moles of oxygen evolved could be ascertained. From this value and also the original sample weight, the atomic O/K ratio of the oxide liquid could be calculated. Next, a known amount of oxygen was bled out of the system, and the system allowed to come to equilibrium again. Again the oxygen pressure was measured, and the liquid O/K ratio calculated. The data indicate that at any given temperature level the oxygen partial pressure depends only on the liquid O/K ratio. Data are shown below at 500, 600, and 650°C for various O/K ratios.

O/K ratio	Partial Pressure of Oxygen, atm. 500°C	600°C	650°C
1.0	0.018	0.070	0.13
1.1	0.10	0.13	0.21
1.2	0.26	0.26	0.31
1.3	0.43	0.40	0.43
1.4	0.61	0.55	0.60

There is essentially nothing known about the structure of the liquid phase. It is black, probably has a high electrical conductivity, and contains some or all of the following species, K^+, O_2^-, K_2O, K_2O_2, KO_2, etc.

We need, immediately, an accurate value for the energy evolved or absorbed if a reaction occurs so that the liquid melt absorbs oxygen isothermally at 600°C and changes the O/K ratio from 1 to 1.4. Express your answer on a basis of 1 gram-atom of potassium.

Also, from the data given, please formulate a simple process flow diagram to remove oxygen from air and indicate possible problem areas.

4. Concentrated sulfuric acid (100%) is to be mixed with water before being added to a batch reactor. For optimum control of the reactor, the dilute acid should be fed between 5 and 10°C. The inlet reactor concentration is to be 20 wt % acid. To minimize heat exchange equipment, it has been suggested that the dilution step be carried out by pouring the concentrated acid over the requisite amount of ice (4 lbs.). Assuming we adopt this scheme and also precool the concentrated acid originally to 0°C, what specifications would you place on the heat exchange equipment to bring the dilute acid to 10° C?

Freezing points of sulfuric acid solutions, partial pressures of water over sulfuric acid solutions, and ice vapor pressure data are attached if needed.

THEOFANOUS

(Continued from page 177)

3. Boundary layers

The classic *exact* solution for laminar flow induced by an infinite rotating disc is derived in detail to illustrate more clearly how convection may limit the growth of a diffusion layer. At this point the student is ready to be convinced of the rationale for the boundary layer assumptions. Laminar boundary layers of momentum, mass, energy are considered in detail for flat plates and solid spheres. The role of the Reynolds, Schmidt and Prandtl numbers in these phenomena is emphasized, especially as a means to understand the limitations of the boundary layer assumptions.

Previously tackled problems of transfer at turbulent interfaces are re-examined in terms of boundary layer concepts and solutions. In particular, renewal concepts are discussed in terms of the small penetration approximations as well as eddy models.

4. Negligible diffusion

The complete solution of a boundary layer situation requires adequate consideration of the diffusion-free region of the domain. The usually non-trivial case is concerned with the fluid mechanical problem. The concepts of inviscid (ideal) flow and irrotational flow are introduced and contrasted. The vorticity-free flow ($W \equiv 0$) around a growing bubble in a *viscous* fluid illustrates this distinction and elucidates how solid surfaces, in general, act as vorticity sources for viscous fluids. Here the ideas are clarified by considering the boundary conditions required for a well-posed problem of a flow starting from rest when it is cast as ideal flow in terms of the velocity potential on the one hand or is described by the Navier-Stokes equation on the other.

The remainder of the material covered in this section is concerned with construction of irrotational flows while the depth and extent of coverage depend largely on how far behind schedule we are at this point.

5. Hydrodynamic Stability—Turbulence

The physical concepts associated with system isolation from surroundings and random inputs form the basis for application of small perturbation analysis of stability. Due to time limitations, a semi-rigorous derivation of the Orr-Sommerfeld equation is given, and the origin of turbulence is discussed in terms of random inputs at random time. Statistical and phenomenological approaches as well as physical models are illustrated and contrasted in terms of potential and