

# ENERGY, MASS AND MOMENTUM TRANSPORT -

## The Treatment Of Jump Conditions At Phase Boundaries And Fluid-dynamic Discontinuities

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**T**HE ABILITY TO DEAL quantitatively with *transport* phenomena accompanying phase and chemical transformations is the hallmark of the chemical engineer. But since the essentials of transport phenomena are, accordingly, a central

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part of every ChE's *undergraduate* education, what then is the purpose of a *graduate* course in this subject? The answer lies in the fact that undergraduate courses tend to emphasize the solution of "classical" problems whereas, in practice, the solution to such problems has already been thoroughly computerized. The situation is what D. Gabor calls the "aristocratic revolution" within the engineering profession [1]—*viz.* the principal need in the future will be for creative engineers able to formulate and program the solution to challenging *novel* problems, not the now-routine problems which characterized (chemical) engineering earlier this century. This is our underlying premise at Yale and, in what follows, I illustrate how this influences my teaching of our graduate course in energy and mass transport. For definiteness, I have selected the treatment of "boundary conditions", one of the "Achilles' heels" of most undergraduate courses in transport phenomena.

### COURSE CONTENT

**T**HE PLACE OF OUR topic within the context of the one semester lecture course (EAS 254) is evident in Table 1. This course is not only taken by all graduate students in ChE but, each year, attracts students from other graduate majors at Yale (*eg.* Geology, Forestry, Materials Science, Fluid Physics, Physiology). As will become clear

TABLE 1  
COURSE OUTLINE: Heat, Mass and  
Momentum Transport Processes\*

1. CONSERVATION PRINCIPLES  
(Continuum Approach)
    - Fixed and moving macroscopic control volumes
    - Conservation relations in partial differential form
    - Jump conditions at phase boundaries, discontinuities
  2. PHENOMENOLOGICAL TRANSPORT LAWS AND COEFFICIENTS
    - Linear flux-driving force laws
    - Molecular level approach to transport coefficients
    - Actual and effective transport coefficients; turbulent transport
    - Similitude methods, implications
  3. ENERGY AND MASS TRANSPORT IN QUIESCENT MEDIA
    - Steady state conduction, diffusion
    - Transient conduction/diffusion; analytical methods
    - Numerical methods; finite differences, finite elements
  4. ENERGY AND MASS TRANSPORT IN MOVING MEDIA
    - Transport to/from submerged surfaces
    - Transport to/from duct surfaces
    - Transport in packed beds
    - Transport in jets, plumes, wakes; pollutant dispersion modeling
  5. SPECIAL TOPICS (as time permits)
    - Transport with simultaneous phase change
    - Transport with simultaneous chemical reaction
    - Low density flows (non-continuum effects)
    - High speed flows (viscous dissipation effects)
- \*Textbook: Bird, R. B., Stewart, W. and Lightfoot, E. N., Transport Phenomena J. Wiley (1963) (Supplemented by papers from the current research/engineering literature)

via our example, this broad appeal follows from our emphasis on fundamental principles common to transport phenomena in these fields. Specific applications including numerical calculations, are covered mainly via graded homework sets (about 9) and 2 take-home open book examinations. Moreover, the course is not only intended for tomorrow's "computer modelers" of chemical processes—it has proved useful to students designing and interpreting experiments in chemical kinetics, both laboratory and pilot plant scale.

Our approach to the treatment of boundary conditions is not that they are a set of *ad hoc* prescriptions (usually stated without their underlying restrictions), but rather that they follow from the same conservation principles used to generate global conditions on chemical reactors or differential equations applicable within each region of the ChE's interest. This is shown in the "road map" (Fig. 1), which reveals that we formulate the conditions to be imposed at interfaces separating continua by applying "battle-tested" conservation (balance) principles (mass, energy, momentum, entropy) to a special type of semi-differential control volume (a "pillbox") straddling the moving interface. It is remarkable that while this approach is quite familiar to EE's studying electromagnetism, most ChE's have not been introduced to it.

#### LIMITATIONS OF THE USUAL APPROACH

**U**NDERGRADUATE ChE's typically feel comfortable imposing continuity of normal velocity, tangential velocity (no "slip"), tangential shear stress, normal pressure, temperature, heat flux and chemical potential across interfaces (usually phase boundaries, but here broadened to include fluid-dynamic discontinuities such as detonation waves in gases, or the interface between immiscible liquids). To illustrate the serious limitations of these "commonly encountered" prescriptions, consider the following student exercises:

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Dr. Rosner's research interests include convective heat and mass transport, interfacial chemical reactions, phase transformations, combustion and aerosol phenomena, on which he has published over 90 papers. He received his Ph.D. in Aeronautical Engineering from Princeton University in 1961 following a bachelor's degree in Mechanical Engineering (*summa cum laude*) from City College of New York in 1955. Prior to joining the Yale faculty as an Associate Professor of Engineering and Applied Science in 1969, he headed a research group on interfacial chemical kinetics and transport at AeroChem Div. Sybron Corporation, Princeton, New Jersey. He has also been a Visiting Professor of Mechanical Engineering at Polytechnic Institute of Brooklyn-Graduate School, and a Visiting Scholar at Stanford University (Chem. Eng. 1968) and Imperial College—London (Mech. Eng. 1973). He is presently Professor of Chemical Engineering and Applied Science and Director of the High Temperature Chemical Reaction Engineering laboratory at Yale University.

- E1. It is often stated that at solid/fluid interfaces the fluid velocity equals the velocity of the surface itself (p. 37, BSL [2] and p. 94 WWW [3]). Moreover, Batchelor (Ref. [4], p. 68) states that "unless rupture occurs" at the interface between two contacting media, the normal component of fluid velocity must be continuous across the interface. Suppose, however, that a solid is subliming into the gas (eg. naphthalene in air). Would this above statement be true for the velocity components normal to the surface?
- E2. The shear stress is often considered to be negligible at gas/liquid interfaces (p. 37, BSL and p. 110 WWW). When wind drives a film of rainwater up your car windshield against the pull of gravity, would this assumption be justified?
- E3. For the energy equation one can frequently impose the condition of continuity of heat flux and temperature across an interface (p. 267, BSL). Would continuity of heat flux be valid if the interface were the site of a phase change?
- E4. A theoretician has argued that a conjectured fluid dynamic discontinuity is possible ("exists") since it is compatible with the laws of mass, momentum and energy conservation. Is his proof complete? Can a discontinuity exist if the specific entropy of the fluid decreases across the discontinuity (as in a solidification wave)?
- E5. For systems which need not be in mechanical, thermal or chemical equilibrium: a) would a discontinuity in tangential mass-averaged velocity,  $v_t$ ,

across an interface (eg. phase boundary) violate any basic conservation principle? b) Would a discontinuity in temperature,  $T$ , across an interface (eg. a shock wave) violate any conservation principle? c) Would a discontinuity in chemical potential across an interface (eg. a phase boundary) violate any conservation principle? d) What kind of restrictions do the conservation equations impose in such cases?

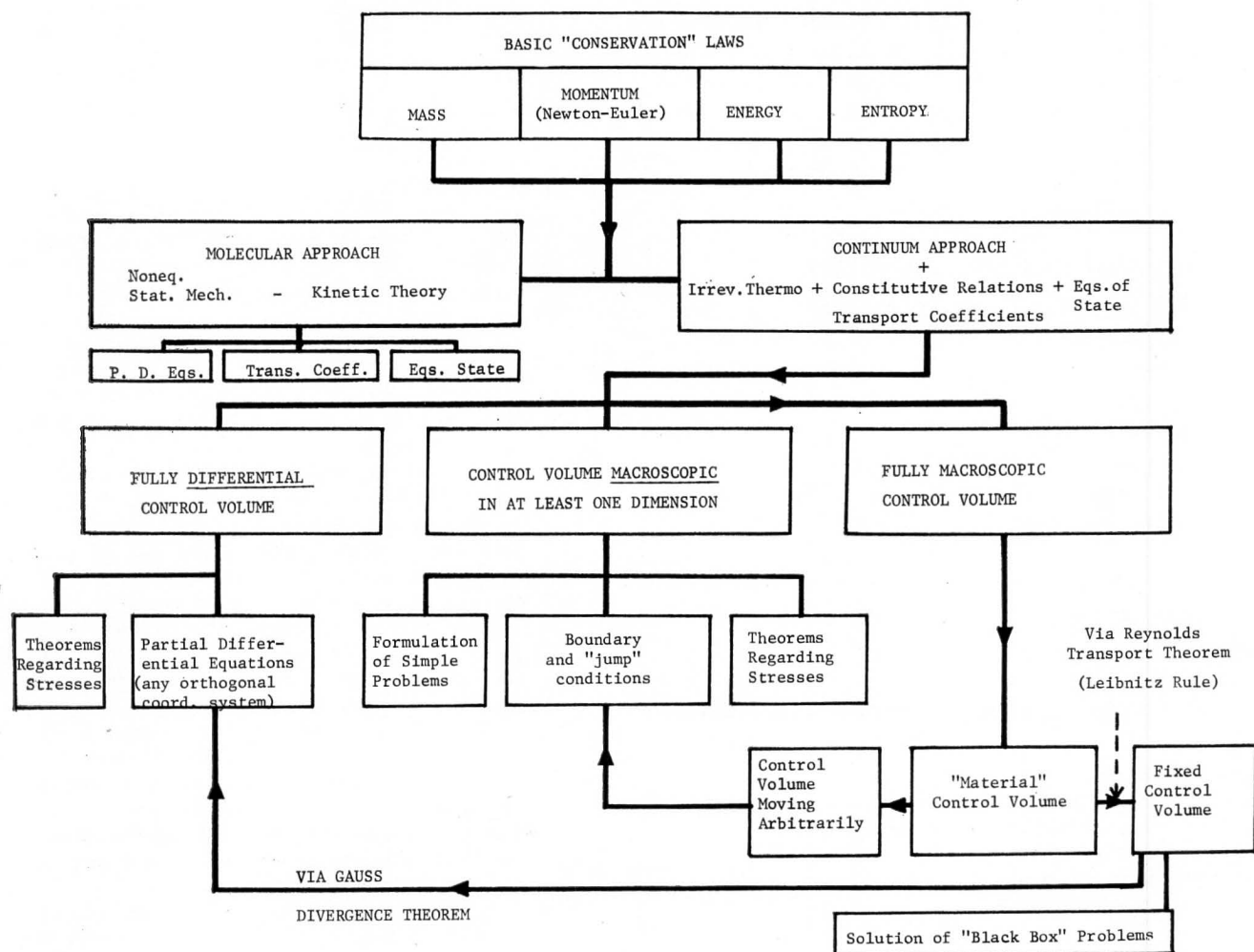
### LECTURE EMPHASIS: A GENERAL METHOD

**I**N THE OUTLINE for this lecture (including a list of useful references [5, 6]), distributed to each student, a systematic procedure for deriving relations between field quantities on either side of surfaces of discontinuity is sketched. During the lecture this procedure is illustrated for each primary "balanced" quantity (chemical elements, chemical species mass, total mass, linear momentum, angular momentum, total energy and specific entropy) and then specialized to cases of practical

importance. For brevity we here outline the procedure as applied to chemical species conservation at interfaces, the relevant field "density" being the scalar partial density of each chemical species. Our result can then be compared to various degenerate cases stated in classical treatises on surface chemistry—e.g. Hayward and Trapnell's monograph [7] on chemisorption on solid surfaces. Using examples from recent research carried out in the Yale High Temperature Chemical Reaction Engineering Laboratories, we then consider some implications of the general boundary condition, emphasizing the important question of departures from chemical equilibrium at surfaces.

We adopt the view that the interface separates two regions (designated by  $\pm$ ) each governed by continuum laws, but avoid prescribing the form of the transport laws *within* the interfacial region (owing to the magnitude of local gradients therein).\*

FIGURE 1



Then:

1. Write the relevant conservation equation for an arbitrarily moving *macroscopic* control volume (since the interface motion is generally different from that of the fluid on either side of it).
2. Specialize the control volume to a "pillbox" (of arbitrary area) always moving so as to straddle the interface.
3. Evaluate all terms in the resulting integral equation [using mathematical theorems (Leibnitz, Gauss), exploiting the fact that, for sufficiently thin interfaces, the pillbox top and bottom become locally parallel (hence their unit outward normals  $\mathbf{n}_+$ ,  $\mathbf{n}_-$  are opposite in sign)].

When applied to a chemical species  $i$  present with instantaneous mass  $\rho_i''$  per unit area of interface† and produced at the instantaneous (heterogeneous reaction) rate  $r_i''$  per unit (projected) interface area, we obtain

$$\underbrace{\partial \rho_i'' / \partial t}_1 + \underbrace{\text{div}'' \cdot (\rho_i'' \mathbf{v}_{s,t} + \mathbf{j}_i')}_2 + \underbrace{[\rho_i''' (\mathbf{v} - \mathbf{v}_s) + \mathbf{j}_i''] \cdot \mathbf{n}_+}_{3} = r_i'' \quad (1)$$

where term 1 is the accumulation rate, 2 is the net outflow of species  $i$  per unit interfacial area due to both tangential *surface* convection  $\mathbf{v}_{s,t}$  and *surface* diffusion  $\mathbf{j}_i'$  3 (involving the "jump" operator [ ]  $\equiv ( )_+ - ( )_-$ ) is the net outflow of species  $i$  due to relative convection and diffusion normal to the interface. In comparing this relation to its better known three-dimensional analog:

$$\partial \rho_i''' / \partial t + \text{div}''' \cdot (\rho_i''' \mathbf{v} + \mathbf{j}_i''') = r_i''' \quad (2)$$

note that, in effect, the net outflow (by convection and diffusion) term per unit interfacial area in Eq. (1) has been decomposed into a tangential contribution 2 and a normal contribution 3.

## IMPLICATIONS

**D**ISSOCIATIVE chemisorption of oxygen on solid surfaces is an important elementary step in solid-catalyzed oxidation reactions. The kinetics of this step are often studied under transient conditions such that only term 1 contributes to the

\*Alternate methods can be used if the "interface" is itself a continuum zone with merely large spatial gradients in one (normal) direction, and moderate spatial gradients in the tangential directions. Decomposition of the  $\nabla$  operator into normal (n) and tangential (t) contributions then allows formal integration of the presumed differential equations to obtain the desired "jump" relations. [8]

†We adopt the useful convention that triple primed ('''), double primed (') and single primed (') quantities refer, respectively, to quantities reckoned per unit volume, area and length.

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left hand side of Eq. (1)—*ie.* the net rate of formation of adsorbed O-atoms is then proportional to the instantaneous rate of increase of surface coverage. [7] But if O-atom diffusion into the bulk "solvent" is important, term 3 contributes, and in molecular beam studies (in which only a portion of the target is "illuminated") [10] term 2 (surface diffusion) must be considered. We recently completed a kinetic study of the oxygen/tantalum reaction in the temperature range 1200-3000K using a transient (resistance "relaxation") method. [9] In considering Eq. (1) for atomic oxygen, term 1 contributed due to the transient, term 2 contributed due to the continuous shrinkage of the tantalum filament associated with metal gasification, and term 3 contributed due to internal dissolution of oxygen in the metal. This system\* provides a dramatic illustration of the moral: be wary of unrestricted statements of highly degenerate cases of Eq. (1), such as the commonly seen forms:

$$\partial \rho_i'' / \partial t = r_i'' \quad (\text{in chemisorption}) \quad (3)$$

or

$$\mathbf{j}_{i+}'' \cdot \mathbf{n}_+ = r_i'' \quad (\text{in steady-state catalysis}) \quad (4)$$

It should also be remarked that a systematic formulation of jump conditions such as Eq. (1) provides insight into failure of the commonly encountered assumption of interphase local chemical equilibrium despite conditions of net chemical species transport. For when one descends to the molecular level one finds that each  $r_i''$  is itself the algebraic sum of positive and negative contributions which vanish only at equilibrium. It follows that when the left hand side of Eq. (1) is non-zero then local interface equilibrium cannot be strictly valid. Thus, in any particular application the importance of this departure can be assessed, provided the relevant kinetic and transport coefficients are known or estimable. Moreover, while

\*An analogous situation, recently treated by Pierson and Whitaker [11], is the surfactant (heptanoic acid) absorption mass balance for a growing droplet (water).

discussed here for the case of chemical equilibrium, similar arguments apply to the case of mechanical equilibrium (via momentum conservation) and thermal equilibrium (via energy conservation). Indeed, in a recent study [12] of the non-equilibrium crystallization of pure  $ZrO_2$ , liquid/solid interface temperatures some 570K below the equilibrium melting point have been encountered!

## CONCLUSIONS

**T**HE TREATMENT of boundary conditions briefly described above [13] has been used to illustrate our approach to the teaching of energy, mass and momentum transport at the graduate level. We believe that such a fundamental approach to each of the topics (Table 1) is essential to the development of PhD chemical engineers who will be able to deal rationally with novel chemical processes involving extreme conditions.

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## REYNOLDS: Engineer as Entrepreneur Continued from page 189.

development to commercialization.

One of the problems which necessarily arises in a one-semester course of this type is that four months is really inadequate to carry out the development and preliminary commercialization satisfactorily. Serious consideration is being given to the extension of the one-semester course to a two-semester course in which at time intervals, prototype devices could be manufactured and test marketing carried out. The current one-semester course carried three credits and has generated a great deal of interest.

The Chemical Engineering Department feels that this type of innovative course could have major beneficial effects for the Commonwealth of Massachusetts by drawing attention of engineering students to the field of entrepreneurship and to give embryonic entrepreneurs a real-life experience in the development and marketing of new products. It is hoped that as time goes on, funding may be available for "seed money" in which to take one or more of the more promising products or services into at least preliminary commercialization. □

## ACADEMIC POSITIONS

For advertising rates contact Ms. B. J. Neelands, CEE c/o Chemical Engineering Dept., University of Florida, Gainesville, FL. 32601.

### CHEMICAL ENGINEERING CHAIRPERSON POSITION

Candidates for the chairperson of the Department of Chemical Engineering at the State University of New York at Buffalo are being sought. Persons interested are invited to send their credentials, and persons wishing to nominate others are invited to send names and addresses to: McAllister H. Hull, Jr., Dean, Graduate School, State University of New York at Buffalo, Buffalo, NY 14214. The university is aggressively engaged in an affirmative action program and is an equal opportunity employer.