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Five Decades of Transport Phenomena

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Surveying the progress made in transport phenomena in the past half-century is an impossible task. Fully half of the publications in the chemical engineering journals have something to do with transport phenomena, and, in addition, there are many other disciplines where transport phenomena arise. In this summary we try to give the flavor of the developments by citing typical textbooks, review articles, and research publications—but the choices are often capricious. To some extent we try to put the emphasis on works that involve two or more of the transport mechanisms.

In reviewing the *AIChE Journal* for the last 50 years, the author must confess to having a feeling of nostalgia as he came across names like Allan Colburn, Olaf Hougen, W. R. ("Bob") Marshall, R. L. ("Bob") Pigford, T. K. ("Tom") Sherwood, and R. H. ("Dick") Wilhelm; he had to pause and contemplate the many contributions of these fine people. We have indeed profited in many ways from the contributions and wisdom of our predecessors.

[*Note:* The references in §1 are numbered. In subsequent sections the references are labeled with lowercase letters. If a reference is made to another section, both the section and letter are given; thus, 16*f* means "reference *f*" of §16.]

§1. The Status of Transport Phenomena Fifty Years Ago

The subject of transport phenomena is a very old one,[1] with some of the topics dating back several centuries. By 1955, much of the theory for homogeneous fluid mixtures had been developed. The equations of change were well known from continuum mechanics, and because of the development of the thermodynamics of irreversible processes during the two preceding decades,[2,3,4] the linear expressions for the fluxes as functions of the driving forces were also well understood. Consequently, the existence of the cross effects (thermal diffusion, the diffusion-thermo effect, and the relations among the multicomponent diffusivities) had been firmly established.

In addition, the Chapman-Enskog kinetic theory of dilute monatomic gases had been presented in great detail by Chapman and Cowling[5] for pure gases and binary mixtures. The analogous kinetic theory for multicomponent mixtures had also been worked out by Curtiss and Hirschfelder[6] and calculations based on the theory had been made for the Lennard-Jones 6–12 potential.[7] Some work had also been done on the kinetic theory of polyatomic molecules, loaded spheres, rough spheres, and rigid ovaloids. A beginning had been made on the kinetic theory of monatomic liquids.[8] These molecular theories give flux expressions that are consistent with those obtained from the thermodynamics of irreversible processes.

Also, a number of analytical solutions of the equations of change were available. In fluid dynamics, the field of inviscid flow had been well developed, and, for viscous Newtonian flow, there were many analytical solutions that were useful in engineering and the applied sciences. For heat conduction, there was the first edition of Carslaw and Jaeger's excellent compilation of thousands of solutions of the heat-conduction equation.[10] For heat conduction, convection, and radiation, there was the book by Gröber and Erk,[11] as well as several others. For diffusion, the situation was rather bleak, since that subject was newer than fluid dynamics and heat transfer, and is more difficult. There were books by Jost[12] and Barrer[13] on diffusion in solids, and for liquids and gases, the Eucken-Jakob treatise[11] provided some guidance. But these references were incomplete inasmuch as the distinctions among the reference frames for the mass and molar fluxes were not made clear, and the nature of the driving forces for diffusion was not carefully discussed. In addition, the heat generated by viscous dissipation was usually omitted from the energy equation.

As far as turbulent flows are concerned, considerable effort had been expended to provide an understanding of this very difficult subject. The status of this topic as of 50 years ago was pretty well summarized by Prandtl[14] and Schlichting,[9] who considered both isothermal and nonisothermal systems.

The macroscopic balances were part of the everyday tools of the civil, mechanical, aeronautical, and chemical engineers. These balances could be found in many handbooks, although the origins of some of the equations were difficult to trace, and often the assumptions inherent in them were not given or had been forgotten. Actually, it was probably this part of the subject

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of transport phenomena that had proven to be of greatest value to engineers in the 19th century and the first half of the 20th.

Because of the great utility of the macroscopic balances, designers found it imperative to understand the interphase transfer coefficients (friction factors, heat-transfer coefficients, and mass-transfer coefficients). Engineers could find in their handbooks the dimensionless plots of friction factor vs. Reynolds number and heat-(mass-) transfer coefficient vs. Reynolds and Prandtl (Schmidt) numbers, along with additional useful information.

By 1954, the science of transport phenomena had been almost completely developed, and the reference work *Molecular Theory of Gases and Liquids*[7] had been published. This volume, directed primarily at physicists, theoretical chemists, aeronautical engineers, and combustion specialists, provided a unified treatment of equilibrium statistical mechanics, nonequilibrium statistical mechanics (kinetic theory), the use of the equations of change, electrical properties, and intermolecular forces. It was mainly Professor J. O. ("Joe") Hirschfelder, the senior author, who determined the contents of the book, and Professor C. F. ("Chuck") Curtiss provided the mathematical agility and intuition for working through some of the more complex theoretical developments.

1. R. B. Bird, *Chem. Eng. Educ.,* 256–265 (Fall 2001); this contains a set of "microbiographies" of the most important people who, during their lifetimes, contributed to the development of the theory of transport phenomena.
2. L. Onsager, *Phys. Rev.,* **37,** 405–426 (1931); **38,** 2265–2279 (1931); C. H. Eckart, *Phys. Rev.,* **58,** 267–268, 269–275, 919, 924 (1940).
3. C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.,* **18,** 171–173 (1950).
4. J. G. Kirkwood and B. L. Crawford, Jr., *J. Phys. Chem.,* **56,** 1048–1051 (1952).
5. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases,* Cambridge University Press (1939, 1970).
6. C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.,* **17,** 550–555 (1949).
7. See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids,* Wiley, New York (1954, 1964), Chapters 7 and 8.
8. J. H. Irving and J. G. Kirkwood, *J. Phys. Chem.,* **18,** 817–829 (1950).
9. See, for example, H. L. Dryden, F. D. Murnaghan, and H. Bateman, *Hydrodynamics,* Bulletin #84 of the National Research Council (1932); of course, there were many other treatises, notably the classics of the German research literature, such as H. Schlichting, *Grenzschicht-Theorie,* G. Braun, Karlsruhe (1951).
10. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids,* Oxford University Press (1946, 1959).
11. H. Gröber and S. Erk, *Die Grundgesetze der Wärmeübertragung,* Springer, Berlin (1933); see also the 13-volume combined transport-phenomena-plus-unit-operations treatise by A. Eucken and M. Jakob, *Der Chemie-Ingenieur: Ein Handbuch der physikalischen Arbeitsmethoden in Chemischen und verwandten Industriebetrieben,* Akademische Verlagsgesellschaft, Leipzig (1933–1940); M. Jakob, *Heat Transfer,* Wiley, New York (Vol. 1, 1949, Vol. 1957).
12. W. Jost, *Diffusion und chemische Reaktion in festen Stoffen,* Leipzig-Dresden (1937).
13. R. M. Barrer, *Diffusion in and through Solids,* Cambridge University Press (1952).
14. L. Prandtl, *Essentials of Fluid Dynamics,* Hafner, New York (1952), a translation of *Führer durch die Strömungslehre* (1949).

§2. Textbooks

Fifty years ago, in colleges of engineering all over the world, there were generally satisfactory courses available on fluid dynamics and heat transfer, often taught by faculty members in mechanical or civil engineering. The subjects of diffusion, mass transfer, and flow with chemical reactions were usually taught only in chemical engineering departments. Courses that presented all three transport phenomena (mass, momentum, and energy) were few and far between. There were several groups of people that realized the advantages of a transport phenomena course and were preparing class notes and experimenting with ways of organizing the material, notably R. R. White and S. W. Churchill[a] at the University of Michigan. In 1956, the 387-page book by Bosworth[b] was published, which was a step in the right direction, but not appropriate as an elementary textbook. It resembled a long review article, treating a wide variety of topics rather superficially, including informational entropy, electrical transport, microscopic reversibility, efficiency of prime movers, and factory operations as "grand transport processes." In 1956 Kramers[c] published a set of stenciled notes for his students at the Technical University of Delft that covered roughly the right material for chemical engineers, with, appropriately, emphasis primarily on the macroscopic balances and transfer coefficients.

The story of how the triumvirate of BS&L[d] teamed up to write the paperback edition *Notes on Transport Phenomena* in 1958, followed by two hardback editions of *Transport Phenomena* in 1960 and 2002 has been published elsewhere[e] and will not be repeated here. In addition, Crosby's cleverly designed experiments and a laboratory manual[f] contributed much to the instructional programs in the United States and abroad.

The primary reason for combining momentum, heat, and mass transfer into one introductory course is the fact that, in many industrial processes and in nature, the transport of all three entities occurs simultaneously. Also, in the three areas the same kinds of equations appear, and some of these can be solved by standard mathematical methods. That others were thinking along the same line is evidenced by the appearance of two other introductory textbooks within a few years,[g] as well as the English translations of two very fine Russian treatises, one by Landau and Lifshitz,[h] and one by Levich,[i] which are suitable as graduate textbooks.

By 1980, there were no less than 23 textbooks[e] on transport phenomena on the market, and since then the number has grown. There are now *introductory* books for chemical engineers, metallurgical engineers, biomedical engineers, and other groups. One has but to search on the Web under the term "transport phenomena" to be greeted by a plethora of choices. At the *advanced* level, several textbooks are available, which put the emphasis on the mathematical aspects of the subject: one by Leal,[j] restricted to laminar flow (without and with heat transfer), that gives a thorough discussion of singular perturbation theory, matched asymptotic expansions, and boundary-layer theory; another by Deen,[k] that emphasizes the finite Fourier transform technique for solving partial differential equations; and another by Slattery[l] that has more extensive discussions of multispecies flow systems and presumes more maturity in tensor analysis than do the other two books. There are also some *treatises* in various specific fields that are discussed under the relevant topics below.

a. J. O. Wilkes, *A Century of Chemical Engineering at the University of Michigan,* Department of Chemical Engineering, University of Michigan, Ann Arbor (2002), p. 66.

b. R. C. L. Bosworth, *Transport Processes in Applied Chemistry,* Halstead Press, Sydney (1956).

c. H. Kramers, *Physische Transportverschijnselen* (1956); revised and published by Delftsche Uitgevers Maatschappij, N. V., Delft (1961).

d. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Notes on Transport*

Phenomena, Wiley, New York (1958); R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, New York (1960, 2002); the 2nd edition is referred to as BS&L.

e. R. B. Bird, *Recent Advances in the Engineering Sciences,* McGraw-Hill, New York (1958), pp. 155–177; R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *History of Chemical Engineering,* Advances in Chemistry Series #190, American Chemical Society, Washington, DC (1980), pp. 153–165; R. B. Bird, *Appl. Mech. Rev.,* **55,** #1, R1–R4 (2002).

f. E. J. Crosby, *Experiments in Transport Phenomena,* Wiley, New York (1961).

g. W. M. Rohsenow and H. Y. Choi, *Heat, Mass, and Momentum Transfer,* Prentice-Hall, Englewood Cliffs, New Jersey (1961); C. O. Bennett and J. E. Myers, *Momentum, Heat, and Mass Transfer,* McGraw-Hill, New York (1962).

h. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics,* Addison-Wesley, Reading Massachusetts (1959, 1987).

i. V. G. Levich, *Physicochemical Hydrodynamics,* Prentice-Hall, Englewood Cliffs, New Jersey (1962).

j. L. G. Leal, *Laminar Flow and Convective Transport Processes: Scaling Principles and Asymptotic Analysis,* Butterworth-Heinemann, Boston (1992).

k. W. M. Deen, *Analysis of Transport Phenomena,* Oxford University Press (1998).

l. J. C. Slattery, *Advanced Transport Phenomena,* Cambridge University Press (1999).

§3. Transport Property Measurements

Fifty years ago, a small band of chemical engineers was dedicated to providing the community with high-quality experimental data and "generalized charts"[a] on transport properties, and these data found their way into the *AIChE Journal.* With the passage of time, the funding agencies unfortunately began to look with disfavor on physical property measurements as being "routine" and "repetitive," and, therefore, unworthy of funding.

For gasesous diffusion coefficients, the correlation and prediction of diffusivities was discussed by Marrero and Mason.[b] Other correlations of self-diffusivity at high pressures were published by Stewart[c] and collaborators.

An early book dealing with the measurement of diffusivity, thermal conductivity, and thermal diffusion in liquids and electrolytes is that of Tyrrell[d]; this monograph also contains much information about the thermodynamics of irreversible processes and the hydrodynamic theories of diffusion.

Chemical engineers have contributed much to the experimental determination of diffusivities. Newman and Chapman[e] showed how to measure diffusion coefficients of electrolytes by measuring accurately the concentrations at long times in a vertical cell closed at both ends (restricted diffusion). Dullien[f] and collaborators prepared a lengthy review article on diffusion of nonelectrolytes and summarized the theories, empiricisms, and data; they also measured self-diffusivities and viscosities of liquids as a function of temperature and developed a correlation that works for 21 liquids within 4%.

Gulari, Brown, and Pings[g] measured diffusivities by quasi-elastic light scattering. Vrentas and Duda[h] prepared a review of the methods for estimating diffusion coefficients for polymer-solvent systems and recommended methods for predicting the temperature, concentration, and molecular weight dependences of diffusivities in dilute and concentrated solutions.[i]

The *Journal of Chemical and Engineering Data* is currently a repository for data on physical properties. Of course, there are numerous handbooks that contain data, particularly the impressive multivolume *Landolt-Börnstein Physicochemische Tabellen.*

a. One of the most conscientious generalized-chart makers was George Thodos at Northwestern University. A few of his charts for viscosity and thermal conductivity are given in the following references: E. J. Owens and G. Thodos, *AIChE Journal,* **3,** 454–461 (1957), **6,** 676–681 (1960); H. Shimotake and G. Thodos, *AIChE Journal,* **4,** 257–262 (1958); C. A. Schaefer and G. Thodos, *AIChE Journal,* **5,** 367–372 (1959); J. T. Kennedy and G. Thodos, *AIChE Journal,* **7,** 625–631 (1961).

b. T. R. Marrero and E. A. Mason, *AIChE Journal,* **19,** 498–503 (1973).

c. L. S. Tee, G. F. Kuether, R. C. Robinson, and W. E. Stewart, *API Proceedings,* Division of Refining, 235–243 (1966); R. C. Robinson and W. E. Stewart, *Ind. Eng. Chem. Fundamentals,* **7,** 90–95 (1968); see also Fig. 17.2-1 in BS&L and the references cited there.

d. H. J. V. Tyrrell, *Diffusion and Heat Flow in Liquids,* Butterworths, London (1961).

e. J. Newman and T. W. Chapman, *AIChE Journal,* **19,** 343–348 (1973).

f. R. K. Ghai, H. Ertl, and F. A. L. Dullien, *AIChE Journal,* **19,** 881–900 (1973), **20,** 1–20 (1974); H. Ertl and F. A. L. Dullien, *AIChE Journal,* **19,** 1215–1223 (1973).

g. E. Gulari, R. J. Brown, and C. J. Pings, *AIChE Journal,* **19,** 1196–1204 (1973).

h. J. S. Vrentas and J. L. Duda, *AIChE Journal,* **25,** 1–24 (1979).

i. J. M. Zielinski and J. L. Duda, *AIChE Journal,* **38,** 405–415 (1992).

§4. Molecular Theories

Although engineers are generally concerned with the continuum aspects of transport phenomena, they need some familiarity with the molecular underpinnings of the subject. This is certainly true when it comes to physical property estimation or calculation. Furthermore, the molecular theory offers a deeper understanding of the continuum equations.

In 1964 there appeared an English translation[a] of Boltzmann's *Vorlesungen über Gastheorie* (complete with a lengthy introduction and numerous helpful notes), thereby making Boltzmann's fundamental work more widely available to the English-speaking world.

In 1958 two extensive reviews[b] by Grad and by Waldmann appeared in the multivolume *Handbuch der Physik.* Grad's article dealt with mathematical matters and made use of an expansion in Hermite polynomials (a generalization of which Curtiss and Bird later used in their development of polymer kinetic theory[13j]) and his "thirteen-moment approximation." Waldmann's article began with a lengthy discussion of measurement methods and then gave a rather full account of the molecular theory of the transport properties.

The publications of Kirkwood and his collaborators[c] were reprinted in his collected works; of relevance here are the volumes dealing with statistical mechanics and polymers. These contain many novel ideas and established the fundamental kinetic theories for liquids, liquid mixtures, and macromolecules. The kinetic theory of polyatomic gases was developed by Wang, Chang, and Uhlenbeck[d] in 1970.

The 1970 edition of Chapman and Cowling[5] (first published in 1939) was a welcome updating of a classic work. It included new material on multicomponent mixtures, molecules with internal degrees of freedom, quantum mechanical calculations, a short presentation of the BBGKY theory of dense gases, and several discussions of approximate theories. In 1972, Ferziger and Kaper[e] published a carefully written and readable account of the kinetic theory of dilute and dense gases. The book by Cunningham and Williams[f] covers a wide variety of topics, but emphasizes the role of the bounding surfaces; it includes Graham's laws for diffusion and effusion, Knudsen diffusion, flow through porous media, slip effects, surface diffusion, Mason's dusty gas model, and a host of other topics not to be found elsewhere in book form. It also contains a chapter dealing with the history of diffusion. Many of these same topics had been covered a few years earlier in a monograph by Jackson, dealing with transport in porous catalysts.[g]

In 1981 a rather novel view of kinetic theory of gases[h] appeared in Volume 10 in the Landau-Lifshitz *Course of Theoretical Physics.* Chapter I includes an abbreviated discussion of the Chapman-Enskog theory for the viscosity and thermal conductivity of pure gases, as well as the diffusivity of binary mixtures. Then, slightly rarefied gases (i.e., Knudsen gases) and highly rarefied gases are discussed, along with some interesting worked-out problems. Then, Bogoliubov's transport equation is given, as well as the transport equation for three-particle collisions. Chapter II starts off with a discussion of the Fokker-Planck equation and the weakly ionized gas in an electric field. The remainder of the book includes plasmas, quantum liquids, metals, superconductors, and the kinetics of phase transitions.

A rather different approach to kinetic theory was taken by Zwanzig,[i] who summarized the method in a review article of considerable didactic value. In that article he gives the transport properties in terms of time-correlation functions.

a. L. Boltzmann, *Lectures on Gas Theory* (translated by Stephen G. Brush), University of California Press, Berkeley (1964).

b. H. Grad, *Principles of the Kinetic Theory of Gases,* Handbuch der Physik, Band XII, Springer, Berlin (1958), pp. 205–294; L. Waldmann, *loc. cit.,* pp. 295–514.

c. J. G. Kirkwood, *Selected Topics in Statistical Mechanics,* Gordon and Breach, New York (1967); *Macromolecules,* Gordon and Breach, New York (1967).

d. C. S. Wang Chang and G. E. Uhlenbeck, in *Studies in Statistical Mechanics,* Vol. V (J. de Boer and G. E. Uhlenbeck, eds.), North Holland, Amsterdam (1970).

e. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases,* North Holland, Amsterdam (1972).

f. R. E. Cunningham and R. J. J. Williams, *Diffusion in Gases and Porous Media,* Plenum, New York (1980).

g. R. Jackson, *Transport in Porous Catalysts,* Elsevier, Amsterdam (1977).

h. E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics,* Pergamon Press, New York (1981).

i. R. Zwanzig, *Ann. Rev. Phys. Chem.,* **16,** 67–102 (1965).

§5. Molecular Dynamics and Brownian Dynamics

As the speed of computing devices has become greater, two techniques have become popular for solving transport problems at the molecular level by simulation techniques. The first of these is *molecular dynamics,* in which the locations and velocities of all the particles (molecules) in a system are followed as functions of time, by using Newtonian mechanics. Often, periodic boundary conditions are introduced, in order to minimize the number of particles that are needed. One example of a molecular dynamics calculation is Gottlieb's simulation,[a] which proved that, strictly speaking, dilute solutions of bead-rod chains do not obey the random-walk chain distribution. In this, he put 47 solvent molecules, represented as "beads," and a 3-bead-2-rod "flexible polymer" into a box, and allowed all 50 beads to interact with one another according to a Lennard-Jones function (except for the beads joined by the rods), and allowed for a similar interaction between all beads and the walls of a cubical box. He found that the distribution of angles between the two rods was not consistent with the random walk chain, but did agree with the exact results predicted by Kramers[b] from statistical mechanics.

The *Brownian dynamics* method is particularly useful for simulating polymer motions by suspending the chains in a solvent, whose structure is not specified. The thermal motion of the solvent then exerts random forces on the "beads" of the molecular model. In this way it is not necessary to follow the motions of the individual solvent molecules. An early example of this was Liu's (1989) sampling of the chain conformations and the subsequent calculation[c] of the viscosity and normal-stress coefficients for a Kramers chain consisting of 20 beads and 19 rigid-rod connectors.

In the same year a Brownian-dynamics clarification of the coil-stretch transition[d] in polymer chains, after inception of a sudden elongational flow, was presented. This established that the dumbbell theory presented earlier by de Gennes[e] was incorrect. In 1992, de Pablo, Öttinger, and Rabin[f] studied changes, with increasing shear rate, in the thickness of the depletion layer of a dilute polymer solution in the neighborhood of the wall; the presence of the wall prevents the polymer molecules from going through all possible configurations. In this work, the authors used the rigid dumbbell and rigid multibead rod models and compared their results with experiments on xanthan solutions. In working through these (and other examples), the monographs by Gardiner, van Kampen, and by Öttinger[g] were most helpful.

There are several review articles[h] of interest dealing with simulations of molecular processes at various stages of the development of the subject. The most recent one (1995) discusses the use of molecular dynamics to deduce some continuum properties of flow systems, such as the details of the fluid-boundary interaction, the nature of interfaces, and wetting mechanisms.

Currently, there is much activity in Brownian dynamics, and particularly, in the flow of polymers in very narrow channels,[i] and in the clarification of the orientation effects[j] for macromolecules in flow systems. A successful numerical algorithm, called CONNFFESSIT (Calculation of non-Newtonian flows: finite elements and stochastic simulation technique), was proposed by Öttinger and Laso[k] for solving simultaneously the equations of motion and the equations for the molecular dynamics of a polymer molecule; as an example, two-dimensional, time-dependent viscoelastic flow calculations have been made, using the FENE and FENE-P models of polymer molecules.

a. M. Gottlieb, *Computers in Chemistry,* **1,** 155–160 (1977).

b. H. A. Kramers, *Physica,* **11,** 1–19 (1944); this is a landmark publication in the kinetic theory of polymers.

c. T. W. Liu, *J. Chem. Phys.,* **90,** 5826–5842 (1989).

d. J. M. Wiest, L. E. Wedgewood, and R. B. Bird, *J. Chem. Phys.,* **90,** 587–594 (1989).

e. P.-G. de Gennes, *J. Chem. Phys.,* **60,** 5030–5042 (1974).

f. J. J. de Pablo, H. C. Öttinger, and Y. Rabin, *AIChE Journal,* **38,** 273–283 (1992).

g. C. W. Gardiner, Handbook of Stochastic Methods, Springer, New York (1983, 1985); N. G. van Kampen, *Stochastic Processes in Physics and Chemistry,* Noord-Holland, Amsterdam (1981, 1992); H. C. Öttinger, *Stochastic Processes in Polymeric Fluids: Tools and Examples for Developing Simulation Algorithms,* Springer, Berlin (1996).

h. B. J. Alder, *Ann. Rev. Phys. Chem.,* **24,** 325–337 (1973); W. G. Hoover, *Ann. Rev. Phys. Chem.,* **34,** 103–127 (1983); D. J. Evans and W. G. Hoover, *Ann. Rev. Fluid Mech.,* **18,** 243–264 (1986); J. Koplik and J. R. Banavar, *Ann. Rev. Fluid Mech.,* **27,** 257–292 (1995).

i. R. M. Jendrejack, E. T. Dimalanta, D. C. Schwartz, M. D. Graham, and J. J. de Pablo, *Phys. Rev. Letters,* **91,** Paper No. 038102 (2003); R. M. Jendrejack, D. C. Schwartz, M. D. Graham, and J. J. de Pablo, *J. Chem.*

Phys., **119,** 1165–1173 (2003); R. M. Jendrejack, D. C. Schwartz, J. J. de Pablo, and M. D. Graham, *J. Chem. Phys.,* submitted.

j. J. K. C. Suen, Y. L. Joo, and R. C. Armstrong, *Ann. Rev. Fluid Mech.,* **34,** 417–444 (2002).

k. M. Laso, M. Picasso, and H. C. Öttinger, *AIChE Journal,* **43,** 877–892 (1997).

§6. Nonlinear Irreversible Thermodynamics

It is often said that classical thermodynamics deals with systems at equilibrium, whereas transport phenomena involve systems that are not at equilibrium (because of gradients in velocity, temperature, and concentration). However, thermodynamics can be extended to describe irreversible processes, by introducing some additional postulates.

In constructing the linear thermodynamic theory[a,2] of nonequilibrium systems, one adds four postulates to those of equilibrium thermodynamics: the quasi-equilibrium postulate (local equilibration), the linearity postulate (for the fluxes), Onsager's reciprocal relations (for the coupling of the forces and fluxes), and Curie's postulate (specifying restrictions on the coupling). One can then understand the flux expressions for thermal diffusion (Soret) and the diffusion-thermo (Dufour) effects, for example. One can also study the behavior viscoelastic materials.[b]

If one wishes to go beyond the linear force-flux relations, it becomes necessary to introduce a new set of postulates, and various proposals have been made, including those by Beris and Edwards,[c] by Jongschaap,[d] and by Öttinger and Grmela.[e] The various proposed postulates have had to be deduced by patiently "working backwards" from existing kinetic theory results (mainly for polymers) and experimental data. In addition one has to strive to set up a theory that has a sense of beauty and exhibits the proper symmetry properties.[d] This theory should ultimately provide an "umbrella theory," capable of linking together many different phenomena.

(As an aside, Dirac's value function, which is used for comparing effectiveness of different separation processes (see Example 23.1–3 of BS&L), can be derived from straightforward equilibrium thermodynamic arguments.[f])

a. K. B. Denbigh, *AIChE Journal,* **5,** 20–25 (1959); S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics,* North Holland, Amsterdam (1962).

b. G. D. C. Kuiken, *Thermodynamics of Irreversible Processes,* Wiley, New York (1994).

c. A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems with Internal Microstructure,* Oxford University Press (1994).

d. R. J. J. Jongschaap, *J. Non-Equilibrium Thermodynamics,* **27,** 356–373 (1997).

e. M. Grmela and H. C. Öttinger, *Phys. Rev.,* **E56,** 6620–6632 (1997); H. C. Öttinger and M. Grmela, *Phys. Rev.,* **E56,** 6633–6655 (1997); H. C. Öttinger, *Phys. Rev.,* **E57,** 1416–1420 (1998); H. C. Öttinger, *Beyond-Equilibrium Thermodynamics* (2004).

f. J. B. Opfell, *AIChE Journal,* **24,** 726–728 (1978).

§7. Some Heat Conduction Problems

According to Carslaw and Jaeger[10] problems involving the solidification of a liquid have been of interest since the 1860s (the Neumann-Stefan problem). There are, of course, heat effects associated with the change of phase, and, during the cooling process, the phase boundary moves with time. There is a similar class of problems involving diffusion with a chemical reaction at the phase boundary. The literature on the mathematical methods available for these moving-boundary problems has been reviewed by Bankoff[a] up to 1964: analytical, integral equations, quasi-steady-state, variational, boundary layer, and matched asymptotic expansions. Since that time, three full-length books[b] have appeared on the subject of analytical solutions. The book by Davis is quite different from the first two, in that the effect of instabilities on the microstructure of resulting crystalline material is considered in depth. Although the Neumann-Stefan problem has been studied extensively, the analytical solutions may not be applicable (and certainly not for polymers), because the kinetics[c] of the phase change has been ignored. Clearly more attention needs to be paid to the latter point. Pangrle, Ayappa, Davis, Davis, and Gordon[d] in an article entitled "Microwave Thawing of Cylinders" pointed out that the interaction between the media and the electromagnetic radiation causes internal heat generation; this problem also involves the "Stefan problem," but there may be a "mushy" region corresponding to the fact that a phase change takes place over a temperature range.

Although the presence of the viscous-dissipation term in the energy equation was known to kinetic theorists for some time (see, for example, p. 52 of the 1939 edition of Chapman and Cowling[5]), scientists and engineers seem to have ignored it until viscous heating became important in high-speed boundary-layer problems in aerodynamics and in high-viscosity problems that occur in lubrication and in polymer processing. As late as 1949, Jakob's first volume[11] makes no mention of viscous heating, and the subject is mentioned only briefly in the second volume (1957). By the mid-1950s, chemical engineers[e] were computing temperature rises for non-Newtonian (power-law) fluids, and by the end of the century for oscillatory viscoelastic flows[f] as well. In 1974 Sukanek and Laurence[g] summarized the experimental and theoretical literature and contributed new data on several flow systems. Dinh and Armstrong[h] solved the problems of viscous heating in slit flow by the WKB-J method and compared their results with the numerical solution of Ybarra and Eckert.[h] Stewart and McClelland[i] gave asymptotic solutions for forced convection in three-dimensional flows with viscous heating; specifically, they solved the problems of flow around a sphere, wedge flows, the wire-coating problem, and the flow near a rotating disk. Viscous dissipation heating was discussed in the textbook by Whitaker,[j] one of the few heat-transfer books prepared by a chemical engineer.

Many non-Newtonian heat-transfer problems have been solved by chemical engineers. For example, the extended Graetz problem with prescribed wall heat flux was solved by Papoutsakis, Ramkrishna, and Lim.[k] Also, numerous investigations have been carried out on the problem of flow in a curved pipe, such as the publication of Hsu and Patankar.[l]

An excellent general reference for solution to heat conduction problems, correlation of mass-transfer coefficients, and tabular information on physical properties is the *Handbook of Heat Transfer.*[m]

a. S. G. Bankoff, in *Advances in Chemical Engineering, Vol. 5* (T. B. Drew, J. W. Hoopes, Jr., T. Vermeulen, and G. R. Cokelet, eds.) Academic Press, New York (1964), pp. 75–150.

b. J. Crank, *Free and Moving Boundary Problems,* Oxford University Press (1984); J. M. Hill, *One-Dimensional Stefan Problems,* Longmans (1987); S. H. Davis, *Theory of Solidification,* Cambridge University Press (2001).

c. H. Janeschitz-Kriegl, *Plastics and Rubber Processing and Applications,* 4, 145–158 (1984); H. Janeschitz-Kriegl, E. Ratajski, and G. Eder, *Ind. Eng. Chem. Res.,* **34,** 3481–3487 (1995).

d. B. J. Pangrle, K. G. Ayappa, H. T. Davis, E. A. Davis, and R. Gordon, *AIChE Journal,* **37,** 1789–1800 (1991); errata: *AIChE Journal,* **38,** 318–319 (1992).

e. R. B. Bird, *Society of Plastics Engineers Journal,* **11,** 35–41 (1955); H. L. Toor, *Trans. Soc. Rheol.,* **1,** 177–190 (1957); H. L. Toor, *AIChE Journal,* **4,** 319–323 (1958).

f. F. Ding, A. J. Giacomin, R. B. Bird, and C.-B. Kweon, *J. Non-Newtonian Fluid Mech.,* **86,** 359–374 (1999).

g. P. C. Sukanek and R. L. Laurence, *AIChE Journal,* **20,** 474–484 (1974).

h. S. M. Dinh and R. C. Armstrong, *AIChE Journal,* **28,** 294–301 (1982; R. M. Ybarra and R. E. Eckert, *AIChE Journal,* **26,** 5, 751 (1980).

i. W. E. Stewart and M. A. McClelland, *AIChE Journal,* **28,** 947–956 (1982).

j. S. Whitaker, *Fundamental Principles of Heat Transfer,* Krieger Publishing Company, Malabar, Florida (1977).

k. E. Papoutsakis, D. Ramkrishna, and H. C. Lim, *AIChE Journal,* **26,** 779–787 (1980); see also A. S. Jones, *AIChE Journal,* **28,** 350 (1982).

l. C.-F. Hsu and S. V. Patankar, *AIChE Journal,* **28,** 610–616 (1982).

m. W. M. Rohsenow, J. P. Hartnett, and Y. I. Cho (eds.), *Handbook of Heat Transfer,* McGraw-Hill, New York (1998).

§8. Some Diffusion Problems

In 1956, a summary of solutions to diffusion problems[a] was compiled; this article was intended to help chemical engineering students understand the origin of the equations in several unit operations textbooks. In the same year, a book[b] summarizing the methods of solving diffusion problems became available. Later in the century the massive two-volume treatise by Aris[c] appeared, and at the end of the century a textbook[d] devoted to the theory and applications of diffusion appeared. Also, a monograph[e] published in 1988 (and again in 2001) puts the emphasis on the solutions of problems dealing with the electronics industry using Fick's second law. For persons wishing the physicochemical point of view of diffusion, the book by Giddings[f] provides valuable information, primarily on separation methods: field flow fractionation, chromatography, electrophoresis, zone formation, and others.

A fascinating phenomenon involving diffusion, chemical reaction, and noninstantaneous periodic precipitation is that of Liesegang[g] ring formation, first discovered in 1896. The formation of Liesegang rings is of interest in geology, biology, and medicine. This phenomenon is normally not discussed in books on diffusion.

The diffusion caused by a temperature gradient—thermal diffusion—was worked on by chemical engineers in the 1950s, but interest waned after a period of initial enthusiasm; most of the work centered on the operation of the Clusius-Dickel column.[h]

The use of "smoothed particle hydrodynamics" for solving diffusion problems has been developed by Nitsche and Zhang[i]; the method is then illustrated by solving four simple problems.

Of considerable interest in the field of mass transfer is the subject of diffusion across interfaces whose shapes and sizes are time dependent. This problem area was discussed at great length by Angelo, Lightfoot, and Howard[j] and others. Diffusion into falling films has also been of interest; for the diffusion into a non-Newtonian falling film (of interest in blood oxygenation) see the article by Mohr and Williams.[k]

There is also a review article by Deen[l] on "hindered transport of large molecules in liquid-filled pores," which is important in the diffusion of molecules through membranes, where the passages are of the same size as the diffusing molecules.

The translational diffusivity tensor of polymers may be defined in three different ways: (1) by the relation between mass flux and concentration gradient, (2) by the relation between the average polymer velocity and an external force, and (3) by the relation for the mean-square displacement of a polymer because of Brownian forces. Öttinger[m] concluded (from considering the diffusion of elastic dumbbells in a solvent) that the definitions (2) and (3) lead to the same diffusion tensors, but that definition (1) leads to a different diffusion tensor. He further concluded that the Nernst-Einstein equation cannot be generalized to flowing solutions.

a. R. B. Bird, in *Advances in Chemical Engineering,* Vol. 1 (T. B. Drew and J. W. Hoopes, Jr., eds.), Academic Press, New York (1956), pp. 155–239.

b. J. Crank, *The Mathematics of Diffusion,* Oxford University Press (1956).

c. R. Aris, *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts,* Oxford University Press (1975).

d. E. L. Cussler, *Diffusion Mass Transfer in Fluid Systems,* Cambridge University Press, Second Edition (1997).

e. R. Ghez, *Diffusion Phenomena: Cases and Studies,* Wiley, New York (1988), Kluwer, Dordrecht (2001).

f. J. C. Giddings, *Unified Separation Science,* Wiley-International, New York (1991).

g. H.-J. Krug and J.-H. Kruhl, Eds., *Nichtgleichgewichtsprozesse und dissipative Strukturen in den Geowissenschaften* (Vol. 11 of *Selbstorganisation. Jahrbuch für Komplexität in den Natur-, Sozial- und Geisteswissenschaften*), Duncker and Humblot, Berlin (2001), 380 pp.; H. K. Henisch, *Crystals in Gels and Liesegang Rings,* Cambridge University Press (1988).

h. J. E. Powers and C. R. Wilke, *AIChE Journal,* **3,** 213–222 (1957); D. R. Longmire, *AIChE Journal,* **6,** 304–311 (1960); J. D. Baldeschwieler, *AIChE Journal,* **7,** 34–37 (1961)—dealing with "the forgotten effect"; D. T. Hoffman, Jr. and A. H. Emery, Jr., *AIChE Journal,* **9,** 653–659 (1963); J. R. Fleming and J. E. Powers, *AIChE Journal,* **9,** 730–740 (1963); P. L. Chueh and H. M. Yeh, *AIChE Journal,* **13,** 37–41 (1967); W. J. Korchinsky and A. H. Emery, Jr., *AIChE Journal,* **13,** 224–230 (1967); E. V. Halle and S. H. Jury, *AIChE Journal,* **13,** 709–717 (1967); S. Dicave and A. H. Emery, Jr., *AIChE Journal,* **13,** 1077–1080 (1967).

i. L. C. Nitsche and W. Zhang, *AIChE Journal,* **48,** 201–211 (2002).

j. J. B. Angelo, E. N. Lightfoot, and D. W. Howard, *AIChE Journal,* **12,** 751–760 (1966); D. W. Howard and E. N. Lightfoot, *AIChE Journal,* **14,** 458–467 (1968); W. E. Stewart, J. B. Angelo, and E. N. Lightfoot, *AIChE Journal,* **16,** 771–786 (1970).

k. C. M. Mohr, Jr., and M. C. Williams, *AIChE Journal,* **19,** 1047–1049 (1973).

l. W. M. Deen, *AIChE Journal,* **33,** 1409–1425 (1987).

m. H. C. Öttinger, *AIChE Journal,* **35,** 279–286 (1989).

§9. Multicomponent Diffusion

Because of the interest of chemical engineers in multicomponent diffusion, several treatises[a,b,c] have been published on this subject. The book by Taylor and Krishna is both a textbook and an encyclopedic reference work, including basic theory, interpretation of experiments, and design of contacting equipment. It also includes simultaneous heat and mass transfer, turbulent transfer processes, and film theories developed by means of matrix methods (introduced by Stewart and Prober[d]).

The thermodynamics of irreversible processes tells us that, in a system with N chemical species, there are $(1/2)N(N - 1)$ independent diffusivities. These may be the Fick diffusivities or the Maxwell-Stefan diffusivities, and the general relations between the two sets of diffusivities were developed by Merk[e] in 1959 for both liquids and gases.

Then, in a series of papers starting in 1957, using the

Maxwell-Stefan diffusivities, Toor[f] showed how to classify and solve a number of three-component gas diffusion problems of engineering interest. In 1973 Newbold and Amundson[g] formulated the problem of finding the concentration and temperature profiles in the evaporation of a multicomponent liquid droplet, and presented a numerical solution for two- and three-component droplets.

Recently, Amundson, Pan, and Paulsen[h] have solved diffusion problems with four chemical species and also with a continuous distribution of components. Nauman and Savoca[i] have evolved an approximate procedure for handling multicomponent diffusion problems with a large number of species. Hsu and Bird[j] showed how to extend the "Arnold problem" to multicomponent systems by use of an approximate boundary-layer method. Rothfeld[k] has shown how to combine the Maxwell-Stefan equation with an equation describing the Knudsen diffusion to obtain a satisfactory theory for diffusion in catalyst pellets. The solution to the problem of the evaporating multicomponent droplet has been sketched by Billingsley.[l]

With regard to the measurement of multicomponent diffusivities in liquids, the Taylor diffusion method[m] has proved to be accurate and reproducible. Applications of the Maxwell-Stefan equations to ionic systems have been given by Graham and Dranoff, and by Pinto and Graham.[n]

a. E. L. Cussler, *Multicomponent Diffusion,* Elsevier, Amsterdam (1976); *Diffusion,* Cambridge University Press, 2nd edition (1997).

b. J. A. Wesselingh and R. Krishna, *Mass Transfer in Multicomponent Mixtures,* Delft University Press (2000).

c. R. Taylor and R. Krishna, *Multicomponent Mass Transfer,* Wiley, New York (1993); for recent demonstrations of the power of their method, see R. Taylor, R. Krishna, and H. Kooijman, *Chem. Eng. Progress,* **99,** 28–39 (July 2003).

d. W. E. Stewart and R. Prober, *Ind. Eng. Chem. Fund.,* **3,** 224–235 (1964); W. E. Stewart, *AIChE Journal,* **19,** 398–400 (1973), erratum **25,** 208 (1979).

e. H. J. Merk, *Appl. Sci. Res.,* **A8,** 73–99 (1959); D. W. Condiff, *J. Chem. Phys.,* **51,** 4209–4212 (1969); C. F. Curtiss and R. B. Bird, *Ind. Eng. Chem. Res.,* **38,** 2515–2522 (1999), erratum, **40** (1791) (2001); K. Ghorayeb and A. Firoozabadi, *AIChE Journal,* **46,** 883–891 (2000).

f. H. L. Toor, *AIChE Journal,* **3,** 198–207 (1959), **10,** 448–455, 460–465 (1964); J. B. Duncan and H. L. Toor, *AIChE Journal,* **8,** 38–41 (1962); F. O. Schuck and H. L. Toor, *AIChE Journal,* **9,** 442–447 (1963).

g. F. R. Newbold and N. R. Amundson, *AIChE Journal,* **19,** 22–30, 1042–1043 (1973).

h. N. R. Amundson, T.-W. Pan, and V. I. Paulsen, *AIChE Journal,* **49,** 813–830 (2003).

i. E. B. Nauman and J. Savoca, *AIChE Journal,* **47,** 1016–1021 (2001).

j. H.-W. Hsu and R. B. Bird, *AIChE Journal,* **6,** 551–553 (1960).

k. L. B. Rothfeld, *AIChE Journal,* **9,** 19–24 (1963).

l. D. S. Billingsley, *AIChE Journal,* **20,** 183–184 (1974).

m. Ph. W. M. Rutten, *Diffusion in Liquids,* Delft University Press, The Netherlands (1992).

n. E. E. Graham and J. S. Dranoff, *Ind. Eng. Chem. Fundam.,* **21,** 360–369 (1982); N. DeG. Pinto and E. E. Graham, *AIChE Journal,* **32,** 291–296 (1986).

§10. Heat and Mass Transfer

Several teams of people have written books with "heat and mass transfer" in the title, such as Incropera and DeWitt,[a] Kays and Crawford,[b] and Baehr and Stefan.[c] The first two of these (written by professors of mechanical engineering) relegate diffusion and mass transfer to the end of the book and give those subjects only a brief treatment. The third does a somewhat better job of discussing the diffusional processes; in addition, it contains many useful references to the German literature.

Ruckenstein[d] has written a very long review of the use of dimensional analysis and scaling methods for estimating Nusselt and Sherwood numbers; the article is well illustrated with numerous practical examples and the documentation is extensive. Comparisons are made between his results and analytical solutions or experimental data. The compilation of Whitaker[e] of correlations for Nusselt numbers as functions of the Reynolds number, the Prandtl number, and a viscosity ratio is well done and reliable. In 1977, Stewart[f] prepared an overview of the field of heat- and mass-transfer correlations for three-dimensional flows of three types: steady forced convection, steady free convection, and transient systems; the tabular material and bibliography are particularly useful.

An impressive review of Sherwood-number measurements has been given by Selman and Tobias[g] (see particularly the 29-page summary in Table VII). The use of the limiting current technique, which is described in considerable detail, has provided Sherwood-number correlations for a wide variety of geometries for laminar, oscillating, and turbulent flows. The authors are careful to list the limits over which the correlations are valid.

For mass transfer, there are two general categories for which analytical solutions can be obtained: liquid-liquid interfaces with no velocity gradient at the interface (often referred to as the "penetration model"[h]), and liquid-solid interfaces, with a non-zero velocity gradient at the interface (see BS&L §22.2). For these two classes of flows, formal expressions for the Sherwood number can be written for boundary layers in flow around arbitrarily shaped objects. In the first case the local Sherwood number Sh for developed laminar flow or for creeping flow is proportional to the square root of the product $ReSc,$ and in the second case to the cube root of the product $ReSc.$

Mass-transfer problems with interfacial motions are important in chemical engineering. Simple examples are the mass transfer into a circulating bubble and into an expanding interface. A more complicated situation is the diffusion during a coalescence process. These types of problems have been extensively studied by Lightfoot, Stewart, and their students[i] (see BS&L §22.2).

A rather thorough study has been made by Dudukovic of heat conduction or diffusion problems for laminar flow past a surface, with a wall boundary condition of the third kind (i.e., a first-order reaction at the wall, or the analogous condition for heat conduction). Although this problem had been solved before, the solution was found not to be in convenient form for use; an article by Basic and Dudukovic[j] has provided some useful power-series solutions and given examples to illustrate their use.

Interphase heat and mass transfer in pulsatile flow has been studied computationally by McMichael and Hellums.[k] Over some ranges of the operating variables, the net heat or mass transfer is increased, whereas, in other ranges, it is decreased.

In an extensive article, Fortuin, Musschenga, and Hamersma[l] review various models for heat, mass, and momentum transfer in turbulent pipe flow. Then, they present a summary of their "extended random surface renewal" model, for which they claim great success in fitting the experimental data, as well as providing a corroboration of the Chilton-Colburn analogy.

An article by Laso[m] points out a new way to look at solving the equations of change of transport phenomena. The method involves making use of the fact that many transport equations are in fact closely related to a Fokker-Planck equation, and use can be made of this to devise a numerical solution procedure that is easier to implement than the finite difference method or the finite-element procedure. The author then illustrates the method by solving eight problems, with a wide range of boundary conditions.

a. F. P. Incropera and D. P. DeWitt, *Fundamentals of Heat and Mass Transfer,* Wiley, New York (1981, 1985, 1990, 1996, 2002).

b. W. M. Kays and M. E. Crawford, *Convective Heat and Mass Transfer,* McGraw-Hill, New York (1966, 1980, 1993).

c. H. D. Baehr and K. Stephan, *Heat and Mass Transfer,* Springer, Berlin (1998), an English translation of *Wärme und Stoffübertragung* (1994 and 1996).

d. E. Ruckenstein, in *Advances in Chemical Engineering,* Vol. 13 (J. Wei, J. L. Anderson, K. B. Bischoff, M. M. Denn, and J. H. Seinfeld, Eds), Academic Press, New York (1987), pp. 11–112.

e. S. Whitaker, *AIChE Journal,* **18,** 361–371 (1972).

f. W. E. Stewart, in *Physicochemical Hydrodynamics,* Vol. 1 (D. B. Spalding, ed.), Advanced Publications Ltd., London (1977), pp. 23–63.

g. J. R. Selman and C. W. Tobias, in *Advances in Chemical Engineering,* Vol. 10 (T. B. Drew, G. R. Cokelet, J. W. Hoopes, Jr., and T. Vermeulen, eds.), Academic Press, New York (1978), pp. 211–318.

h. P. V. Danckwerts, *AIChE Journal,* **1,** 456–463 (1955).

i. J. B. Angelo, E. N. Lightfoot, and D. W. Howard, *AIChE Journal,* **12,** 751–760 (1966); E. N. Lightfoot, in *Lectures in Transport Phenomena,* AIChE Continuing Education Series No. 4 (1969), W. E. Stewart, J. B. Angelo, and E. N. Lightfoot, *AIChE Journal,* **16,** 771–786 (1970); W. E. Stewart, *AIChE Journal,* **33,** 2008–2106 (1987); **34,** 1030 (1988).

j. A. Basic and M. P. Dudukovic, *AIChE Journal,* **37,** 1341–1344 (1975).

k. W. J. McMichael and J. D. Hellums, *AIChE Journal,* **21,** 743–752 (1991).

l. J. M. H. Fortuin, E. E. Musschenga, and P. J. Hamersma, *AIChE Journal,* **38,** 343–362 (1992).

m. M. Laso, *AIChE Journal,* **40,** 1297–1311 (1994).

§11. Chemically Reacting Systems

Flow systems with chemical reactions inevitably involve transport phenomena, since multicomponent mixtures with thermal and concentration gradients are present. These are generally extremely difficult problems, and, therefore, the numerous books available stress different aspects of the subject.

Hougen and Watson's pioneering (graduate) kinetics textbook[a] contained just enough transport phenomena principles for developing design equations for catalytic and noncatalytic reactors: calculation of pressure drops through packed beds, heat- and mass-transfer coefficients, the Colburn-Chilton "*j*-factors," the Maxwell-Stefan equations for multicomponent diffusion, "effectiveness factors," and methods for estimating viscosities, diffusivities, and thermal conductivities.

The first extensive discussion[b] of the subject of simultaneous absorption and chemical reactions appeared in Chapter IX of a book by Sherwood and Pigford. In 1955, Frank-Kamenetskii's treatise[c] on the interaction of diffusion and heat conduction with chemical kinetics appeared; this book, containing much material on flames, combustion, and explosions, is a good source on the early Russian literature. In 1967, Astarita[d] published a small book dealing with the effect of chemical reactions on mass transfer, and Danckwerts[e] in 1970 published a monograph dealing with solutions of the diffusion equations for various kinds of geometrical arrangements and kinetic relations, somewhat in the spirit of Carslaw and Jaeger's book on heat conduction. Finally, in 1975 a two-volume treatise[8c] on solutions to the diffusion equation in catalytic systems was published by Aris, complete with literature references and bibliographical notes.

A number of chemical engineering kinetics textbooks have been published in the last half-century, each one with its own particular emphasis and prejudice; as examples, we may cite those by Levenspiel,[f] Hill,[g] and Smith.[h] The textbook by Rawlings and Ekerdt[i] is rather different from its predecessors in that it places more emphasis on teaching by numerical problem solving. All these are aimed at the design and operation of chemical reactors. A notable exception is that by Rosner,[j] which attempts to set forth the subject of transport phenomena for people working in the general area of combustion, shock waves, and flames. This book makes full use of the equations of change, the thermodynamics of irreversible processes, and elementary ideas of turbulence. An introductory textbook by Belfiore[k] covering somewhat the same area was recently published. In addition, there are three review articles[l] that cover the subjects of combustion and flames.

Although not particularly devoted to the subject of transport phenomena, the comprehensive work[m] by Doraiswamy should be mentioned. This massive reference work contains much useful information about experimental details and analysis of experiments, along with extensive bibliographical references.

One area of research that makes full use of transport phenomena and chemical kinetics is that of chemical vapor deposition[n] and the simulation and design of CVD reactors. In the CVD process, chemically reacting gases form a thin solid film, the reaction occurring in the gas phase or on the surface of a substrate.

Homsy and Strohman[o] studied diffusion and chemical reaction in a tubular reactor with a non-newtonian annular flow; they modeled the non-Newtonian fluids by the Ostwald-de Waele and Prandtl-Eyring models.

a. O. A. Hougen and K. M. Watson, *Kinetics and Catalysis,* Wiley, New York (1947).

b. T. K. Sherwood and R. L. Pigford, *Absorption and Extraction,* McGraw-Hill, New York (1952); T. K. Sherwood, R. L. Pigford, and C. R. Wilke, *Mass Transfer,* McGraw-Hill, New York (1975).

c. D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics,* Princeton University Press (1955); 2nd enlarged edition, Plenum Press, New York (1969); 3rd edition in Russian, Nauka, Moscow (1987).

d. G. Astarita, *Mass Transfer with Chemical Reactions,* Elsevier, Amsterdam (1967).

e. P. V. Danckwerts, *Gas Liquid Reactions,* McGraw-Hill, New York (1970).

f. O. Levenspiel, *Chemical Reaction Engineering,* Wiley, New York (1967, 1972, 1999).

g. C. G. Hill, *An Introduction to Chemical Engineering Kinetics and Reactor Design,* Wiley, New York (1977).

h. J. M. Smith, *Chemical Engineering Kinetics,* McGraw-Hill, New York (1956, 1970, 1981).

i. J. B. Rawlings and J. G. Ekerdt, *Chemical Reactor Analysis and Design Fundamentals,* Nob Hill Publishing, Madison, Wisconsin (2002).

j. D. E. Rosner, *Transport Processes in Chemically Reacting Flow Systems,* Butterworths (1986), Dover, New York (2000).

k. L. A. Belfiore, *Transport Phenomena for Chemical Reactor Design,* Wiley, New York (2003).

l. C. E. H. Bawn and C. F. H. Tipper, *Ann. Rev. Phys. Chem.,* **6,** 231–259 (1957); H. G. Wolfhard and D. S. Burger, *Ann. Rev. Phys. Chem.,* **8,** 389–412 (1957); E. Becker, *Ann. Rev. Fluid Mech.,* **4,** 155–194 (1972).

m. L. K. Doraiswamy, *Organic Synthesis Engineering,* Oxford University Press (2001); see pp. 172 et seq., for more on the Hougen-Watson models and their extensions.

n. K. F. Jensen, E. O. Einset, and D. I. Fotiadis, *Ann. Rev. Fluid Mech.,* **23,** 197–242 (1991).

o. R. V. Homsy and R. D. Strohman, *AIChE Journal,* **17,** 215–219 (1971).

§12. Turbulence

For an authoritative and readable summary of the turbulence literature for the last century, see the review article by Lumley and Yaglom.[a] Each of these authors has published, with others, books[b] on turbulence.

The book by Friedlander and Topper is a collection a dozen key classical papers on the statistical theory of turbulence.[c] A classic guide to the literature of the first three-quarters of the 20th century is the 800-page tome of Hinze;[d] Chapter 5 of this book is devoted to the transport of mass and heat, treated as completely analogous phenomena. For turbulent shear flow, the monograph of Townsend,[e] can be recommended, and for homogeneous flow, there is the monograph of Batchelor.[f] An advanced book that includes numerical simulation of turbulence, coherent structures, drag reduction by polymers, and closure methods for the Navier-Stokes equations discussed is that by McComb.[g] Some of the same material is covered in the treatise by Holmes, Lumley, and Berkooz.[h] At the other end of the spectrum, there is the colorful book of Lesieur,[i] with beautiful photographs and simulations intended to give the reader a good qualitative understanding of the subject.

Despite the intense effort made in the past half-century on the fundamentals of turbulence, in many engineering calculations mixing-length theories or K, ε-theories are still being used, and with some success. For example, the classical Prandtl mixing-length empiricism for the turbulent momentum flux, with the mixing length l given by a modified van Driest[j] expression, can describe the time-smoothed velocity profiles for turbulent flow in tubes, all the way from the wall to the tube center-line. This same empiricism can also be used for predicting heat and mass transfer rates.[j] Alternatively, one may deduce by elementary arguments (as did Wasan, Tien, and Wilke[k]) that the eddy viscosity very near the wall is proportional to the third power of the distance from the wall. [As an aside, this relation had been suggested three decades earlier by E. V. Murphree, *Ind. Eng. Chem.*, **24,** 726–736 (1932), a reference that has often been overlooked.]

A unique approach to turbulent heat and mass transfer was pioneered by Stewart.[l] He avoided time smoothing and worked instead with the Fourier transforms of the velocity, temperature, and concentration fields. Then, at high Prandtl (or Schmidt) numbers, he showed that the Nusselt (or Sherwood) number is equal to a constant times the one-third power of the Prandtl (or Schmidt) number, plus another constant times the zero-th power of the Prandtl (or Schmidt) number, and so on. This result checks well with the experimental data[m] of Shaw and Hanratty on mass transfer. A related analysis had been made earlier by Notter and Sleicher[n] to deduce that the eddy diffusivity near a wall is proportional to the third power of the distance from the wall.

In another effort to provide a useful equation for the Reynolds stresses, the classical von Kármán-Prandtl universal logarithmic velocity distribution was modified by replacing the constants in the latter by functions of the Reynolds number; this leads to the Barenblatt-Chorin[o] equation.

One problem of continuing interest is that of "drag reduction" in turbulent flow.[p] This is the lowering of the friction factor vs. Reynolds number curve in the turbulent region because of the presence of small amounts of high polymers. The molecular mechanism for this phenomenon is not yet well understood. The reduction in the drag force, as well as the analogous heat-transfer effect, can nonetheless be described rather satisfactorily using a "random surface renewal" model to describe the increase of the mean age of the fluid elements very near the wall; see the publication of Hamersma and Fortuin,[q] as well as the earlier articles by Fortuin and collaborators. Other discussions of the turbulent heat transfer in drag-reducing fluids have been given by Wells[r] and by Virk and others.[s]

Another problem of interest to chemical engineers is atmospheric turbulent diffusion. Seinfeld[t] has prepared an informative review of this topic, including a number of solutions to the turbulent diffusion equation.

The onset of turbulence in falling liquid films has been covered in a summary article by Fulford.[u] This includes the onset of rippling, the effect of wall roughness, and film flow with an adjacent stream. The rather complete literature search (with comments) should be very helpful to workers in mass transfer. The interaction between homogeneous turbulence and chemical reactions has been reviewed by Hill.[v]

A fascinating apparatus involving turbulent flow is the Ranque-Hilsch vortex tube (see Hinze,[d] pp. 473–477), which is used to separate a gas into a hot stream and a cold stream. The gas enters the tube tangentially at sonic or supersonic velocity through a nozzle, and leaves at the two ends—one with a central orifice (where the cooled gas escapes) and the other with a throttle valve (where the heated gas leaves).

a. J. L. Lumley and A. M. Yaglom, *Flow, Turbulence, and Combustion,* **66,** 241–286 (2001).

b. H. Tennekes and J. L. Lumley, *A First Course in Turbulence,* MIT Press, Cambridge, Massachusetts (1972); A. S. Monin and A. M. Yaglom, *Statistical Fluid Mechanics,* MIT Press, Cambridge, Massachusetts (Vol. 1, 1971; Vol. 2, 1972).

c. S. K. Friedlander and L. Topper, *Turbulence,* Interscience, New York (1961).

d. J. O. Hinze, *Turbulence,* McGraw-Hill, New York (1959, 1975).

e. A. A. Townsend, *The Structure of Turbulent Shear Flow,* Cambridge University Press (1956).

f. G. K. Batchelor, *The Theory of Homogeneous Turbulence,* Cambridge University Press (1953).

g. W. D. McComb, *The Physics of Fluid Turbulence,* Oxford University Press (1990).

h. P. Holmes, J. L. Lumley, and G. Berkooz, *Turbulence, Coherent Structures, Dynamical Systems, and Symmetry,* Cambridge University Press (1996).

i. M. Lesieur, *La Turbulence,* Presses Universitaires de Grenoble (1994); see also M. Lesieur, *Turbulence in Fluids,* Kluwer, Dordrecht, 3rd edition (1997).

j. E. R. van Driest, *J. Aero Sci.,* **23,** 1007–1011 (1956); the original van Driest equation was modified by O. T. Hanna, O. C. Sandall, and P. R. Mazet, *AIChE Journal,* **27,** 693–697 (1981), to make the turbulent viscosity be proportional to the third power of the distance from the wall; O. C. Sandall, O. T. Hanna, and P. R. Mazet, *Canad. J. Chem. Engr.,* **58,** 443–447 (1980).

k. D. T. Wasan, C. L. Tien, and C. R. Wilke, *AIChE Journal,* **9,** 567–569 (1963).

l. W. E. Stewart, *AIChE Journal,* **33,** 2008–2016 (1987); errata, *ibid.,* **34,** 1030 (1988); W. E. Stewart and D. G. O'Sullivan, *AIChE Journal,* to be submitted; see also §13.6 of BS&L.

m. D. A. Shaw and T. J. Hanratty, *AIChE Journal,* **28,** 23–37, 160–169 (1977).

n. R. H. Notter and C. A. Sleicher, *AIChE Journal,* **15,** 936–939 (1969).

o. G. I. Barenblatt and A. J. Chorin, *Proc. Nat. Acad. Sci. USA,* **93,** 6749–6752 (1996).

p. F. T. M. Nieuwstadt and J. M. J. den Toonder, in *Turbulence Structure and Modulation* (eds. A. Soldati and R. Monti), Springer, New York (2001); M. D. Graham, *British Rheology Review,* **2,** 00–00 (2004).

q. P. J. Hamersma and J. M. H. Fortuin, *AIChE Journal,* **49,** 335–349

(2003); J. M. H. Fortuin and P.-J. Klijn, *Chem. Eng. Sci.,* **37,** 611–623 (1982).

r. C. S. Wells, Jr., *AIChE Journal,* **14,** 406–410 (1968).

s. K. A. Smith, G. H. Keuroghlian, P. S. Virk, and E. W. Merrill, *AIChE Journal,* **15,** 294–299 (1969); P. S. Virk, *AIChE Journal,* **21,** 625–656 (1975).

t. J. H. Seinfeld, *Atmospheric Diffusion Theory,* in Vol. 12 of *Advances in Chemical Engineering* (J. Wei, K. B. Bischoff, T. B. Drew, and J. H. Seinfeld, eds.), Academic Press, New York (1983), pp. 209–299.

u. G. D. Fulford, *The Flow of Liquids in Thin Films,* in Vol. 5 of *Advances in Chemical Engineering* (T. B. Drew, J. H. Hoopes, T. Vermeulen, and G. R. Cokelet, eds.), Academic Press, New York (1964), pp. 151–236.

v. J. C. Hill, *Ann. Rev. Fluid Mech.,* **8,** 135–161 (1976).

§13. Polymeric Liquids

Chemical engineers, because of the growing importance of the plastics industry, were rather quick to jump into the emerging field of polymer rheology. The lengthy review article of Metzner[a] identified a number of key problems and set the tone for much of the research that followed. The first textbook in this area authored by a chemical engineer was that of Fredrickson,[b] who capitalized on Oldroyd's use of convected coordinate systems,[c] as well as convected differentiation and integration. Various corotating coordinate systems have also been introduced.[d]

In both turbulent flow and non-Newtonian flow, the major problem is to find suitable expressions for the stress tensor that can be substituted into the equation of motion so that flow and transport problems can be solved. There is one important difference between the two types of problems: the non-Newtonian fluids can be described by means of molecular theory (at least for polymeric fluids), so that forms of the empiricisms have some structural basis, whereas in turbulent flows there are no suitable molecular theories.

Several books[e,f,g,h,i] have appeared in recent years that provide the molecular-continuum connection. There are two main classes of molecular theories: network theories, for polymer melts; and single-molecule theories, mainly for dilute solutions, or used for polymer melts by describing the motion of one molecule moving in the "mean field" of the surrounding molecules. The latter theories have been more highly developed, particularly as regards the formulation of the stress tensor and the heat and mass flux vectors,[j] along with the various "cross effects." For example, these theories suggest that a tensorial modification of the Maxwell-Stefan equations should be valid for polymers, and that velocity gradients should produce both heat and mass fluxes. Such cross effects have not been studied experimentally to any significant extent.

For a polymer in a dilute solution, the diffusivity of the polymer is proportional to the inverse square root of the molecular weight according to the theory of Kirkwood,[k] which has been confirmed by experiment. The theory has been refined by Öttinger[l] to account for the fact that the polymer molecules, during a diffusion process, are not quite in an equilibrium conformation. For polymer melts, a reasonable theory was proposed by de Gennes,[m] who suggested that a "marked" molecule will undergo reptational (i.e., snake-like) motion, as though it sloshes back and forth within a "tube" formed by its nearest neighbors. In this way he showed that the self diffusivity should be proportional to the inverse square of the molecular weight, more or less in agreement with experiment.

Doi and Edwards[n] then took de Gennes' ideas, which are pretty good near equilibrium, and cleverly applied them to the calculation of the stress tensor of flowing polymers. The Doi-Edwards papers were received by the rheological community with considerable excitement. On closer examination, however, it appeared that the theory had some unfortunate defects;[o] these could be remedied by introducing additional assumptions into the theory, and a flood of publications ensued. To cite just one example, Neergaard and Schieber[p] have tested recently a modified reputation model (including chain stretching, chain-length fluctuations, segment connectivity, and constraint release) and evaluated the behavior of the model in steady and unsteady shearing flows.

For some purposes, various dumbbell and chain models with nonlinear springs give plausible results[q] for a wide variety of phenomena. However, Curtiss, Bird, and Beers[j] found that the thermal conductivity is extremely sensitive to the nature of the spring force; when a Fraenkel spring is used in an elastic dumbbell model, the theoretically predicted thermal conductivity increases by many orders of magnitude as the spring is "tightened up," causing it to go from a Hookean dumbbell to a nearly rigid dumbbell.

Williams[r] reviewed the current status of molecular theories of rheology of polymers from the chemical and chemical engineering viewpoints in 1975. A review article[s] written in 1992 summarizes the molecular theory of transport phenomena in polymers up to that time; another, in 1995, summarizes the "constitutive equations" used for polymers.[s] In addition, an article by Truesdell and Toupin[t] gives an exhaustive discussion of continuum mechanics and is famous for its extensive bibliography.

With regard to the experimental measurement of rheological properties of polymers, the works of Meissner[u] are highly recommended, and for both rheological and optical properties, the publications of Janeschitz-Kriegl.[v] The classic work on linear viscoelastic properties is the book by Ferry.[w]

Squeezing flows between parallel plates are encountered in various industrial situations, such as lubrication and plastics molding operations. Squeezing flow seven of polymeric liquids was analyzed experimentally by Grimm,[x] who concluded that the squeeze-flow device was not suitable as a viscometer. Co and Stewart[y] solved the problem of the flow from tube into a radial slit by orthogonal collocations; they did this for one non-Newtonian model with elasticity and one without.

In 1964, Lodge[e] published his famous *Elastic Liquids* book, which provided an excellent organizational tool for the entire field of polymer rheology; he also emphasized the utility of the "network" model for molten polymers. The main deficiency of this model was its inability to predict a decrease of the viscosity with increasing shear rate. This was remedied by introducing "network rupture" by Tanner[z,g] in 1969 and by others in the years following. Somewhat before, Spriggs[aa] had proposed his 4-constant model, which was inspired by the Rouse theory for dilute solutions; it proved to be reasonably good for describing the behavior of polymer melts.[bb]

A number of books have appeared on the subject of polymer processing or polymer unit operations, the most authoritative one of which is probably that of Tadmor and Gogos.[cc]

a. A. B. Metzner, in *Advances in Chemical Engineering* Vol. 1 (T. B. Drew and J. W. Hoopes, Jr., eds.), Academic Press, New York (1956), pp. 77–153.

b. A. G. Fredrickson, *Principles and Applications of Rheology,* Prentice Hall, Englewood Cliffs, New Jersey (1964).
c. J. G. Oldroyd, *Proc. Roy. Soc.,* **A200,** 523–541 (1950).
d. L. E. Wedgewood, *Rheol. Acta,* **38,** 91–99 (1999).
e. A. S. Lodge, *Elastic Liquids,* Academic Press, New York (1964); *An Introduction to Elastomer Molecular Network Theory,* Bannatek Press, Madison, Wisconsin (1999).
f. R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics,* Wiley, New York (1977, 1987); R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory,* Wiley, New York (1977, 1987).
g. R. I. Tanner, *Engineering Rheology,* Oxford University Press (1985).
h. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics,* Oxford University Press (1986).
i. R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions,* Butterworths, Boston (1988).
j. C. F. Curtiss and R. B. Bird, *Adv. Polym. Phys.,* **125,** 1–101 (1995); *J. Chem. Phys.,* **106,** 9899–9921 (1997); *J. Chem. Phys.,* **107,** 5254–5267 (1997), *J. Chem. Phys.,* **111,** 10362–10370 (1999); R. B. Bird, C. F. Curtiss, and K. J. Beers, *Rheol. Acta,* **36,** 269–276 (1997); R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.,* **79,** 255–259 (1998).
k. J. G. Kirkwood, *Macromolecules,* Gordon and Breach, New York (1967), pp. 13, 25, 41, 76–77, 95, 101–102.
l. H. C. Öttinger, *J. Chem. Phys.,* **87,** 3156–3165 (1987).
m. P.-G. de Gennes, *Phys. Today,* **36,** 33–39 (1983).
n. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics,* Oxford University Press (1986).
o. For example, the Doi-Edwards theory does not predict "rod-climbing" [O. Hassager, *J. Rheol.,* **29,** 361–364 (1985); A. S. Lodge, J. D. Schieber, and R. B. Bird, *J. Chem. Phys.,* **88,** 4001–4007 (1988); see also H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.,* **77,** 4747–4766 (1982).]
p. J. Neergaard and J. D. Schieber, *J. Non-Newtonian Fluid Mech.,* **105,** 111–130 (2002).
q. Q. Zhou and R. Akhavan, *J. Non-Newtonian Fluid Mech.,* **109,** 115–155 (2003).
r. M. C. Williams, *AIChE Journal,* **21,** 1–25 (1975).
s. R. B. Bird and H. C. Öttinger, *Ann. Revs. Phys. Chem.,* **43,** 371–406 (1992); R. B. Bird and J. M. Wiest, *Ann. Rev. Fluid Mech.,* **27,** 169–193 (1995).
t. C. Truesdell and R. Toupin, in *Handbuch der Physik,* Volume III/1 (S. Flügge, ed.), pp. 226–793 (1960).
u. J. Meissner, *Ann. Rev. Fluid Mech.,* **17,** 45–64 (1985).
v. H. Janeschitz-Kriegl, *Polymer Melt Rheology and Flow Birefringence,* Springer, Berlin (1983).
w. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York (1961, 1970, 1980).
x. R. J. Grimm, *AIChE Journal,* **24,** 427–439 (1978).
y. A. Co and W. E. Stewart, *AIChE Journal,* **28,** 644–655 (1982).
z. R. I. Tanner, *AIChE Journal,* **15,** 177–183 (1969).
aa. T. W. Spriggs, *Chem. Eng. Sci.,* **20,** 931–940 (1965).
bb. C. D. Denson, W. M. Prest, Jr., and J. M. O'Reilly, *AIChE Journal,* **15,** 809–814 (1969).
cc. Z. Tadmor and C. G. Gogos, *Principles of Polymer Processing,* Wiley, New York (1979).

§14. Transport Phenomena in Electrolytic Solutions

When dealing with ionic systems, one needs not only the equations of change for mass, momentum, and energy, but also a statement of electric neutrality for the solution, and the Maxwell equations of electromagnetism (usually in abbreviated form). Also, the equation of motion may need to be modified if there are electrical and magnetic forces acting on the fluid. Most general textbooks on transport phenomena do not discuss ionic systems, notable exceptions being those of Probstein[a] and Plawsky.[b]

Perhaps the first book of interest to chemical engineers dealing with ionic transport was that of Levich.[2i] Several years after that, there were review articles by Newman[c] and by Chapman,[c] and then the first edition of the textbook by Newman.[d]

The field of "electrohydrodynamics" was summarized in a review article by Melcher and Taylor;[e] in this field one has to introduce the Maxwell equations and also to modify the equation of motion to include the electrical effects. This article includes a description of a number of effects along with some photographs and line drawings. A later review, by Saville,[f] was devoted to the "Taylor-Melcher leaky dielectric model" in electrohydrodynamics.

DiBenedetto and Lightfoot,[g] in a publication that combined theoretical analysis and experiment, verified that the Nernst-Planck equations are suitable for describing the behavior of ions in aqueous solutions surrounding a membrane during electrodyalysis. Crosser, Powers, and Prabhudesai[h] analyzed the separation that occurs in a thermoelectrogravitational electrophoresis column.

a. R. F. Probstein, *Physicochemical Hydrodynamics,* Wiley, New York, 2nd edition (1994).
b. J. L. Plawsky, *Transport Phenomena Fundamentals,* Dekker, New York (2001).
c. J. S. Newman, *Advances in Electrochemistry and Electrochemical Engineering,* **5,** 87–135 (1967); J. S. Newman, *Ind. Eng. Chem.,* **60,** 12–27 (1968); T. W. Chapman, in *Lectures in Transport Phenomena,* AIChE Continuing Education Series #4, AIChE, New York (1969), Chapter 3.
d. J. S. Newman, *Electrochemical Systems,* Prentice Hall, Englewood Cliffs, New Jersey (1973, 1991).
e. J. R. Melcher and G. I. Taylor, *Ann. Rev. Fluid Mech.,* **1,** 111–146 (1969).
f. D. A. Saville, *Ann. Rev. Fluid Mech.,* **29,** 27–64 (1997).
g. A. T. DiBenedetto and E. N. Lightfoot, *AIChE Journal,* **8,** 79–86 (1962); see also E. N. Lightfoot and E. M. Scattergood, *AIChE Journal,* **11,** 175–176, 185–187 (1962).
h. O. K. Crosser, J. E. Powers, and R. K. Prabhudesai, *AIChE Journal,* **19,** 38–57 (1973).

§15. Surface and Interfacial Phenomena

When discussing interfacial phenomena, a whole new set of physical properties has to be taken into account, the most important of which is the interfacial tension,[a] which was studied in 1955 from the point of view of the principle of corresponding states. A method of measuring the surface tension from the shape of the meniscus was developed by Biery.[b]

In addition, there are the interfacial viscosity and the interfacial dilatational viscosity, as well as other mechanical properties, described in the textbooks of Slattery[c] and of Edwards, Brenner, and Wasan.[c] The latter two books contain a wealth of information about the entire field of interfacial transport phenomena.

In Chapter VII of the first edition of Landau and Lifshitz's[2h] *Fluid Mechanics* the subject of surface-driven flows was discussed and illustrated by a handful of examples. Then, in 1959 and 1960 publications[d] appeared by Sternling and Scriven, dealing with the Marangoni effect. In 1996, another effect, evaporative convection,[e] was discussed in some detail. In these phenomena, one has to deal with the interaction of interfacial dynamics, fluid dynamics, diffusion, and heat conduction. The hydrodynamic stability of Marangoni films was studied experimentally and theoretically by Ludviksson and Lightfoot.[f]

Interfacial effects are important in any systems dealing with bubbles and drops. A review article in 1970 by Kumar and Kuloor,[g] and a monograph by Clift, Grace, and Weber[h] in 1978 are devoted to the subject of the formation and behavior of drops and bubbles. In the latter, heat- and mass-transfer effects, internal circulation, motions near confining walls, oscillatory motion, and numerous other topics are covered.

a. J. R. Brock and R. B. Bird, *AIChE Journal,* **1,** 174–177 (1955).

b. J. C. Biery, *AIChE Journal,* **16,** 787–792 (1970).

c. J. C. Slattery, *Interfacial Transport Phenomena,* Springer-Verlag, New York (1990); J. C. Slattery, L. M. C. Sagis, and E.-S. Oh, *Interfacial Transport Phenomena,* 2^{nd} edition, Springer-Verlag, New York (2005); D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Processes and Rheology,* Butterworth-Heinemann, Boston (1991).

d. C. V. Sternling and L. E. Scriven, *AIChE Journal,* **5,** 514–523 (1959); L. E. Scriven, *Chem. Eng. Sci.,* **12,** 98–108 (1960).

e. J. C. Berg, A. Acrivos, and M. Boudart, *Evaporative Convection,* in Vol. 6 of *Advances in Chemical Engineering* (T. B. Drew, J. W. Hoopes, Jr., T. Vermeulen, and G. R. Cokelet, eds.), Academic Press, New York (1966), pp. 61–123.

f. V. Ludviksson and E. N. Lightfoot, *AIChE Journal,* **14,** 620–626 (1968). *AIChE Journal,* **17,** 1166–1173 (1971).

g. R. Kumar and N. R. Kuloor, *The Formation of Bubbles and Drops,* in Vol. 8 of *Advances in Chemical Engineering* (T. B. Drew, G. R. Cokelet, J. W. Hoopes, Jr., and T. Vermeulen), Academic Press, New York (1970).

h. R. Clift, J. R. Grace, and M. E. Weber, *Bubbles, Drops, and Particles,* Academic Press, New York (1978).

§16. Two-Phase Systems

The monograph of Happel and Brenner[a] dealing with "Stokes flow" problems has become a much-cited reference for those working in the low Reynolds number area. This was followed by a comprehensive article by Brenner,[b] and thereafter many more. The Happel-Brenner book was supplemented later by the monograph[c] of Kim and Karilla. There is another book, by Drew and Passman,[d] whose title is misleading, at least to chemical engineers who feel that "multicomponent fluids" are fluids containing a variety of chemical species—and not, as the authors intend, a variety of objects suspended in a medium. The book covers various kinds of averaging and possible methods for modeling suspensions. An extensive review of the rheological properties of suspensions of neutrally buoyant particles was published by Jeffrey and Acrivos.[e]

Colloids are another class of two-phase systems,[f] and these materials involved fluid dynamics, surface interactions, Brownian motion, electrical transport, and rheology. The rheology of suspensions has been discussed by Brenner[g] and by Adler, Nadim, and Brenner.[g] The phenomena associated with suspensions of particles in flowing fluids in tubes have been summarized by Cox and Mason.[h] The literature on one-dimensional flow of liquids containing small gas bubbles[i] has been surveyed by van Wijngaarden.

None of these references deal with heat and mass transfer. However, in Marble's article[j] discussing the fluid dynamics of dusty gases, he includes all of the transport phenomena. Another review covers the method of "Stokesian dynamics,"[k] a molecular-dynamics type of approach that is capable of handling multiphase flow problems, thermal phenomena, diffusive systems, and rheological problems.

An extensive review article by Brown[l] deals with the role of transport phenomena in crystal growth from the molten state. Here fluid dynamics, heat conduction, and diffusion all come into play.

Greenkorn[m] prepared a review article on the flow through porous media, and a few years later (in 1983) published a book on the same subject. Whitaker[n] studied diffusion in packed beds of porous particles, and described how to extract the particle effective-diffusivity from the overall effective-diffusivity of a packed bed. Lin and Slattery[o] studied the two-phase flow in a 3-dimensional, randomized, network model for a porous medium. This is the first model that has successfully predicted the hysteresis loops for the capillary pressure and for the relative permeabilities; it is also the first model that has been developed within the context of local volume averaged equations of motion. In porous media problems, there is always the problem of what kind of boundary condition to be used at the interface between the porous medium and the external fluid. Ross[p] has worked out equations that go smoothly from Darcy's law within the porous medium to the Navier-Stokes equations in the fluid phase.

Sy, Taunton, and Lightfoot[q] have solved the equations of motion for the motion of a solid sphere or a spherical gas bubble embedded in an external medium, starting from rest and accelerating to steady state. Wagner and Slattery[r] studied the flow of a non-Newtonian fluid past a droplet in steady-state flow. They used a third-order fluid to describe the non-Newtonian behavior.

Another problem is that of the liquid film falling on a vertical wall with interphase mass transfer at the gas-liquid interface which was studied by Wang, Ludviksson, and Lightfoot.[s] There was interphase mass transfer and surface-tension gradients. They investigated the stability of the interface.

Mixing, with or without diffusion and chemical reactions, is important in many of the unit operations of chemical engineering. In 1981, a key paper by Ottino, Ranz, and Macosko[t] was published, based on the principles of continuum mechanics, which established the mathematical framework for future work in this subject. This was followed by Ottino's monograph[u] dealing more exhaustively with the subject of mixing.

a. J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics,* Prentice-Hall, Englewood Cliffs, New Jersey (1965), First paperback edition, Martinus Nijhoff, The Hague (1983).

b. H. Brenner, *Advances in Chemical Engineering,* Vol. 6 (T. B. Drew, J. W. Hoopes, Jr., T. Vermeulen, G. R. Cokelet, eds.), Academic Press, New York (1966), pp. 287–438.

c. S. Kim and S. J. Karilla, *Microhydrodynamics,* Butterworth-Heinemann, Boston (1991).

d. D. A. Drew and S. L. Passman, *Theory of Multicomponent Fluids,* Springer, New York (1999).

e. D. J. Jeffrey and A. Acrivos, *AIChE Journal,* **22,** 417–432 (1976).

f. R. J. Hunter, *Foundations of Colloid Science* (2 vols.), Oxford University Press (1987, 1992).

g. H. Brenner, *Ann. Rev. Fluid Mech.,* **2,** 137–176 (1970); P. M. Adler, A. Nadim, and H. Brenner, *Advances in Chemical Engineering,* Vol. 15 (J. Wei, J. L. Anderson, K. B. Bischoff, and J. H. Seinfeld, eds.), Academic Press, New York (1990), pp. 1–72.

h. R. G. Cox and S. G. Mason, *Ann Rev Fluid Mech.,* **3,** 291–316 (1971).

i. L. van Wijngaarden, *Ann. Rev. Fluid Mech.,* **4,** 369–396 (1972).

j. F. Marble, *Ann. Rev. Fluid Mech.,* **2,** 397–446 (1970).

k. J. F. Brady and G. Bossis, *Ann. Rev. Fluid Mech.,* **20,** 111–157 (1988).

l. R. A. Brown, *AIChE Journal,* **34,** 881–911 (1988).

m. R. A. Greenkorn, *AIChE Journal,* **27,** 529–545 (1981); R. A. Greenkorn, *Flow Phenomena in Porous Media,* Marcel Dekker, New York (1983).

n. S. Whitaker, *AIChE Journal,* **34,** 679–683 (1988).

o. C.-Y. Lin and J. C. Slattery, *AIChE Journal,* **28,** 311–324 (1982).

p. S. M. Ross, *AIChE Journal,* **28,** 840–846 (1982).

q. F. Sy, J. W. Taunton, and E. N. Lightfoot, *AIChE Journal,* **16,** 386–391 (1970); F. Sy and E. N. Lightfoot, *AIChE Journal,* **17,** 177–181 (1971).

r. M. G. Wagner and J. C. Slattery, *AIChE Journal,* **17,** 1198–1207 (1971).

s. R. H. Wang, V. Ludviksson, and E. N. Lightfoot, *AIChE Journal,* **17,** 1402–1408 (1971).

t. J. M. Ottino, W. E. Ranz, and C. W. Macosko, *AIChE Journal,* **27,** 565–577 (1981).

u. J. M. Ottino, *The Kinematics of Mixing: Stretching, Chaos, and Transport,* Cambridge University Press (1989).

§17. Mesoscopic Analyses

To get the macroscopic balances, one integrates the equations of change over the entire volume of a flow system. There are, however, situations in which we need to integrate over all the variables, except for one or two, and then solve the resulting differential equation. This is well illustrated by the topic of Taylor dispersion.[a] Instead of solving the complete diffusion equation for the concentration in a circular tube as a function of time, radial coordinate, and axial coordinate, one can integrate over the radial coordinate and get an equation involving time and the axial coordinate, which describes the "axial dispersion." Other examples are cited in BS&L §20.5. The book by Brenner and Edwards[b] gives an encyclopedic coverage of this very useful topic. Recently, the extension of Taylor diffusion to two-phase systems has been used to develop a novel two-fluid Taylor vortex extractor.[c]

Another mesoscopic analysis example is typified by the von Kármán boundary-layer balances. For the flow along a flat plate in the x-direction, an integration of the boundary-layer equations over the y-coordinate gives an integral equation for the velocity profile. One can then "guess" a reasonable form for the velocity profile $v_x(y)$, containing the boundary-layer thickness $\delta(x)$. When this is substituted into the integral equation, one can solve for the boundary-layer thickness and, thus, get an approximate expression for the velocity profile and the drag force (see BS&L, Problem 4B.2). Similar approximate procedures may be used for transient diffusion and heat-conduction problems to get heat- and mass-transfer coefficients.

A third example of a mesoscopic analysis is the solution by means of the method of moments. In 1958, Spalding[d] proposed this method for solving certain kinds of diffusion problems. Here, one writes the equation for the zeroth, first, second, etc., moments of the equation, and then solves the sequence of equations. Often, only a few terms in the sequence are actually needed (see BS&L, Example 23.6-3).

a. G. I. Taylor, *Proc. Roy. Soc.,* **A219,** 186–203 (1953); **A225,** 473–477 (1954); see also R. A. Aris, *Proc. Roy. Soc.,* **A235,** 6667 (1956).

b. H. Brenner and D. A. Edwards, *Macrotransport Processes,* Butterworth-Heinemann, Boston (1993).

c. G. Baier, M. D. Graham, and E. N. Lightfoot, *AIChE Journal,* 2395–2407 (2000).

d. D. B. Spalding, *Chem. Eng. Sci.,* **9,** 74–77 (1958); E. N. Lightfoot, A. M. Lenhoff, and R. I. Rodriguez, *Chem. Eng. Sci.,* **36,** 954–956 (1982).

§18. Energy Transport by Radiation

This topic in transport phenomena was studied intensively at the end of the 19th century. When Planck tried to resolve the problem of black-body radiation distribution, he was forced to introduce the notion of quantization of energy. This led to the new science of quantum mechanics, and, for his contribution, he received a Nobel Prize in 1918.

In 1967, the comprehensive text by Hottel and Sarofim[a] appeared; this was a revision and expansion of Hottel's chapter in McAdams' text *Heat Transmission.* In the last three decades, four editions of the book by Siegel and Howell[b] have appeared; this is an excellent source of references and tabular material. There has been much activity[c,d,e,f] in the field of solar energy use, starting with the establishment of the Solar Energy Research Laboratory at the University of Wisconsin about 50 years ago.

The subject of "radiation hydrodynamics," presented in Pomraning's monograph,[g] concerns itself with the propagation of thermal radiation through a moving fluid and the effect of the radiation on the motion of the fluid. It includes the incorporation of relativistic effects, electromagnetic energy transport, and stimulated emission and scattering of radiation.

Radiant heat transfer in packed beds was discussed by Beek[h] in 1962.

a. H. C. Hottel and A. F. Sarofim, *Radiative Transfer,* McGraw-Hill, New York (1967).

b. R. Siegel and J. R. Howell, *Thermal Radiation Heat Transfer,* Taylor and Francis (1971, 1981, 1992, 2001).

c. F. Daniels and J. A. Duffie, *Solar Energy Research,* University of Wisconsin Press, Madison (1955).

d. J. A. Duffie and W. A. Beckman, *Solar Energy Thermal Processes,* Wiley, New York (1974); German Edition (1976), Russian Edition (1977), Italian Edition (1978).

e. W. A. Beckman, S. A. Klein, and J. A. Duffie, *Solar Heating Design by the f-Chart Method,* Wiley, New York (1977); German Edition (1979).

f. J. A. Duffie and W. A. Beckman, *Solar Engineering of Thermal Processes,* Wiley, New York (1980, 1991).

g. G. C. Pomraning, *The Equations of Radiation Hydrodynamics,* Pergamon Press, New York (1973).

h. J. Beek, in *Advances in Chemical Engineering,* Vol. 3 (ed. T. B. Drew), Academic Press, New York (1962), pp. 203–271; see also W. E. Stewart, Chapter 4 in *Selected Topics in Transport Phenomena,* Chem. Engr. Prog. Symposium Series #58, Vol. 61 (1965).

§19. Angular Momentum Transport

Except for some civil and mechanical engineering textbooks,[a] the subject of angular momentum has been generally ignored, although later books[b] contain brief discussions. The first publication by chemical engineers on this subject was (as far as we know) a short article by Dahler and Scriven,[c] which called attention to the continuum-mechanics aspects of the subject; this was followed by the derivation of the macroscopic angular momentum balance[21b] by Slattery and Gaggioli, as well as by the nonequilibrium thermodynamic[d] discussion. The literature[e] up to 1995 has been summarized by Kuiken.

One application of the macroscopic angular momentum balance is in the computation of torques on pipe bends. Another is the calculation of the rotation speed of tangential spray devices. Also, chemical engineers occasionally have to be able to calculate the torque on towers where the feedstream is introduced tangentially at high speed and then the exit stream leaves vertically. In this situation, a large amount of angular momentum may be introduced via the feedstream and none removed in the exit stream. There is, then, a resultant torque on the tower. If there is not sufficient bracing, then the tower may wobble, possibly with disastrous results. The author recalls sitting in on an industrial discussion pertaining to just this situation, in which the tower was filled with carbolic acid, the tower was swaying, and a technician was sent up to the top to look in through an opening to see what was happening!

If the stress tensor is symmetric, then it may be shown that the equation of change for angular momentum is identical with that obtained by taking the cross product of the position vector $\boldsymbol{r}$ with the equation of motion (i.e., the equation of change for linear momentum). However, for solving problems, it may sometimes be advantageous to work with the angular momentum equation rather than the linear momentum equation. One might wonder whether macromolecular materials would have a stress tensor that is symmetric; the kinetic theory of polymers (including polymer melts) does gives a symmetric stress tensor.[13j]

a. J. C. Hunsaker and B. G. Rightmire, *Engineering Applications of Fluid Dynamics,* McGraw-Hill, New York (1947).

b. F. M. White, *Fluid Mechanics,* McGraw-Hill (1979), §3.6; R. L. Panton, *Incompressible Flow,* Wiley, New York (1996), §5.8.

c. J. S. Dahler and L. E. Scriven, *Nature,* **192,** 36–37 (1961); this is the first of a series of articles.

d. S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics,* North Holland, Amsterdam (1962), Chapter XII.

e. G. D. C. Kuiken, *Ind. Eng. Chem. Res.,* **34,** 3568–3572 (1995).

20. Transport Phenomena in Living Systems

During the 1970s, four textbooks by chemical engineers appeared, which to a greater or lesser extent dealt with transport phenomena in living systems. Seagraves'[a] small book was intended to be an introduction to heat and mass transfer. Lightfoot's[b] book gave very little attention to heat transfer, but emphasized fluid mechanics and mass transfer; the discussion of multicomponent diffusion was well thought out, and the subjects of convective mass transport and transport across membranes—all with biological applications—were extensively covered. Lih's[c] book was intended to bridge the "language barrier" between the biological community and the chemical engineers. The textbook of Bailey and Ollis,[d] which covers all aspects of biochemical engineering, contains one chapter (Chapter 8) devoted to applied transport phenomena.

In 1972 Jahn and Votta[e] reviewed the subject of the locomotion of protozoa; anyone who has been captivated by the ways amoebae and paramecia propel themselves will find this article fascinating. Another review on the same subject by Pedley and Kessler[f] appeared in 1992, and in 2000, a review on fish-like swimming[g] was published.

Pedley's 1977 review[h] discusses the subject of pulmonary fluid dynamics and mass transfer in the pulmonary system. Steady and unsteady flows in branching networks are discussed, and the associated convection-diffusion processes. Similar topics are discussed in another review in 1994 by Grotberg.[i]

The pulsatile flow of blood in the arteries has been summarized by Ku[j] in 1997; this article shows how far we have come since Poiseuille's original interest in the physics of blood flow.

In the coming years, it is expected that much more will be done in this area, as more and more departments of Chemical Engineering transform themselves into "Chemical and Biological Engineering."

a. R. C. Seagrave, *Biomedical Applications of Heat and Mass Transfer,* Iowa State University Press, Ames (1971).

b. E. N. Lightfoot, *Transport Phenomena in Living Systems,* Wiley, New York (1974).

c. M. M. Lih, *Transport Phenomena in Medicine and Biology,* Wiley, New York (1975).

d. J. E. Bailey and D. F. Ollis, *Biochemical Engineering Fundamentals,* McGraw-Hill, New York (1977, 1986).

e. T. L. Jahn and J. J. Votta, *Ann. Rev. Fluid Mech.,* **4,** 93–116 (1972).

f. T. J. Pedley and J. O. Kessler, *Ann. Rev. Fluid Mech.,* **24,** 313–358 (1992).

g. M. S. Triantafyllou, G. S. Triantafyllou, and D. K. P. Yue, *Ann. Rev. Fluid Mech.,* **32,** 33–53 (2000).

h. T. J. Pedley, *Ann. Rev. Fluid Mech.,* **9,** 229–274 (1977).

i. J. B. Grotberg, *Ann. Rev. Fluid Mech.,* **26,** 329–371 (1994).

j. D. N. Ku, *Ann. Rev. Fluid Mech.,* **29,** 399–434 (1997).

§21. Macroscopic Balances

Prior to 1957, the momentum and mechanical energy balances had been used widely for solving steady-state problems. The macroscopic balances for energy and the masses of various chemical species had been used for some time in unsteady-state versions, in order to show how the temperature and the species concentrations in mixed vessels change evolve with time.

In 1957, an article was published[a] showing how the unsteady-state macroscopic balances for mass, momentum, and energy could be obtained by straightforward integrations of the equations of change. It was further shown how the macroscopic mechanical-energy balance could be obtained by dotting the equation of motion with the velocity vector and integrating the resulting equation over the volume of the flow system; no thermodynamics is used in that derivation. Several years later, Slattery and Gaggioli[b] published an analogous derivation of the macroscopic angular momentum balance, thereby completing the set of macroscopic balances.

The derivation of the mechanical energy balance was repeated in various forms[c] since 1957. However, many textbook authors have persisted in reciting the misleading sentence,[d] "An adequate appreciation of the underlying significance of Bernoulli's theorem cannot be had except in the light of the second law," from a well-known unit operations book. The insertion of thermodynamics into the derivation only serves to obfuscate. Others, notably Bliss[e] and Whitaker,[f] seem to agree with this point of view.

a. R. B. Bird, *Chem. Eng. Sci.,* **6,** 123–131 (1957).

b. J. C. Slattery and R. A. Gaggioli, *Chem. Eng. Sci.,* **17,** 893–895 (1962).

c. BS&L (1960, 2002); R. B. Bird, *Chem. Eng. Educ.,* **27**(2), 102–109 (Spring 1993); *NPT Procestechnologie,* **1**(5), 6–10 (1995); *Korean J. Chem. Eng.,* **15,** 105–123 (1998). See also R. B. Bird and M. D. Graham, *The Handbook of Fluid Dynamics,* CRC Press, Boca Raton, Florida (1998), Ch 3.

d. W. H. Walker, W. K. Lewis, W. H. McAdams, and E. R. Gilliland, *Principles of Chemical Engineering,* McGraw-Hill (1937).

e. H. Bliss, *AIChE Journal,* **2,** 429 (1956). [*Note:* Harding Bliss was the first editor of the *AIChE Journal*]

f. S. Whitaker, in *One Hundred Years of Chemical Engineering* (N. A. Peppas, ed.), Kluwer, Dordrecht (1989), pp. 47–108 (see particularly comments on pp. 90–93).

§22. Then and Now

Fifty years ago:

(a) There were no undergraduate textbooks on transport phenomena.

(b) The use of the equations of change to solve problems was limited to those classes of problems that could be attacked analytically, that is, those that were trivial one-dimensional problems, or more complex problems that required a certain amount of mathematical know-how. A few problems could be done numerically, but only with an enormous amount of programming effort.

(c) The lack of experimental data on diffusivities was often the limiting factor in mass-transfer calculations for separation processes.

(d) S. R. de Groot's *Thermodynamics of Irreversible Processes,* North-Holland Publishing Company (1951) had appeared just a few years before, and there was much discussion about the importance and future of the subject.

(e) J. G. Kirkwood and his students were churning out publications on the kinetic theory of liquids and polymers, but these had attracted little interest among engineers, inasmuch as most of them were highly theoretical and seemed to hold little promise for making practical calculations.

(f) Molecular dynamics had probably been dreamt of, but the idea was discarded on account of the very limited power of computers.

(g) Polymer flow problems were generally solved by using simple models, such as the "power law" or "Bingham" models. If the flows were nonisothermal, the usual equations for heat convection + conduction were used, since nothing else was available. Nothing was known about the molecular theory of heat conduction for polymers.

(h) Solving multicomponent diffusion problems was avoided, and empirical "effective binary diffusion" schemes were resorted to. In this way diffusion in porous catalysts could be handled approximately.

(i) Turbulence was regarded as the "Mt. Everest" of fluid dynamics and transport phenomena. Little was accessible to the engineer, and dimensionless correlations of experimental data were generally resorted to.

(j) Little had been done in understanding the nature of instabilities.

At the present (here we list some of the challenges in the form of questions):

(a) Who is going to make measurements of diffusivities and other transport properties? Who is going to develop a database for three- and four-component diffusing systems (complete with the activity data)?

(b) Can we learn how to predict turbulent flows, using "significant structures"? What needs to be done to develop a viable theory for drag reduction in turbulent flows?

(c) Will nonlinear irreversible thermodynamics take its place as a fundamental study, capable of making useful predictions? If so, what problems should be attacked?

(d) How much work would be involved in evaluating the polymer-polymer interaction terms for the stress tensor and the heat flux vector in the Curtiss-Bird kinetic theory of polymers (1996)? What could we learn about polymer melt rheology and heat conduction if these were evaluated?

(e) What boundary and interfacial conditions in transport phenomena need to be clarified by use of molecular dynamics? Does more research need to be done on the question of equilibrium at the interface of a rapidly evaporating liquid?

(f) Are the mechanism of Liesegang ring formation and the operation of the Ranque-Hilsch tube sufficiently well explained?

(g) What experiments should be done on the steady-state and unsteady-state macroscopic balances, in order to assess the limits of their applicability?

(h) What is the correct velocity boundary condition at the tube wall when a homogeneous mixture is flowing through the tube? Does the mass-average velocity equal zero, or the molar average, or the volume average?

(i) What heat- and mass-transfer problems taking place in an ultrasonic field need to be explored?

(j) What new textbooks, monographs, and treatises are needed for organizing and consolidating parts of the subject that at present are spread out over the research literature?

Certainly investigators working in specific areas will be able to come up with additional crucial questions. There are so many combinations of fluids, modes of transport, boundary conditions, and potential applications that we are well supplied with problems to work on in the future.

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